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UNIT 1

Organic Chemistry

OVERALL EXPECTATIONS

- assess the social and environmental impact of organic compounds used in everyday life, and propose a course of action to reduce the use of compounds that are harmful to human health and the environment
- investigate organic compounds and organic chemical reactions, and use various methods to represent the compounds
- demonstrate an understanding of the structure, properties, and chemical behaviour of compounds within each class of organic compounds

BIG IDEAS

- Organic compounds have predictable chemical and physical properties determined by their respective structures.
- Organic chemical reactions and their applications have significant implications for society, human health, and the environment.

UNIT TASK **PREVIEW**

In the Unit Task, you will explore organic solvents. You will research their properties and their health and environmental implications; then you will consider alternatives. Taking the role of a delegate at a conference on green alternatives, you will suggest less harmful solvents that could replace the toxic organic options.

The Unit Task is described in detail on page 116. As you work through the unit, look for Unit Task Bookmarks to see how information in the section relates to the Unit Task.

FOCUS ON **STSE**

THE MEDICINE HUNTER

The world's forests are not only beautiful, but they also contain natural and complex treasures. Plants, like all living things, contain carbon-based compounds. Plants and plant extracts have been used to treat human ailments since prehistoric times. Ancient Egyptians chewed willow bark to cure fever and headaches. Atropine, derived from the nightshade plant, is a drug used today to treat heart conditions. Plant sources provide a significant amount of all prescription medications, which are typically carbon-based compounds. In addition, one in five of today's pharmaceutical drugs comes from the world's rainforests. These rainforests flourish in temperate areas, such as the Pacific Rim National Park Reserve of Canada, and tropical regions.

One of the most exciting areas of plant-based pharmaceutical research is the search for a cancer cure. Vinblastine and vincristine, which are derived from periwinkle plants from Madagascar, are used in chemotherapy to treat certain cancers. Taxol, a drug derived from the Pacific yew tree, is used in the treatment of breast and ovarian cancers.

The healing power of the Pacific yew was known to the indigenous peoples of the Pacific Northwest. They made teas and poultices from the tree's needles to treat many ailments, including various tumours, cancers, and skin lesions. Scientists have spent years isolating, studying, and testing compounds from the Pacific yew. Once a compound that exhibited anti-cancer activity was isolated, scientists began to study the mechanism by which the compound worked.

Harvesting Pacific yew bark to produce Taxol for cancer patients threatens the balance in the ecosystem. The promise of plant-based pharmaceuticals is accompanied by environmental concerns about the damage to ecosystems. Losing ecosystems may also mean losing sources of medications—possibly even medications that we do not yet know about.

When chemists have figured out the chemical structure of an effective chemotherapy drug, pharmaceutical companies may choose to manufacture it rather than continue extracting the natural product from harvested plants. This relieves the pressure on the environment. However, there is some concern that pure, synthetic compounds may not be as effective as natural extracts.

Questions

1. There are millions of organic compounds that occur naturally, and many more that can be synthesized. They generally consist of just three or four elements. How can so few elements form so many compounds?
2. How might unknown organic compounds be relevant to medical researchers?
3. As more plant-based compounds are discovered to have medicinal qualities, how important is environmental diversity?
4. Tropical rainforests are destroyed by overharvesting and by converting the forests to farmland. Given that there is a possibility of finding useful compounds in rainforests, what should we do to save forest ecosystems?

UNIT 1 ARE YOU READY?

CONCEPTS

- Lewis structures
- electronegativity
- relationship between intermolecular forces and properties
- polar bonds and polar molecules
- ionization or dissociation of acids and bases

SKILLS

- identify WHMIS symbols and safety instructions
- build molecular models
- review molecular shapes
- identify acids and bases

Concepts Review

1. Provide an example of each of the following methods of representing entities: K/U C
   (a) molecular formula
   (b) Lewis structure
   (c) structural formula
2. (a) Explain what is meant by the term "electronegativity."
   (b) Describe the trend of electronegativity in the periodic table.
   (c) Describe the effect that electronegativity has on bonding.
   (d) Explain how to use electronegativity values to predict the characteristics of bonds. K/U T/I
3. What are polar covalent bonds? Give an example. K/U
4. Rank the bonds between the following pairs of elements in order of increasing polarity. Show calculations to support your answers.

   LiF; NH; BO; HH K/U
5. (a) Do you agree or disagree with the following statement? "All molecules that contain polar bonds are polar molecules." Support your answer with an example.
   (b) Give an example of a polar molecule. Explain your choice.
   (c) Give an example of a non-polar molecule. Explain your choice. K/U T/I
6. (a) What are the parts of a solution? Give an example of each.
   (b) What is solubility? Give an example.
   (c) Most familiar solutions have solid solutes and liquid solvents. Give three examples of solutions in everyday life that do not fit this description. K/U
7. (a) Using your current knowledge, define the terms "acid" and "base," giving an example of each.
   (b) The general formula of acids is HA(aq). Why is this formula useful? K/U
8. What are intermolecular forces? Give an example. K/U
9. Rank the following types of forces and bonds in order of decreasing strength:

   dipole–dipole; covalent; London dispersion; hydrogen; ionic K/U
10. Which of the following substances form hydrogen bonds?

    NH_3; H_2O; HF; H_2; CH_4; O_3 K/U T/I
11. Draw Lewis structures for the each of the following molecules. Show multiple bonds and correct bond angles where possible. Using a different colour, highlight any polar bonds. Indicate whether each molecule is polar or non-polar. T/I C
    (a) H_2O
    (b) O_2
    (c) C_4H_{10}
    (d) CO_2
    (e) HF
    (f) CH_4
12. Carbon atoms generally form four covalent bonds with other atoms. K/U T/I
    (a) Explain the statement above, referring to the valence electrons of a carbon atom.
    (b) Explain how a carbon atom may bond to only 3 other atoms but still fulfill the requirement of having 4 bonds.
13. The fuels that we most commonly use are hydrocarbons. K/U A
    (a) What is a hydrocarbon?
    (b) What type of reaction occurs when a hydrocarbon is used as a fuel?
    (c) What other reactant is required for this reaction to take place?
    (d) List four possible products of this reaction.
    (e) Identify at least one health concern that may result from this reaction.

Skills Review

14. Identify the following WHMIS symbols. Give one precaution associated with using an item or substance bearing this symbol. K/U

    (a) 

    (b) 

    (c) 

    (d) 

15. List three pieces of personal protective equipment that you might wear in a chemistry laboratory. K/U
16. Describe the safety precautions you should take before handling an acid. K/U
17. Describe the correct technique for smelling a chemical in the laboratory. K/U
18. Describe the procedure for cleaning up spilled solvent. K/U A
19. What is the procedure to clean up a spilled basic solution? K/U A
20. If you were using soft candies to represent atoms, and toothpicks to represent bonds, how many of each would be required to build each of the following molecules? Draw a diagram illustrating each model that you would build. K/U T/I C
    - (a) water, $H_2O(l)$
    - (b) methane, $CH_4(g)$
    - (c) carbon dioxide, $CO_2(g)$
    - (d) oxygen, $O_2(g)$
21. Explain why the boiling point of a pure substance increases as the strength of intermolecular forces increases. K/U T/I
22. (a) Which substance has a higher boiling point: water or oxygen?
    - (b) Justify your answer, using empirical evidence (observations).
    - (c) Give a theoretical explanation for your answer in (a). K/U T/I
23. You are given samples of three colourless aqueous solutions. One is a solution of hydrochloric acid, one is a solution of sodium hydroxide, and the third is a solution of sodium chloride. T/I A
    - (a) Describe how you could safely differentiate between them.
    - (b) List the equipment and materials you would need for your tests.
24. What are van der Waals forces? K/U
25. Write a dissociation or ionization equation (as appropriate) for each of the following acids or bases. Identify each as an acid or a base. K/U
    - (a) $NaOH(aq)$
    - (b) $HCl(aq)$
    - (c) $H_2SO_4(aq)$
    - (d) $HNO_3(aq)$
    - (e) $LiOH(aq)$

CAREER PATHWAYS **PREVIEW**

Throughout this unit you will see Career Links. Go to the Nelson Science website to find information about careers related to Organic Chemistry. On the Chapter Summary page at the end of each chapter you will find a Career Pathways feature that shows you the educational requirements of the careers. There are also some career-related questions for you to research.

CHAPTER 1

Organic Compounds

KEY CONCEPTS

After completing this chapter you will be able to

- describe some impacts of organic compounds on human health, society, and the environment
- use appropriate terminology, including IUPAC nomenclature, to describe organic compounds and their reactions
- safely perform laboratory investigations involving organic compounds
- create molecular models to represent simple organic compounds and their reactions
- compare the structural formulas and properties of different classes of organic compounds
- explain the changes that occur during various organic chemical reactions and predict the products of those reactions
- explain the concept of isomerism and relate variations in the properties of isomers to their structural formulas

Why Is Carbon So Ubiquitous?

As far as we know, life exists only on Earth. Why does life exist on Earth at all? What enables it to exist? The availability of liquid water is essential for life. Equally important are the elements carbon and nitrogen. Together, these elements form most of the thousands of compounds that make up living things. According to Stephen Hawking, "What we normally think of as 'life' is based on chains of carbon atoms, with a few other atoms, such as nitrogen or phosphorous. One can speculate that one might have life with some other chemical basis . . . but carbon seems the most favourable case, because it has the richest chemistry."

Historically, the distinction between inorganic and organic substances was based on whether a compound was produced by living things. Until the early nineteenth century it was believed that organic compounds contained a "life force" and could only be made by living organisms. In 1828, German chemist Friedrich Wöhler (1800–1882) changed that belief: he successfully prepared urea, a component of urine, from inorganic ammonium cyanate. This proved that organic compounds can be made from inorganic materials.

The definition of organic chemistry has since changed. It is now the study of carbon-containing compounds and their properties. There are a few carbon compounds, including carbon oxides and carbonates, that we consider to be inorganic. The vast majority of carbon-containing compounds, however, contain chains or rings of carbon atoms and are considered to be organic compounds. Why can carbon atoms form long chains, rings, and double and triple bonds when other elements cannot? Each atom of carbon has the ability to form four stable covalent bonds resulting in molecules with a variety of unique shapes and sizes. Organic molecules may contain one carbon atom or tens of thousands of carbon atoms, or any number in between. Many carbon-based molecules are involved in complex tasks of life. DNA, a large biological molecule found in plant and animal cells, stores genetic information. Organic molecules in plant chloroplasts transform light energy from the Sun into chemical energy during photosynthesis. Fatty acids are long-chained carbon molecules that make up cell membranes.

In this chapter we will explore how carbon atoms bond to each other and to other atoms to form the molecules that enable life to exist on our planet.

STARTING **POINTS**

Answer the following questions using your current knowledge. You will have a chance to revisit these questions later, applying concepts and skills from the chapter.

1. What does the term "organic" mean in everyday language? How does this definition relate to "organic chemistry"?
2. Consider the physical and bonding properties of carbon. What other element(s) on the periodic table demonstrate(s) similar properties? Justify your answer.
3. Many organic compounds used in everyday applications are extracted from natural sources. Give two examples of such compounds.
4. In addition to carbon, what other elements are commonly found in organic compounds? How do these elements affect the properties of organic compounds?

Mini Investigation

An Enlightening Organic Compound (Teacher Demonstration)

Skills: Questioning, Observing, Evaluating

SKILLS HANDBOOK **A1, A2.3**

In this demonstration you will observe an unusual reaction in which luminol, an organic compound, reacts to produce a new substance that emits light. The glow of fireflies at night comes from a similar reaction.

Equipment and Materials: chemical safety goggles; lab apron; two 1 L Erlenmeyer flasks; retort stand and ring clamp; funnel; 3 utility clamps; 1 m length of clear plastic tubing; distilled water; Solution A (2.0 g sodium carbonate, $Na_2CO_3(s)$; 0.1 g luminol, $C_8H_7O_2N_3(s)$; 12.0 g sodium bicarbonate, $NaHCO_3(s)$; 0.25 g ammonium carbonate monohydrate, $(NH_4)_2CO_3{\cdot}H_2O(s)$; 0.2 g copper(II) sulfate pentahydrate, $CuSO_4{\cdot}5H_2O(s)$); Solution B (25 mL 3 % hydrogen peroxide, $H_2O_2(aq)$)

Copper(II) sulfate pentahydrate is toxic and an irritant. Avoid skin and eye contact. In the case of contact, wash the affected area with lots of cool water and inform your teacher.

1. Put on your safety goggles and apron.
2. Dissolve the first two ingredients for Solution A in a 1 L flask containing 250 mL of distilled water.
3. Dissolve the remaining ingredients for Solution A in the flask.
4. Dilute Solution A to 500 mL by adding distilled water.
5. Prepare Solution B by diluting 25 mL of 3% hydrogen peroxide to 500 mL with distilled water.
6. Attach a 1 m coil of clear plastic tubing to a retort pole with clamps.
7. Place a funnel in a ring clamp attached high on the retort pole. Place the lower end of the tubing in the second Erlenmeyer flask.
8. Dim the room lights.
9. Slowly pour Solution A and Solution B into funnel.

A. During this reaction, luminol is changed into an ion called aminophthalate. Which entity has more chemical energy associated with its structure: luminol or aminophthalate? How can you tell? T/I

B. Suggest applications for this reaction. A

1.1 Alkanes

organic compound a molecular compound of carbon, not including $CO(g)$, $CO_2(g)$, and $HCN(g)$

Organic chemistry is the study of carbon compounds. As a general definition, an **organic compound** is a molecular compound containing carbon with the exception of carbon monoxide, $CO(g)$, carbon dioxide, $CO_2(g)$, and hydrogen cyanide, $HCN(g)$. Since carbon has 4 valence electrons, its atoms tend to form 4 covalent bonds. Carbon atoms often bond with one another to form chains. These chain structures become the backbones of a range of molecules, some of them very complex. Carbon-based molecules are the building blocks for life on Earth.

Most fuels are hydrocarbons, whose molecules consist only of carbon atoms and hydrogen atoms connected by covalent bonds. Hydrocarbon fuels include natural gas, gasoline, fuel oil, and diesel fuel. NASCAR racing cars burn an unleaded fuel similar to that used in most cars on the street (**Figure 1**). Natural gas, which is primarily methane, is a major fuel for electric power plants. Butane and propane are used to heat homes and to fuel tools such as soldering torches.

Figure 1 Hydrocarbons are sources of fuel all over the world.

Burning carbon-based fuels is a major contributor to global warming, according to most scientific models, due to the release of carbon dioxide into the atmosphere. Other environmental problems have also been associated with the release of carbon-containing compounds to our atmosphere and oceans. The use of hydrocarbons as fuel needs to be balanced with the ability of Earth's carbon cycle to remove carbon dioxide from the atmosphere.

Alkanes: Saturated Hydrocarbons

hydrocarbon a compound containing only carbon and hydrogen atoms

saturated hydrocarbon a hydrocarbon with only single covalent bonds between its carbon atoms

alkane a saturated hydrocarbon

A **hydrocarbon** is a compound that is composed only of carbon and hydrogen atoms. A **saturated hydrocarbon**, also known as an **alkane**, is a hydrocarbon in which all bonds between the carbon atoms are single bonds. The simplest saturated hydrocarbon (alkane) is methane, CH_4, with just 1 carbon atom bonded to 4 hydrogen atoms. Methane has a tetrahedral structure (**Figure 2**).

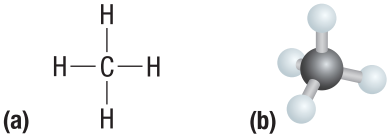


Figure 2 Two representations of the methane molecule: (a) the structural formula and (b) the ball-and-stick model

Ethane, C_2H_6, contains 2 carbon atoms. Each carbon atom in ethane is bonded to 4 atoms in a tetrahedral arrangement. **Figure 3** shows three ways of depicting ethane. Figure 3(a) is a structural formula that uses chemical symbols to represent atoms, and lines to represent individual bonds between atoms. Figure 3(b) is a ball-and-stick model that represents the atoms as spheres and incorporates "sticks" to represent the bonds between them. Figure 3(c) is a space-filling model in which atoms are depicted as spheres proportional to the actual size of the atoms. Models (b) and (c) show the three-dimensional arrangement of atoms in the molecule, which is not evident in the structural formula.

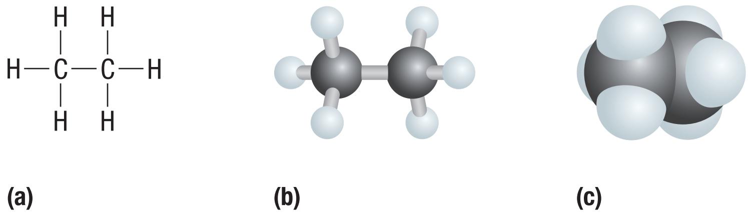


Figure 3 Three representations of ethane, C_2H_6: (a) the structural formula, (b) the ball-and-stick model, and (c) the space-filling model

Table 1 shows the first ten alkanes. As you can see, the compound names all have a prefix, which indicates the number of carbon atoms, and the suffix *-ane*. The general chemical formula for an alkane is C_nH_{2n+2}. Notice how the subscript indicating the number of CH_2 groups increases with the number of carbon atoms in the molecule.

Table 1 The First Ten Alkanes

Number of C atoms	Name	Molecular formula	Condensed formula
1	methane	CH_4	
2	ethane	C_2H_6	CH_3CH_3
3	propane	C_3H_8	$CH_3CH_2CH_3$
4	butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$
5	pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$
6	hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
7	heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$
8	octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
9	nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
10	decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$

Alkanes in which the carbon atoms form long chains are called straight-chain alkanes. Structural formulas of alkanes typically show the carbon atoms lying along a straight line (**Figure 4(a)**). Empirical evidence indicates, however, that the angle between any two carbon bonds in a chain is 109.5°, not 180°. The physical arrangement of carbon atoms in a straight-chain alkane therefore has a zigzag configuration (**Figure 4(b)**).

LEARNING TIP

Line Diagrams
In a line diagram, imagine that there is a carbon atom at the end of every line and at the intersection of every line. Each one is surrounded by the maximum number of hydrogen atoms. For example, there are 8 carbon atoms and 18 hydrogen atoms in Figure 4(c).

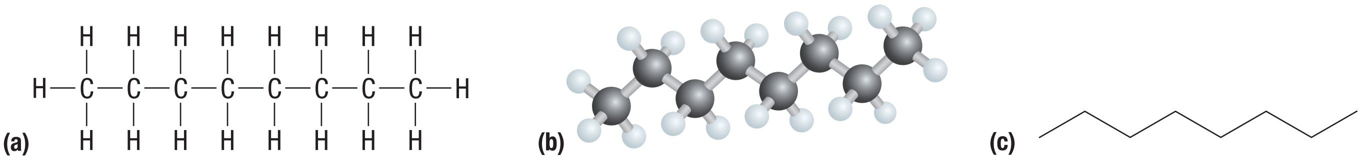


Figure 4 (a) The structural formula, (b) the ball-and-stick model, and (c) the line diagram of octane, C_8H_{18}

Not all alkanes are based on straight chains. Their carbon atoms can also join to form rings and branches. A **cyclic alkane**, or cycloalkane, is a hydrocarbon in which the carbon atoms form a closed loop instead of a chain. Cyclopropane, C_3H_6, is the simplest cyclic alkane. Its carbon atoms form an equilateral triangle with bond angles of 60° (**Figure 5**). The general formula of cyclic alkanes is C_nH_{2n}. WEB LINK

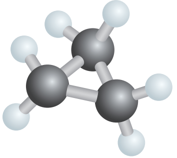


Figure 5 Cyclopropane, C_3H_6

cyclic alkane a hydrocarbon in which the main structure consists of a chain of carbon atoms joined to form a closed ring

Mini Investigation

Arranging Carbon Atoms

Skills: Performing, Observing, Communicating

SKILLS HANDBOOK A2.4

Each carbon atom can bond with 4 different atoms. Carbon chains form a variety of configurations, such as long chains, branched chains, and cyclic structures. In this investigation, you will construct models of some different carbon compound structures.

Equipment and Materials: molecular modelling kit

1. Use the molecular modelling kit to build a model of a molecule that contains 5 carbon atoms and 12 hydrogen atoms.
2. Draw a structural formula of your molecule.
3. Using the same model parts, build another molecule that cannot be twisted into the same shape as the original molecule.
4. Draw a structural formula of this molecule.

A. How many different molecules of C_5H_{12} are possible? K/U

B. Predict the number of arrangements that are possible for C_6H_{14}. Test your prediction. T/I

Structural Isomerism

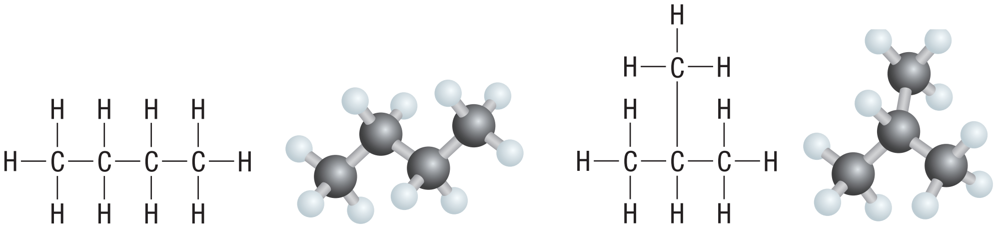
In all of the examples we have examined so far, the molecules form chains or rings in which each carbon atom is bonded to 2 other carbon atoms. The only exceptions are the carbon atoms at the ends of the chains, which are bonded to only 1 other carbon atom. Some hydrocarbons, however, contain one or more hydrocarbon branches attached to the main structure of the molecule. The branch is called an **alkyl group**. Alkyl groups are named with the prefix indicating the number of carbon atoms in the branch (as in Table 1) and a *-yl* suffix. An alkyl group consisting of a single carbon atom and 3 hydrogen atoms (–CH_3) is called a methyl group. A group with a 2-carbon chain (–CH_2CH_3) is an ethyl group. An alkyl group is a type of **substituent group**, which is any atom or group that replaces hydrogen in an organic molecule.

alkyl group one or more carbon atoms that form a branch off the main chain of a hydrocarbon

substituent group an atom or group that replaces a hydrogen atom in an organic compound

Most hydrocarbons with 4 or more carbon atoms exhibit structural isomerism. Structural isomerism occurs when 2 molecules each have the same numbers and types of atoms but these atoms are bonded in different ways. Each molecule is a **structural isomer** of the other. For example, there are 2 alkanes that have the molecular formula C_4H_{10} (**Figure 6**). Butane is a straight-chain molecule, while methyl-propane has a branched structure. Both have the formula C_4H_{10}, but because of their different structures, these compounds exhibit different properties. For example, the boiling point of butane is −0.5 °C, whereas that of methylpropane is −12 °C.

structural isomer a compound that has the same molecular formula as another compound, but a different structure



(a) butane **(b)** methylpropane

Figure 6 (a) Butane (b) The branched isomer of butane: methylpropane. In this structure, one of the C–C bonds appears to be longer than the others. This is only to make the structure easier to interpret. The bonds are actually the same length.

Naming Alkanes

There are millions of organic compounds, so it would be impossible to have—or to remember—simple common names for all of them. The International Union of Pure and Applied Chemistry (IUPAC) has established a system for naming chemicals that is used worldwide. Other naming systems are still used frequently, though, so you may see compounds named differently in contexts outside this course.

The names of the alkanes beyond butane are obtained by adding the suffix *-ane* to the Greek root for the number of carbon atoms (Table 1). For a branched hydrocarbon, we use the longest continuous chain of carbon atoms to determine the root name for the hydrocarbon. We indicate the length of a branch by the name of the alkyl group, and its location by numbering from the shortest end of the parent chain.

Cyclic hydrocarbons are named in a similar way. The name is based on the number of carbon atoms in the ring, with the prefix *cyclo-* added.

In the following tutorial, you will practise drawing and naming several different types of alkanes. WEB LINK

Structure*	**Name†**
$—CH_3$	methyl
$—CH_2CH_3$	ethyl
$—CH_2CH_2CH_3$	propyl
$CH_3\overset{\vert}{C}HCH_3$	propan-2-yl, or isopropyl
$—CH_2CH_2CH_2CH_3$	butyl
$CH_3\overset{\vert}{C}HCH_2CH_3$	butan-2-yl, or sec-butyl

* The bond with one end open shows the point of attachment of the substituent to the carbon chain.

† The first name for each group is the IUPAC name. You may see the other names in other contexts.

Figure 7 Alkyl groups through C_4

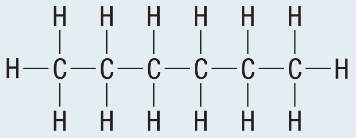
Tutorial 1 Naming and Drawing Alkanes

This tutorial outlines a systematic way of naming an organic compound or drawing its structure. In either case, you need to first recognize the longest carbon chain in the compound and then identify any substituent groups that may be present.

1. Identify the longest carbon chain, called the parent chain.
2. Identify all of the groups (substituents) attached to the parent chain (**Figure 7**).
3. Number the parent chain from the end so that the substituents are attached to the carbon atom with the lowest possible number. If there are two or more groups and the numbering is a tie, the group that comes first alphabetically gets the lowest number.
4. If the same substituent is present more than once, use a prefix to indicate this (*di-*, *tri-*, *tetra-*) and include a number to indicate each substituent's location.
5. When writing the final name, list substituents in alphabetical order, ignoring any prefixes. Separate words by hyphens; separate numbers by commas. If there are two possible ways to arrange a parent chain, use the simplest possible arrangement.

Sample Problem 1: Naming Unbranched Alkanes from Structural Formulas

Determine the correct name for the following compound:



Solution

Step 1. Identify the parent chain.

There are 6 carbon atoms in the chain, so it is hexane.

Step 2. Identify all of the groups (substituents) attached to the parent chain.

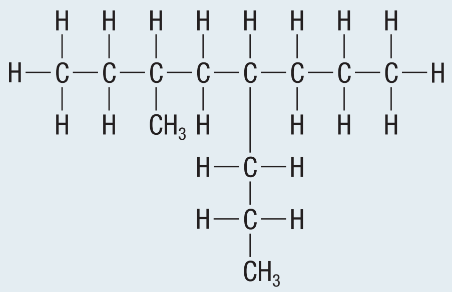
This is an unbranched alkane. It has no substituent groups.

The compound is named hexane.

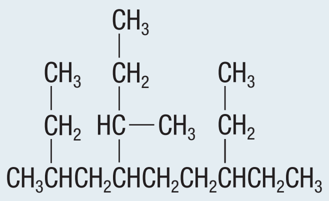
Sample Problem 2: Naming Branched Alkanes from Structural Formulas

Determine the correct name for each of the following compounds:

(a)



(b)



Solution (a)

Step 1. Identify the parent chain.

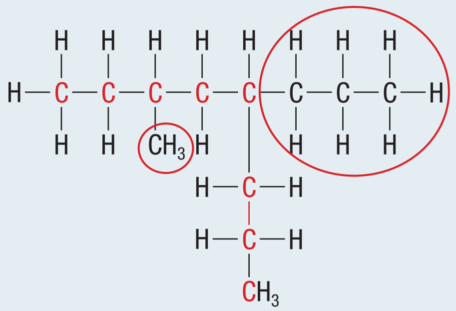
The longest carbon chain has 8 carbon atoms. Its root name is octane.

LEARNING **TIP**

Memory Aid: Table of Terms

You might find it helpful to create a 3-column table summarizing the naming of alkanes with 1 to 10 carbon atoms. List the unbranched straight-chain alkanes, the unbranched cyclo alkanes, and the alkyl groups.

Step 2. Identify all of the groups (substituents) attached to the parent chain.



Step 3. Number the parent chain from the end so that the substituent is attached to the carbon atom with the lowest possible number. If there are two or more groups and the numbering is a tie, the group that comes first alphabetically gets the lowest number.

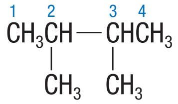
Numbering from the left gives the lowest numbers: 3 for the methyl group and 5 for the propyl group.

Step 4. If the same substituent is present more than once, use a prefix to indicate this (*di-*, *tri-*, *tetra-*) and include a number to indicate each substituent's location.

Methyl groups are attached to carbon atoms 3 and 6, so the prefix is *di-*.

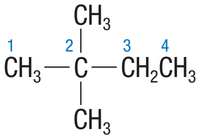
Step 5. When writing the final name, list substituents in alphabetical order, ignoring any prefixes. Separate words by hyphens; separate numbers by commas.

"Methyl" comes before "propyl" in the alphabet, so the name begins with 3-methyl-5-propyl. The compound's name is 3-methyl-5-propyloctane.



$\underset{CH_3}{CH_3CH}-\underset{CH_3}{CHCH_3}$

2,3-dimethylbutane



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2CH_3$

2,2-dimethylbutane

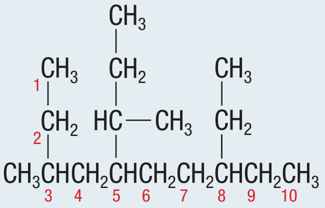
Figure 8 Notice how the two methyl groups are numbered in these structural isomers.

Notice that structural formulas are sometimes condensed, eliminating the bonds around the carbon atoms that do not have substituent groups. This arrangement takes less space and makes it easier to see the substituent groups (**Figure 8**).

Solution (b)

Step 1. Identify the parent chain.

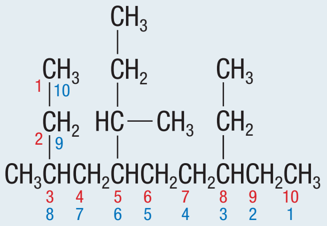
The parent chain has 10 carbon atoms, so its root name is decane.



Step 2. Identify all of the groups (substituents) attached to the parent chain.

This compound has a 1-carbon group, a 4-carbon group, and a 2-carbon group. According to Figure 7, the substituent groups are methyl, butan-2-yl, and ethyl.

Step 3. Number the parent chain from the end so that the substituent is attached to the carbon atom with the lowest possible number. If there are two or more groups and the numbering is a tie, the group that comes first alphabetically gets the lowest number.



Numbering from either end places the first group on carbon atom 3. However, "ethyl" comes before "methyl" in the alphabet, so number from the "ethyl" end of the molecules, using the blue numbers. This places the ethyl group on carbon 3, the butan-2-yl group on carbon 6, and the methyl group on carbon 8.

Step 4. If the same substituent is present more than once, use a prefix to indicate this (*di-*, *tri-*, *tetra-*) and include a number to indicate each substituent's location.

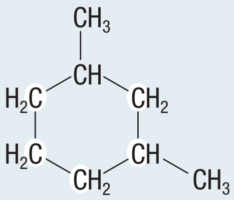
The same substituent does not appear more than once.

Step 5. When writing the name, list substituents in alphabetical order, ignoring prefixes. Separate words by hyphens; separate numbers by commas.

The substituents will be listed in the order butan-2-yl, ethane, and methane. This compound is 6-butan-2-yl-3-ethyl-8-methyldecane.

Sample Problem 3: Naming Cyclic Alkanes from Structural Formulas

Determine the correct name for the compound on the right. Follow the same steps as for naming a branched alkane, except that you are naming the parent carbon ring in Step 1.



Solution

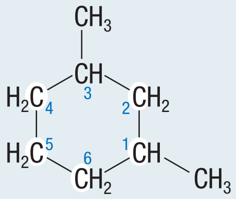
Step 1. Identify the parent carbon ring.

The ring contains 6 carbon atoms, so it is a cyclohexane.

Step 2. Identify all of the groups (substituents) attached to the parent chain.

The ring has two alkyl groups bonded to it: both methyl groups.

Step 3. Number the carbon atoms in the ring to give the two groups the lowest numbers. If there are two or more groups and the numbering is a tie, the group that comes first alphabetically gets the lowest number.



Both groups are “methyl,” so the numbering can start with either group and give the same answer: 1 and 3. Note that you do not have to include the number “1” if only one substituent is present on the ring.

Step 4. If the same substituent is present more than once, use a prefix to indicate this (*di*-, *tri*-, *tetra*-) and include a number to indicate each substituent’s location.

There are two methyl groups, so the name includes “dimethyl.”

Step 5. When writing the name, list substituents in alphabetical order, ignoring prefixes.

The name of the compound is 1,3-dimethylcyclohexane.

LEARNING **TIP**

Numbering Carbon Atoms
Always use the lowest possible numbers. For example, the methyl groups in Sample Problem 3 are on carbon atoms 1 and 3, not 1 and 5.

When you are given the name of an alkane and asked to draw its structure, follow these steps:

1. Draw the parent chain or carbon ring from the last part of the compound name.
2. Identify the carbon atoms where each of the substituents is attached.
3. Draw the substituents attached to the parent chain or ring.

Sample Problem 4: Drawing Alkanes

Draw structural formulas for each of the following compounds:

(a) 4-ethyl-3,5-dimethylnonane

(b) 7-ethyl-2-methyl-4-(propan-2-yl)decane

(c) 1-ethyl-2-propylcyclobutane

Solution (a)

Step 1. Draw the parent chain from the last part of the compound name.

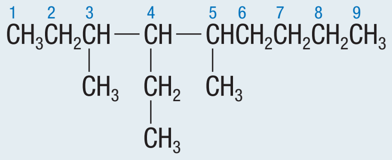
The root name nonane indicates that the compound has a 9-carbon backbone.

Step 2. Identify the carbon atoms where each of the substituents is attached.

The numbers 4, 3, and 5 indicate that substituents are attached at these carbon atoms.

Step 3. Draw the substituents attached to the parent chain.

It has an ethyl group bonded to the fourth carbon atom, and methyl groups bonded to the third and fifth carbon atoms. Therefore, the structure of 4-ethyl-3,5-dimethylnonane is as shown:



$CH_3CH_2\underset{CH_3}{CH}-\underset{\underset{CH_3}{CH_2}}{CH}-\underset{CH_3}{CH}CH_2CH_2CH_2CH_3$

Notice that, in this and later structures, the condensed notation is used.

Solution (b)

Step 1. Draw the parent chain from the last part of the compound name.

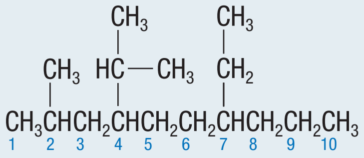
The decane chain has 10 carbon atoms.

Step 2. Identify the carbon atoms where each of the substituents is attached.

There are substituents on carbon atoms 7, 2, and 4.

Step 3. Draw the substituents attached to the parent chain.

The molecule has 3 substituents: a methyl group on carbon 2, a propan-2-yl group (which is a 3-carbon chain bonded at the second carbon atom) on carbon 4, and an ethyl group on carbon 7. 7-ethyl-2-methyl-4-(propan-2-yl)decane therefore has the following structure:



$CH_3\overset{CH_3}{CH}CH_2\overset{\overset{CH_3}{HC-CH_3}}{CH}CH_2CH_2\overset{\overset{CH_3}{CH_2}}{CH}CH_2CH_2CH_3$

Solution (c)

Step 1. Draw the carbon ring from the last part of the compound name.

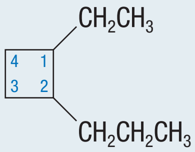
Cyclobutane is a ring of 4 carbon atoms.

Step 2. Identify the carbon atoms where each of the substituents is attached.

The substituents are attached at carbon atoms 1 and 2.

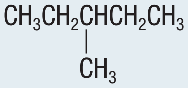
Step 3. Draw the substituents attached to the ring.

This compound has an ethyl group and a propyl group bonded to adjacent carbon atoms on the ring. Because ethyl comes first alphabetically, it is placed on carbon atom 1. Therefore 1-ethyl-2-propylcyclobutane has the following structure:



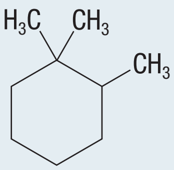
Practice

1. Write the name of each of the following compounds: K/U
   - (a) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
   - (b)

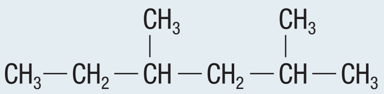


$CH_3CH_2\underset{CH_3}{CH}CH_2CH_3$

   - (c)



   - (d)



$CH_3-CH_2-\overset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-CH_3$

2. Draw a structural formula for each of the following compounds: K/U C
   - (a) decane
   - (b) 3-ethyl-5-methylheptane
   - (c) 2,3-dimethylpentane
   - (d) 1,3-diethylcyclopentane

Properties of Alkanes

The two elements that make up hydrocarbons are carbon and hydrogen. These two elements have similar electronegativities. This means that the bonds between carbon and hydrogen are close to being non-polar. Coupled with the fairly even arrangement of hydrogen atoms within alkane molecules, this causes the molecules to be non-polar. Van der Waals forces are the main intermolecular force in hydrocarbon compounds. These forces are very weak, so alkanes exhibit relatively low boiling and melting points (**Table 2**).

Table 2 Selected Properties of the First Ten Straight-Chain Alkanes

Name	Formula	Molar mass (g/mol)	Melting point (°C)	Boiling point (°C)	Number of structural isomers
methane	CH_4	16	−182	−162	1
ethane	C_2H_6	30	−183	−89	1
propane	C_3H_8	44	−187	−42	1
butane	C_4H_{10}	58	−138	0	2
pentane	C_5H_{12}	72	−130	36	3
hexane	C_6H_{14}	86	−95	68	5
heptane	C_7H_{16}	100	−91	98	9
octane	C_8H_{18}	114	−57	126	18
nonane	C_9H_{20}	128	−54	151	35
decane	$C_{10}H_{22}$	142	−30	174	75

The boiling points of alkanes are related to the length of the carbon chain: as the chain gets longer, the boiling point gets higher. Chemists take advantage of this pattern to separate mixtures of alkanes using a process called fractional distillation. During fractional distillation, the temperature of a mixture of hydrocarbons is slowly increased. As the boiling point of each alkane is reached, the alkane boils out of the mixture. Chemists can collect the vapour and condense it to obtain mixtures of alkanes with similar boiling points and carbon chain lengths.

Fractional distillation (or fractionation) is used on an industrial scale in oil refineries (**Figure 9**). It enables oil and gas companies to separate the crude oil extracted from the ground. Fractional distillation separates the lighter fractions of the crude, such as natural gas and other fuel gases, from the heavier fractions that are used to make waxes, asphalt, and so on. WEB LINK

Figure 9 In a fractionation tower, fractional distillation separates the lighter components of crude oil from the heavier fractions.

Reactions of Alkanes

In general, alkanes are fairly unreactive. For example, at 25 °C, alkanes do not react with acids, bases, or strong oxidizing agents. This chemical inertness makes them valuable as lubricating materials and as the backbone for structural materials such as plastics.

Alkanes are used as fuels because their **complete combustion** releases a lot of energy, along with carbon dioxide and oxygen. For example, the complete combustion of butane with oxygen is represented by the equation

$$2\ C_4H_{10}(g) + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(g) + \text{thermal energy}$$

Although all alkanes burn, some are much more combustible than others. Smaller, gaseous alkanes, such as methane and ethane, are highly flammable. Longer-chain alkanes are difficult to ignite until heated to a temperature at which they vaporize. In addition, different hydrocarbons release different quantities of energy per unit of mass when they burn. These and other properties affect how we use alkanes.

complete combustion a chemical reaction in which a compound reacts with oxygen, O_2; if the compound is a hydrocarbon, the products of the reaction are carbon dioxide, water, and thermal energy

UNIT TASK BOOKMARK

Mixtures of alkanes, such as gasoline, are sometimes used as solvents. Consider their effectiveness and their safety as you work on the Unit Task outlined on page 116.

The combustion of fuels to provide energy for transportation and electricity also produces carbon dioxide and water. Carbon dioxide is a naturally occurring greenhouse gas that helps keep Earth warm by reducing the proportion of the Sun's heat that is reflected back into space. While this greenhouse effect is necessary for life on Earth, too much carbon dioxide contributes to climate change. As a result, many countries are investigating alternative energy sources to reduce the consumption of hydrocarbons for energy.

Table 3 lists some common uses of alkanes.

Table 3 Selected Uses of Alkanes

Length of carbon chain	Uses
1–4	Fuels such as natural gas for heating and cooking, propane for barbecues and soldering torches (**Figure 10**), and butane for lighters
5–12	Fuels such as gasoline
12–18	Fuels such as jet fuel
18–20	Fuels such as home heating oil
20–30	Lubricating oils such as engine oil
30–40	Fuel oils such as ship fuel
40–50	Waxes and thick oils such as paraffin wax and petroleum jelly
More than 50	Tars used in road surfacing

Figure 10 A soldering torch burns propane to produce a flame hot enough to melt some metals.

Alkyl Halides

Sometimes alkanes include substituent groups that are halogens, such as chlorine or fluorine. An alkane that contains a halogen is called an **alkyl halide**. Alkyl halides may be formed by substitution reactions:

alkyl halide an alkane in which one or more hydrogen atoms have been substituted with one or more halogen atoms

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

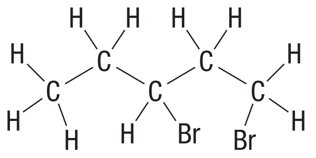
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_2 + HCl$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

Alkyl halides may include more than one halogen element. For example, substituted methanes containing both chlorine and fluorine are called chlorofluorocarbons (CFCs) or Freons. Their general formula is CF_xCl_y. These compounds are non-toxic and mostly unreactive. They have been extensively used as coolant fluids in refrigerators and air conditioners. Unfortunately, their chemical inertness allows Freons to remain in the atmosphere for so long that they eventually reach the stratosphere, where they react with ozone and damage Earth's protective ozone layer. Therefore, the use of these compounds is being rapidly phased out.

Alkyl halides are named by writing the root of the halogen name first, with the suffix -*o*, followed by the name of the parent alkane. If necessary to avoid ambiguity, the position of the halogen is specified with a number **(Figure 11)**. As usual, the substituent groups are written in alphabetical order.

The halogens are much more electronegative than are carbon and hydrogen. When halogens bond to a hydrocarbon chain or ring, they attract electrons, pulling them away from the carbon atoms. This makes the molecule polar. The resulting polarity increases the strength of the intermolecular forces. Since more energy is needed to overcome these forces, the boiling and melting points of alkyl halides are higher than those of the corresponding alkanes.



1,3-dibromopentane

Figure 11 The name of this alkyl halide includes numbers to indicate the position of the 2 bromine atoms.

1.1 Review

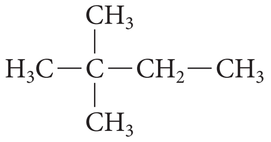
Summary

- Hydrocarbons contain hydrogen and carbon. In a saturated hydrocarbon, the atoms of carbon are bonded to each other by single bonds.
- Structural isomers are compounds that have the same molecular formula but different molecular geometry.
- Alkanes may have a straight-chain structure or a ring structure. Substituent groups may be attached to the parent structure.
- Alkyl halides are alkanes in which halogen atoms have substituted for one or more hydrogen atoms.

Questions

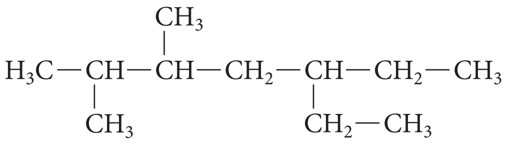
1. Define each of the following terms: K/U
   (a) organic compound
   (b) alkane
   (c) structural isomer
   (d) substituent group
   (e) alkyl group
   (f) alkyl halide
2. Name the following compounds: T/I C

(a)



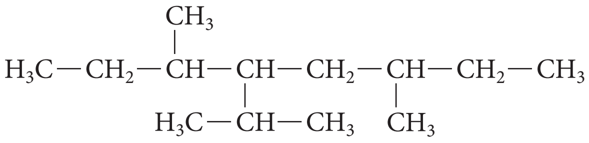
$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$$

(b)



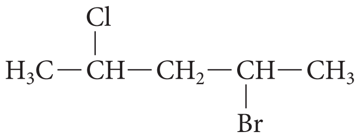
$$H_3C-\underset{CH_3}{CH}-\overset{CH_3}{CH}-CH_2-\underset{CH_2-CH_3}{CH}-CH_2-CH_3$$

(c)



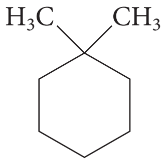
$$H_3C-CH_2-\overset{CH_3}{CH}-\underset{H_3C-CH-CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-CH_3$$

(d)

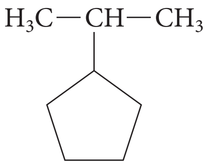


$$H_3C-\overset{Cl}{CH}-CH_2-\underset{Br}{CH}-CH_3$$

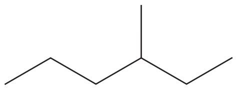
(e)



(f)



(g)



3. Draw and name five structural isomers that all have the molecular formula C_6H_{14}. K/U T/I C
4. Draw the structural formula and write the molecular formula for each of the following alkanes: T/I C
   (a) 3,4-dimethylheptane
   (b) 2,2-dimethylpentane
   (c) 4-propyl-3,5-diethyloctane
   (d) 1-ethyl-3-propylcyclohexane
5. Draw the structural formula for each of the following compounds: T/I C
   (a) 1,3-dibromocyclopentane
   (b) 4-chloro-1-fluorobutane
   (c) 3-iodo-4-methylnonane
6. (a) Why does water not mix with liquid hydrocarbons?
   (b) Most hydrocarbons are less dense than water. How does this difference in density affect the cleanup of an oil spill on a still lake?
   (c) Some liquid organic halides are denser than water. How might this difference affect the cleanup of an organic halide spill in a river? K/U A
7. 2,2,4-trimethylpentane (isooctane) is used as a reference for octane ratings for gasoline. Draw the structural formula for isooctane. T/I C
8. A methane leak can pose an extreme fire and explosion hazard, especially in an enclosed area. In contrast, a leak of paraffin is typically not a significant hazard. Use your knowledge of the properties of different types of alkanes (including the information in Tables 2 and 3) to explain the differences in danger of these two substances. T/I A
9. A chemist burns samples of ethane, pentane, nonane, and dodecane (which contains 12 carbon atoms per molecule) and measures the volume of carbon dioxide produced during each reaction. If the chemist starts with the same amount (in moles) of each compound, which will produce the largest volume of carbon dioxide? Explain your answer. T/I A

1.2 Alkenes and Alkynes

As you learned in Section 1.1, all of the carbon–carbon bonds in an alkane are single bonds. In other organic compounds, however, double or triple covalent bonds connect some of the pairs of carbon atoms. A hydrocarbon containing carbon–carbon double or triple bonds is called an **unsaturated hydrocarbon** because each molecule contains fewer than the maximum number of hydrogen atoms. Unsaturated hydrocarbons have a variety of uses in industry and everyday life. For example, ethyne (commonly known as acetylene) is the fuel used in welding and cutting torches. This molecule contains a triple bond between its 2 carbon atoms (**Figure 1**).

Ethene, another unsaturated hydrocarbon, is used in agriculture to help ripen fruit more quickly. Ethene contains a carbon–carbon double bond (**Figure 2**). Note that each carbon atom always has four bonds. In an ethene molecule each carbon bonds to 3 atoms (1 carbon and 2 hydrogen atoms), but the carbon–carbon bond is a double bond. In ethyne (Figure 1), each carbon atom is bonded to only 1 hydrogen atom; the remaining three bonds connect to the other carbon atom. In this section, you will learn about hydrocarbons that contain multiple bonds.

unsaturated hydrocarbon an organic compound, consisting of carbon and hydrogen, with one or more double or triple bonds joining pairs of carbon atoms within the molecules

(b) $H-C\equiv C-H$

Figure 1 (a) An oxyacetylene torch burns ethyne (acetylene) in oxygen. (b) Ethyne contains a triple bond.

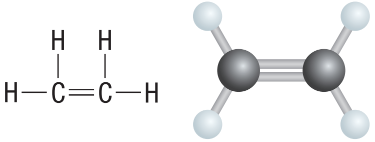


Figure 2 The 2 carbon atoms in ethene are joined by a double bond.

Alkenes and Alkynes: Unsaturated Hydrocarbons

A hydrocarbon that contains at least one carbon–carbon double bond is called an **alkene**. Alkenes with one double bond have the general formula C_nH_{2n}. The simplest alkene is ethene, C_2H_4 (Figure 2).

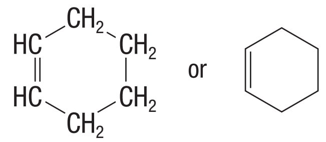
An unsaturated hydrocarbon that contains at least one triple bond between 2 carbon atoms is called an **alkyne**. Alkynes with one triple bond have the formula C_nH_{2n-2}. The simplest alkyne is ethyne (Figure 1).

Longer unsaturated compounds can include both single and multiple bonds. Like alkanes, alkenes and alkynes can form ring structures (**Figure 3**).

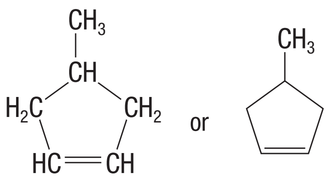
Scientists use the general term **aliphatic hydrocarbon** to refer to a compound that has a structure based on straight or branched chains or rings of carbon atoms. Alkanes, alkenes, and alkynes are all aliphatic hydrocarbons.

alkene a hydrocarbon that contains at least one carbon–carbon double bond

alkyne a hydrocarbon that contains at least one carbon–carbon triple bond



cyclohexane



4-methyl cyclopentene

Figure 3 Structural formulas for two cyclic alkenes

aliphatic hydrocarbon a compound that has a structure based on straight or branched chains or rings of carbon atoms

Naming Alkenes and Alkynes

Like alkanes, unsaturated hydrocarbon names are based on the longest hydrocarbon chain. The name of an alkene ends in *-ene* and the name of an alkyne ends in *-yne*. For example, the alkane C_3H_8 is propane, the alkene C_3H_6 is propene, and the alkyne C_3H_4 is propyne. Tutorial 1 describes in detail the process for naming and drawing unsaturated hydrocarbons using the IUPAC convention. WEB LINK

Tutorial 1 Naming and Drawing Alkenes and Alkynes

The rules for naming alkenes and alkynes are similar to those for alkanes.

1. Identify the parent chain or ring that contains the multiple bond.
2. Identify whether the chain or ring contains a double bond (in which case it is an alkene) or a triple bond (in which case it is an alkyne). If the hydrocarbon chain has more than one double or triple bond, add a suffix to show the number of multiple bonds (such as *-diene* or *-triene*).
3. Number the parent chain or ring so that the first carbon atom involved in a multiple bond has the lowest possible number. Write this number before the suffix. (This is only necessary if there are more than 3 carbon atoms.)
4. Number and name any substituents using the same rules as were used for alkanes. If the double or triple bond is in the middle of a chain, start the numbering from the end nearer the substituent group.

Following these rules, $CH_2{=}CHCH_2CH_3$ is called but-1-ene and $CH_3CH{=}CHCH_3$ is called but-2-ene. You may encounter an older naming method in which the number of the first carbon to include the multiple bond is written at the beginning of the name. For example, but-2-ene would be called 2-butene.

As another example, a chain of 8 carbon atoms with double bonds at the second, fourth, and sixth carbon atoms is named octa-2,4,6-triene. An 8-carbon chain with triple bonds at the second, fourth, and sixth carbon atoms is octa-2,4,6-triyne.

$CH_3CH{=}CHCH{=}CHCH{=}CHCH_3$ octa-2,4,6-triene

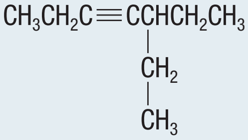
$CH_3C{\equiv}CC{\equiv}CC{\equiv}CCH_3$ octa-2,4,6-triyne

In the following sample problem, you will learn how to name unsaturated hydrocarbons by examining their structural formulas. Next, you will learn how to draw their structural formulas from their names.

Sample Problem 1: Naming Alkenes and Alkynes

Determine the correct name for each of the following compounds:

(a)

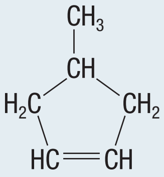


$$\mathrm{CH_3CH_2C{\equiv}C\underset{\substack{|\\ CH_2\\ |\\ CH_3}}{C}HCH_2CH_3}$$

(b) $CH_3CH{=}CHCH{=}CH_2$

(c) $CH_2{=}CHCHClCH_2CH_3$

(d)



Solution (a)

Step 1. Identify the parent chain or ring that contains the multiple bond.

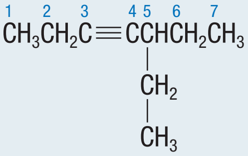
In this compound, the longest chain is 7 carbon atoms with one triple bond, so the root name contains *hept*-.

Step 2. Identify whether the chain contains a double bond (in which case it is an alkene) or a triple bond (in which case it is an alkyne).

The molecule contains a triple bond, so it is an alkyne. Its name contains -*yne*. The root name is therefore heptyne.

Step 3. Number the parent chain so that the first carbon atom involved in a multiple bond has the lowest possible number. Write this number before the suffix.

The triple bond is attached to the third carbon atom: hept-3-yne.



$$\mathrm{\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{C}{\equiv}\overset{4}{C}\underset{\substack{|\\ CH_2\\ |\\ CH_3}}{\overset{5}{C}}H\overset{6}{CH_2}\overset{7}{CH_3}}$$

Step 4. Number and name any substituents using the same rules as were used for alkanes. If the double or triple bond is in the middle of a chain, start the numbering from the end nearer the substituent.

The ethyl group is bonded to the fifth carbon atom in the chain: 5-ethyl.

This compound is 5-ethylhept-3-yne.

Solution (b)

Step 1. Identify the parent chain or ring that contains the multiple bond.

The unbranched chain has 5 carbon atoms: *pent*-.

Step 2. Identify whether the chain contains a double bond or a triple bond.

There are two double bonds, so it is a pentadiene.

Step 3. Number the parent chain so that the first carbon atom involved in a multiple bond has the lowest possible number.

The double bonds are on the first and third carbon atoms so this compound is penta-1,3-diene.

Solution (c)

Step 1. Identify the parent chain or ring that contains the multiple bond.

There are 5 carbon atoms in the chain: *pent*-.

Step 2. Identify whether the chain contains a double bond or a triple bond.

There is one double bond, so the compound is a pentene.

Step 3. Number the parent chain so that the first carbon atom involved in a multiple bond has the lowest possible number.

The double bond is between the first and second carbon atoms: pent-1-ene.

Step 4. Number and name any substituents using the same rules as were used for alkanes. If the double or triple bond is in the middle of a chain, start the numbering from the end nearer the substituent.

This compound contains a chlorine atom bonded to atom 3.

Therefore, this compound is 3-chloropent-1-ene.

Solution (d)

Step 1. Identify the parent chain or ring that contains the multiple bond.

The ring contains 5 carbon atoms: *cyclopent*-.

Step 2. Identify whether the ring contains a double bond or a triple bond.

There is one double bond, so it is a cyclopentene.

Step 3. Number the parent ring so that the first carbon atom involved in a multiple bond has the lowest possible number.

In a ring, the carbon atoms are always numbered so that the multiple bond is between carbon atoms 1 and 2: cyclopent-1-ene.

Step 4. Number and name any substituents using the same rules as were used for alkanes.

Whichever way you count around the ring, the methyl group is attached to carbon atom 4.

This compound is therefore 4-methylcyclopent-1-ene.

When you are given the name of an alkene or alkyne and asked to draw its structure, the steps are similar to those for drawing an alkane:

1. Draw the parent chain or carbon ring from the last part of the compound name.
2. Identify the carbon atom where each of the multiple bonds (and substituents) is attached.
3. Draw the multiple bonds (and substituents) at the appropriate locations.

Sample Problem 2: Drawing Structures of Alkenes and Alkynes

Draw the structural formula of each of the following compounds:

(a) 2-methylpenta-1,4-diene

(b) 4,5-dimethylhept-2-yne

Solution (a)

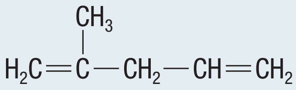
Step 1. Draw the parent chain or carbon ring from the last part of the compound name.

The name *penta-1,4-diene* tells us that the longest carbon chain is 5 carbon atoms.

Step 2. Identify the carbon atom where each of the multiple bonds (and substituents) is attached.

The name *diene* indicates that the compound contains two double bonds. The number 1,4 tells us that these double bonds are between the first and second and fourth and fifth carbon atoms. The *2-methyl* part of the name indicates that the molecule also contains a methyl group bonded to the second carbon atom.

Step 3. Draw the multiple bonds (and substituents) at the appropriate locations.



$$H_2C{=}C(CH_3){-}CH_2{-}CH{=}CH_2$$

Solution (b)

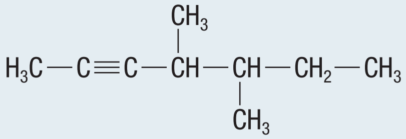
Step 1. Draw the parent chain or carbon ring from the last part of the compound name.

The longest carbon chain is 7 carbon atoms.

Step 2. Identify the carbon atom where each of the multiple bonds (and substituents) is attached.

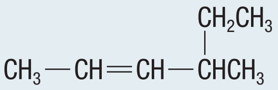
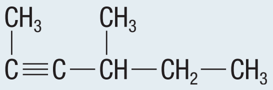
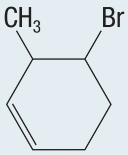
It contains one triple bond between the second and third carbon atoms. It also contains two methyl groups, bonded to the fourth and fifth carbon atoms.

Step 3. Draw the multiple bonds and substituents at the appropriate locations.



$$H_3C{-}C{\equiv}C{-}CH(CH_3){-}CH(CH_3){-}CH_2{-}CH_3$$

Practice

1. Name each of the following compounds: K/U
   (a) $CH_2{=}CH{-}CH_2{-}CH_3$
   (b)
   
   $CH_3{-}CH{=}CH{-}CH(CH_2CH_3)CH_3$
   (c)
   
   $CH_3{-}C{\equiv}C{-}CH(CH_3){-}CH_2{-}CH_3$
   (d)
   

2. Draw the structural formula for each of the following compounds: K/U C
   (a) hex-3-ene
   (b) 6-methylhepta-2,4-diene
   (c) 7-bromooct-3-yne
   (d) 3-ethylcyclopent-1-ene

Mini **Investigation**

Isomers of Pentene

Skills: Performing, Observing, Communicating

SKILLS HANDBOOK **A2.4**

Equipment and Materials: molecular modelling kit

1. Use the molecular modelling kit to build all the possible isomers of pentene.
2. After building each isomer, draw its structural formula and write its molecular formula.

A. How many isomers of pentene are there? K/U

B. Are there more isomers of pentene than pentane? Explain your answer. T/I

C. Look for a predictive pattern based on the number of multiple bonds in a hydrocarbon and the number of possible isomers. Explain your conclusion. T/I

Cis–Trans Isomerism

If you used a molecular modelling kit in Section 1.1 to build isomers of pentane, you probably noticed that you can rotate the carbon "atoms" around the single bonds connecting each atom. As a result, you could create many three-dimensional models that look different but are actually identical, having 5 carbon atoms in a chain. However, when you made the models of pentene, you may have noticed that you cannot rotate the carbon atoms around the double bond. Therefore, the groups on different sides of a double bond are in a fixed position relative to each other (**Figure 4**).

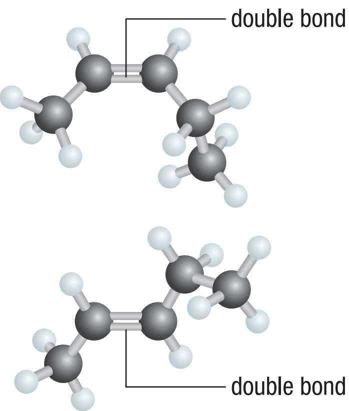


Figure 4 These two pentene structures represent two different compounds because the molecule cannot rotate around the double bond.

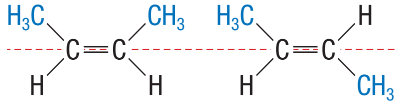
The two pentene structures in Figure 4 are stereoisomers. **Stereoisomers** have the same kind and number of atoms bonded in the same order but have different arrangements in space. Stereoisomers cannot be changed from one to another by simple rotation. Bonds would have to be broken and re-formed. Stereoisomers are distinct compounds with different properties, such as different melting points.

stereoisomers molecules that have the same chemical formula and structural backbone, but with a different arrangement of atoms in space

***cis* isomer** a stereoisomer in which the groups of interest are located on the same side of a double bond

***trans* isomer** a stereoisomer in which the groups of interest are located on opposite sides of a double bond

In this textbook we use the terms *cis* and *trans* to describe the positions of the parts of a molecule around a double bond. A ***cis* isomer** has matching alkyl groups located on the same side of the double bond. The ***trans* isomer** has the groups located on opposite sides of the double bond (**Figure 5**). When we refer to the "sides" of the double bond, we mean the two sides of the molecule divided by a line running along the double bond. We use the *cis/trans* naming system only when two of the substituents are the same (methyl groups in this case), and only for alkenes. IUPAC conventions use a different system, incorporating the letters E and Z, which you may see in other contexts.



(a) *cis*-but-2-ene **(b)** *trans*-but-2-ene

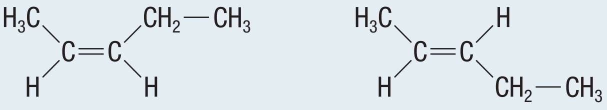
Figure 5 Two stereoisomers of but-2-ene. In *cis*-but-2-ene, the methyl groups are on the same side of the double bond. In *trans*-but-2-ene, the methyl groups are on opposite sides of the double bond.

Tutorial 2 Naming and Drawing *Cis–Trans* Isomers

In this tutorial, you will practise naming and drawing *cis* and *trans* isomers of alkenes.

Sample Problem 1: Naming Stereoisomers

Figure 6 shows two stereoisomers of pent-2-ene. Name each stereoisomer.



(a) **(b)**

Figure 6

Solution

In Figure 6(a), the substituent groups are bonded to the same sides of the pair of double-bonded carbon atoms. Therefore, Figure 6(a) shows *cis*-pent-2-ene. In Figure 6(b), the two substituent groups are on opposite sides of the double bond, so Figure 6(b) shows *trans*-pent-2-ene.

When drawing structural formulas for compounds that are stereoisomers, follow the same steps that you have already practised for drawing structural formulas. The only difference is the position of the parts of the molecule on either side of the double bond.

1. Draw the parent chain or carbon ring from the last part of the compound name. Leave the bonds on either side of the double bond empty for now.
2. Identify the carbon atom where each of the multiple bonds (and substituents) is attached.
3. Draw the substituent groups on either side of the double bond according to whether the name includes *cis* or *trans*.
4. Add any substituents at the appropriate locations.

Sample Problem 2: Drawing Stereoisomers

Draw structural formulas for *cis*-1,2-dichloroethene and *trans*-1,2,-dichloroethene.

Solution

Step 1. Draw the parent chain or carbon ring from the last part of the compound name. Leave the bonds on either side of the double bond empty for now.

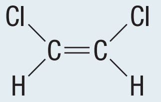
Ethene contains 2 carbon atoms with a double bond between them: $C{=}C$

Step 2. Identify the carbon atom where each of the multiple bonds (and substituents) is attached.

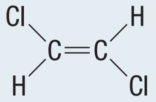
For ethene, the double bond can only be in one place: between the 2 carbon atoms.

Step 3. Draw the substituent groups on either side of the double bond according to whether the name includes *cis* or *trans*.

From the name of the compound, you know that it contains 2 chlorine atoms. You also know that each chlorine atom is bonded to a different carbon atom. Therefore, add 2 chlorine atoms: 1 on each of the carbon atoms. The *cis* isomer will have the chlorine atoms on the same side of the double bond; the *trans* isomer will have the chlorine atoms on opposite sides:



cis-1,2-dichloroethene



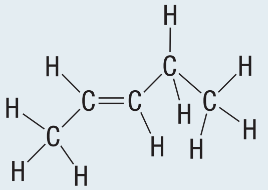
trans-1,2-dichloroethene

Step 4. Add any substituents at the appropriate locations.

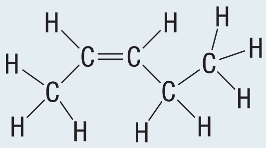
In this case, there are no other substituents to add.

Practice

1. Draw the *cis* and *trans* isomers of the following compounds: K/U C
   (a) hex-3-ene (b) 1-bromoprop-1-ene
2. Name each of the following compounds: K/U
   (a)



   (b)



3. Draw the structural formulas and write the names of the two stereoisomers of 2,4-dimethylhex-3-ene. K/U C

LEARNING TIP

Remembering *Cis* and *Trans*

To use *cis* and *trans* correctly, you could think of *cis* as being like sisters: side by side. And *trans* means "across," as in transatlantic.

Reactions of Alkenes and Alkynes

A **functional group** is a specific group of atoms within a molecule that affects the properties of the compound, such as solubility, melting point, boiling point, and chemical reactivity with other elements or compounds. Multiple bonds are considered to be functional groups because they affect the properties of the molecules that contain them. For example, alkenes and alkynes are more reactive than alkanes. The double-bonded and triple-bonded carbon atoms are more likely to take part in reactions because the multiple bonds are less stable than single bonds between carbon atoms.

functional group a group of atoms within a molecule that determines the properties of the molecule

One common type of reaction that alkenes and alkynes undergo is an addition reaction. In an **addition reaction** two molecules react to form one. The multiple bonds in alkenes and alkynes enable the organic molecules to react with hydrogen. The addition of hydrogen is a type of addition reaction known as hydrogenation, and results in the hydrocarbon becoming saturated (**Figure 7**).

addition reaction a reaction in which the atoms from one molecule are added to another molecule to form a single molecule

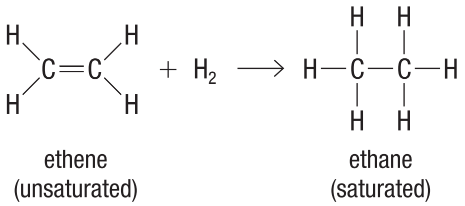


Figure 7 An unsaturated molecule of ethene becomes saturated by the addition of a hydrogen atom on either side of the double bond. A molecule of ethane is formed.

Hydrogenation reactions, in which hydrogen atoms are added on either side of a multiple bond, can occur with alkenes, alkynes, or cyclic alkenes (**Figure 8**).

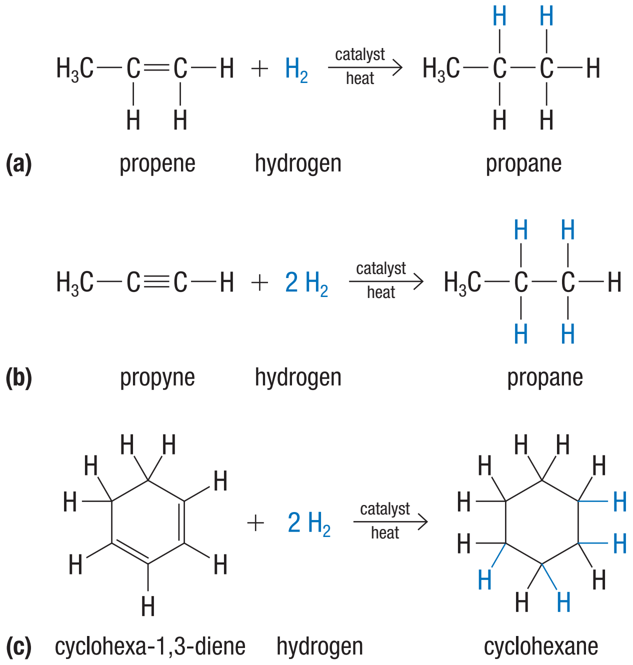


Figure 8 Hydrogenation reactions for alkenes and alkynes in the presence of heat and a catalyst. (a) Propene reacts with hydrogen to form propane. (b) Propyne reacts with two moles of hydrogen per mole of propyne to form propane. (c) Cyclohexa-1,3-diene reacts with hydrogen to form cyclohexane.

The alkene (or alkyne) gains atoms from the reacting molecule but does not lose any atoms. Addition reactions may also occur with halogens, hydrogen halides such as hydrogen chloride, and water.

In a halogenation reaction, a halogen such as bromine or chlorine reacts with an alkene or alkyne (**Figure 9**). The halogenation of an alkene produces an alkyl halide. The halogenation of an alkyne produces a halogenated alkene or, if excess halogen is present, an alkyl halide. A hydrogen halide such as hydrogen chloride or hydrogen bromide may also react with an alkene or alkyne. This reaction is called a hydrohalogenation reaction. The resulting compound includes both the halogen and the hydrogen atoms and may be a halogenated alkene or an alkyl halide.

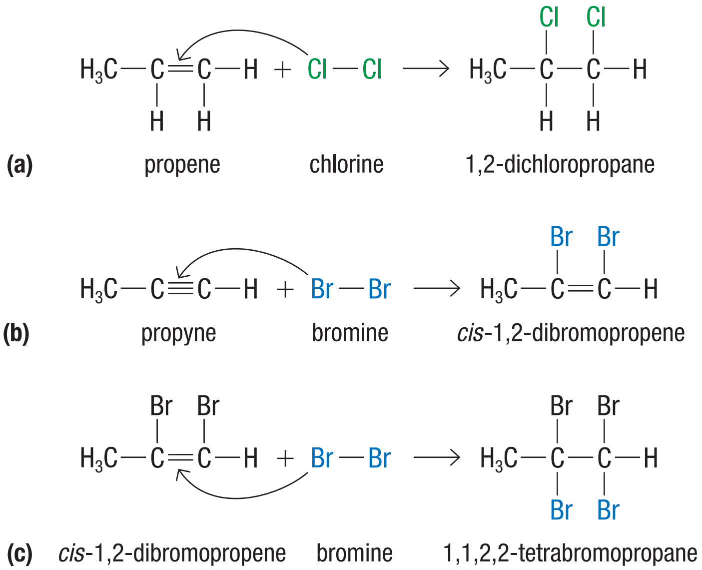
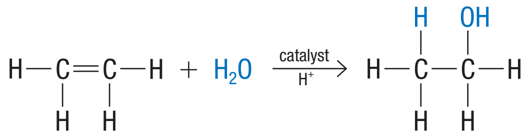


Figure 9 Halogenation reactions for alkenes and alkynes.

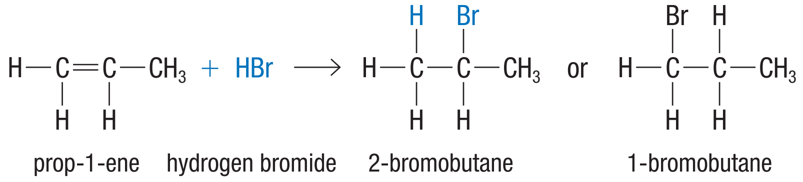
In a hydration reaction (**Figure 10**), water reacts with an unsaturated hydrocarbon. This reaction produces a type of organic compound that contains a hydroxyl group (−OH). This compound is called an alcohol.



$$H-\underset{H}{C}=\underset{H}{C}-H + H_2O \xrightarrow[H^+]{catalyst} H-\overset{H}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-H$$

Figure 10 In this hydration reaction, ethene reacts with water in the presence of a catalyst and acid to form ethanol.

Look again at Figures 8 and 9. In all of these reactions, the substance that is added to the hydrocarbon (H_2, Cl_2, or Br_2) is made up of 2 identical atoms. Therefore, only one possible product can form in each case. For example, you could switch the positions of the 2 chlorine atoms in 1,2-dichloropropane (Figure 9(a)), but the product would be the same substance. In contrast, hydration reactions (Figure 10) and hydrohalogenation reactions add 2 non-identical atoms to the multiple bond. Therefore, more than one product is possible (**Figure 11**).



$$H-\underset{H}{C}=\underset{H}{C}-CH_3 + HBr \longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-CH_3 \text{ or } H-\overset{Br}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CH_3$$

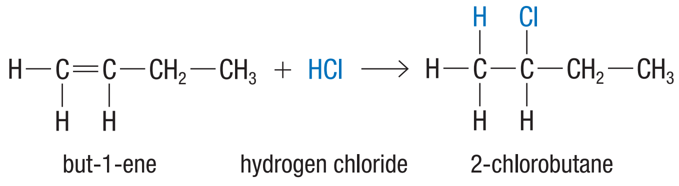
Figure 11 When a hydrogen halide reacts with an alkene, two different products are possible.

How can we predict which product will be formed? **Markovnikov's rule** provides guidance on how the atoms will be added to the double bond. Markovnikov's rule is as follows:

Markovnikov's rule the rule for predicting the products of addition reactions: when a hydrogen halide or water is added to an alkene, the hydrogen atom generally bonds to the carbon atom within the double bond that already has more hydrogen atoms bonded to it

> When a hydrogen halide or water molecule reacts with an alkene, the hydrogen atom will generally bond to the carbon atom in the multiple bond that has the most hydrogen atoms already bonded to it.

Markovnikov's rule applies to hydrohalogenation of both straight-chain and cyclic hydrocarbons (**Figure 12**). It also applies to hydration reactions.



$$H-\underset{H}{C}=\underset{H}{C}-CH_2-CH_3 + HCl \longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-CH_2-CH_3$$

Figure 12 According to Markovnikov's rule, the hydrogen atom from the hydrogen chloride molecule bonds to the carbon atom that has the most hydrogen atoms already attached to it.

Despite Markovnikov's rule, small quantities of the other product will be produced. If both of the carbon atoms have the same number of hydrogen atoms, an equal mixture of products will result.

Sometimes a chemist may need to perform a hydrohalogenation or hydration reaction in which the hydrogen atom is added to the carbon atom that has the fewest hydrogen atoms already bonded to it. Therefore, chemists have developed strategies to overcome Markovnikov's rule. They can use catalysts or other reaction conditions to change the expected outcome of a reaction. CAREER LINK

Tutorial 3 Predicting Products of Addition Reactions

You can use the familiar skills of writing and balancing chemical equations, along with strategies for naming organic compounds, to predict the main products of addition reactions. Remember to look carefully at the multiple bonds in the organic reactant, and consider Markovnikov's rule to establish where each atom will be placed in the product molecule.

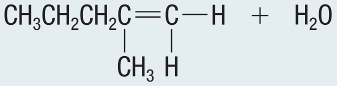
Sample Problem 1: Applying Markovnikov's Rule

Predict the major product of a hydration reaction of 2-methylpent-1-ene.

Solution

Step 1. Draw the substances involved in the reaction.

You will likely find it helpful to draw the structural formula for the organic reactant. Recall that a hydration reaction involves the addition of water to an unsaturated hydrocarbon.

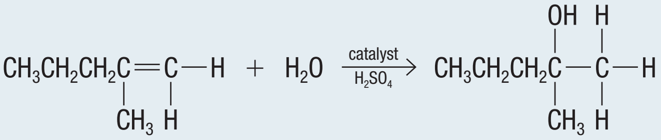


$$CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}-H \quad + \quad H_2O$$

2-methylpent-1-ene water

Step 2. Determine where the added entities will attach.

During the reaction, the water molecule splits into a hydrogen atom and a hydroxyl group (—OH). These two entities will be added to the carbon atoms on either side of the double bond in the organic molecule. According to Markovnikov's rule, the hydrogen atom will be added to the carbon atom that already has the most hydrogen atoms bonded to it. ("The rich get richer!") Therefore, the hydrogen atom will bond to carbon 1, and the hydroxyl group will bond to carbon 2.



$$CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}-H \quad + \quad H_2O \xrightarrow[H_2SO_4]{\text{catalyst}} CH_3CH_2CH_2\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-H$$

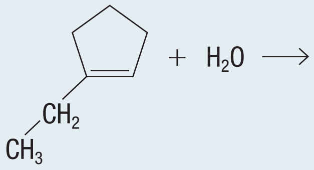
2-methylpent-1-ene water 2-hydroxy-2-methylpentane

Step 3. Name the product.

The major product of the reaction is 2-hydroxy-2-methylpentane.

Practice

1. Draw the structural formula and write the name of the major product in the reaction of 3-methylbut-1-ene and hydrogen chloride. T/I C
2. Predict the major product of the reaction involving the following reactants. (You can ignore the fact that a catalyst is required for this reaction.) T/I C



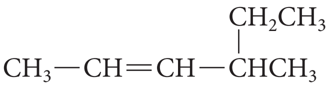
1.2 Review

Summary

- An alkene is a hydrocarbon that has at least one double bond between 2 carbon atoms. The carbon chain is numbered using the lowest number for the double bond. The root name ends in *-ene*.
- An alkyne is a hydrocarbon that has at least one triple bond between 2 carbon atoms. Naming alkynes is similar to naming alkenes. The root name ends in *-yne*.
- *Cis* and *trans* isomers are compounds that are identical except for the position of groups on either side of a double bond. In *cis* isomers, the groups are located on the same side of the double bond. In *trans* isomers, the groups are located on opposite sides of the double bond.
- Hydrocarbons with multiple bonds are more reactive than alkanes and participate in addition reactions in which atoms from one molecule are added to another molecule. Addition reactions include hydrogenation, halogenation, hydrohalogenation, and hydration.
- Markovnikov's rule states that, when two non-identical entities are added at a double bond, the major product will be formed by the hydrogen atom bonding to the carbon atom with more hydrogen atoms attached.

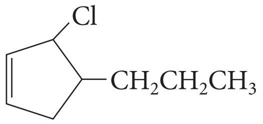
Questions

1. Create a flow chart to summarize the naming of alkenes and alkynes. K/U C
2. Classify each of the following compounds as an alkane, an alkene, or an alkyne. Explain your reasoning. K/U
   (a) $CH_3CH_2CHCHCH_3$
   (b) $CH_2CHCH_2CH_3$
   (c) $CHCCH_2CCH$
3. Name each of the following alkenes. (Ignore *cis–trans* isomerism for now.) K/U T/I
   (a) $CH_2{=}CH{-}CH_2{-}CH_3$
   (b)

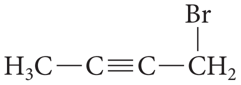


$$CH_3{-}CH{=}CH{-}\underset{}{\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}}HCH_3$$

   (c)

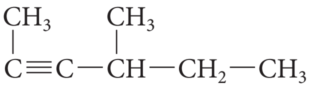


4. Draw the structure of each of the following compounds: T/I C
   (a) 2,5-dimethylhept-3-ene
   (b) 3-bromopropyne
5. Name each of the following alkynes: K/U T/I
   (a)



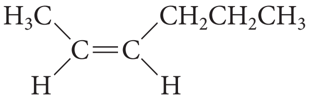
$$H_3C{-}C{\equiv}C{-}\overset{\overset{\displaystyle Br}{|}}{C}H_2$$

   (b)

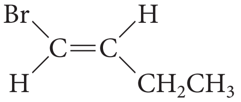


$$\overset{\overset{\displaystyle CH_3}{|}}{C}{\equiv}C{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}CH_3$$

6. Describe how you would identify whether a compound is a *cis* isomer or a *trans* isomer. K/U T/I
7. Name each of the following compounds. Use *cis–trans* conventions. K/U T/I
   (a)



   (b)



8. There is only one compound that is named 1,2-dichloroethane, but there are two distinct compounds that can be named 1,2-dichloroethene. Why? K/U
9. Write chemical equations, using condensed structural formulas, to represent the addition reactions that produce the following compounds. Include the names of the reactants. T/I A
   (a) 2,3-dichlorobutane
   (b) 3-bromohexane
10. Predict the product(s) of the reaction that occurs when the following reactants are combined: T/I A
    (a) pent-1-ene reacts with water and a catalyst.
    (b) Chlorine gas is bubbled through 3-methylcyclohexene.

1.3 Aromatic Hydrocarbons

Michael Faraday (1791–1867) was the first person to isolate and identify benzene from a mixture of oils in 1825 (**Figure 1**). Since then, benzene has been used in many commercial products. One of its first uses was as an aftershave in the nineteenth and early twentieth centuries. In 1903, benzene was used to decaffeinate coffee. It was also used as an anti-knock additive in gasoline to control the ignition of the fuel until the 1950s, when it was replaced by tetraethyl lead. Benzene is also widely used in industry as a solvent in chemical reactions. Testing has identified benzene as a carcinogen and implicated it in other health problems. As the hazards of benzene have become known, many of its commercial uses have been discontinued.

Figure 1 Michael Faraday (left) working in his chemistry lab

What Is an Aromatic Hydrocarbon?

An **aromatic hydrocarbon** is an unsaturated hydrocarbon that has a ring structure and a bonding arrangement that causes it to be chemically stable. Benzene, C_6H_6, is a flat 6-carbon ring with a hydrogen atom bonded to each carbon atom (**Figure 2**). It is the simplest aromatic hydrocarbon. The structural diagram often shows benzene as having three double bonds alternating with three single bonds. Measurements of the bond length between carbon atoms, however, have shown that all six bond lengths are equal. If benzene actually had three double bonds, then those bonds would be shorter than the other three. To indicate that all six bonds are identical, the structure is shown as alternating between two arrangements of double bonds (Figure 2(b)) or as a hexagon with a circle inside (Figure 2(c)). The hexagon with the circle indicates that the electrons in the bonds are shared equally between all 6 carbon atoms.

aromatic hydrocarbon an unsaturated cyclic hydrocarbon with a pattern of bonding that makes it chemically stable

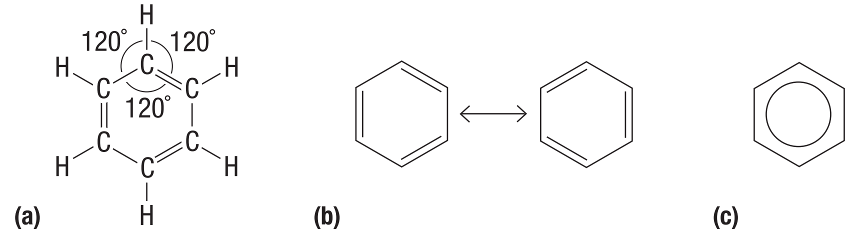
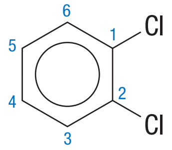
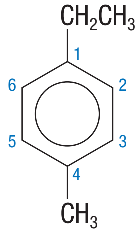


Figure 2 (a) The structure of benzene, a planar ring system in which all bond angles are 120° (b) Two structural formulas implying that the structure of benzene is a combination of them both together (c) The common representation of benzene



1,2-dichlorobenzene



1-ethyl-4-methylbenzene

Figure 3 Substituted benzenes

Naming Aromatic Compounds

There are two conventions for naming compounds that include a benzene ring. Which one we use depends on the structure of the other part of the compound.

We use the first convention when naming aromatic compounds that have non-carbon substituents or a small alkyl group. In this case, the benzene ring is generally considered to be the parent molecule. The attached functional groups are named as substituents to benzene. If a single group is attached to a benzene ring, we put the name of the group before the root *-benzene*. For example, chlorobenzene, C_6H_5Cl, has one chlorine atom replacing a hydrogen atom on the benzene ring. Compounds made up of a benzene ring with one or more halogen atoms attached are called aromatic halides.

If two or more substituents are bonded to the benzene ring, we number the carbon atoms of the benzene ring starting with the first substituent (alphabetically) and continue numbering in the direction of the next closest substituent. **Figure 3** shows some examples.

In the second naming convention, the benzene ring is considered to be a substituent on a hydrocarbon chain. A benzene ring that has lost 1 hydrogen atom is called a **phenyl group**, just as a methyl group is like a methane molecule that has lost 1 hydrogen atom. The compound is named using "phenyl" as the substituent (**Figure 4**). WEB LINK

phenyl group a benzene ring (minus 1 hydrogen atom) that behaves as a substituent in an organic compound

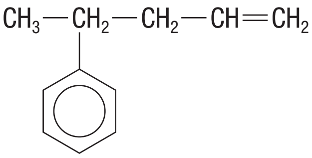


Figure 4 Benzene as a substituent group in 4-phenylpent-1-ene

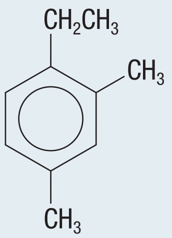
Tutorial 1 Naming and Drawing Aromatic Compounds

Aromatic hydrocarbons with one or more simple substituents are named by adding the substituent name(s) to the root “benzene.” If the substituent is complex, such as a hydrocarbon chain with a multiple bond, consider this the parent group and the benzene ring the substituent. In this tutorial, you will recognize when to use each convention, and practise naming and drawing compounds using both conventions.

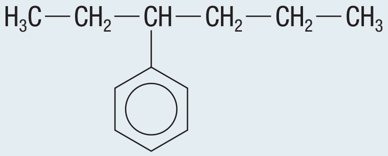
Sample Problem 1: Naming Aromatic Compounds

Name the compounds represented by the following structural formulas:

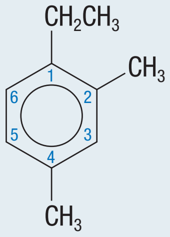
(a)



(b)



Solution (a)



The structure has three simple substituents, so can be named as a substituted benzene. Number the carbon atoms to give the substituents the lowest numbers.

This compound is 1-ethyl-2,4-dimethylbenzene.

Solution (b)

Treat the benzene ring as the substituent. The alkane chain is a hexane and the benzene ring is bonded to the third carbon atom in the chain. Therefore, this compound is 3-phenylhexane.

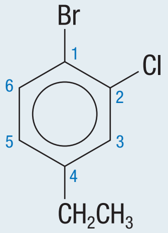
Sample Problem 2: Drawing Aromatic Compounds

Draw the structural formula for each of the following compounds:

(a) 1-bromo-2-chloro-4-ethylbenzene

(b) 4,6-diphenyloct-2-ene

Solution (a)

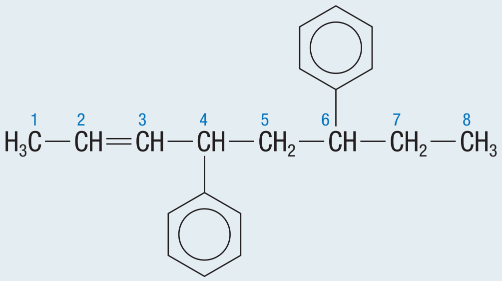


First, draw the benzene ring and number the carbon atoms.

Next, add the substituents as indicated in the name: a bromine atom on carbon 1, a chlorine atom on carbon 2, and an ethyl group on carbon 4.

Solution (b)

First, draw the parent alkene, oct-2-ene. Next, add the benzene rings to the fourth and sixth carbon atoms.



LEARNING TIP

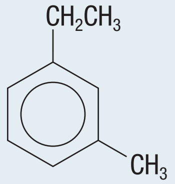
Traditional Names for Aromatic Hydrocarbons

An older naming convention for substituted aromatic compounds used the Greek prefixes *ortho*-, *meta*-, and *para*- to indicate the positions of substituents. Ortho substituents are on adjacent carbon atoms in 1,2 positions. Meta substituents are separated by 1 carbon atom in 1,3 positions. Para substituents are located on opposite sides of the 6-carbon ring in 1,4 positions.

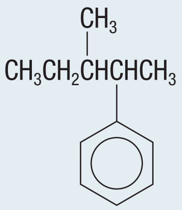
Practice

1. Name each of the following compounds: K/U

(a)



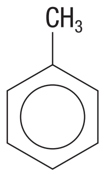
(b)



2. Draw the structural formulas of the following compounds: T/I C
   (a) 1-fluoro-3-methylbenzene
   (b) 2-phenylbut-2-ene

Properties of Aromatic Hydrocarbons

Many aromatic hydrocarbons are liquids at room temperature, while others are crystalline solids. Their symmetrical structure causes them to be non-polar unless they contain an electronegative substituent, so they are generally insoluble in water. From its discovery and well into the second half of the twentieth century, benzene was widely used as a solvent in industrial processes and for dry cleaning clothes. Since the discovery that benzene is carcinogenic, other chemicals have replaced benzene in the workplace. One replacement compound is methylbenzene, commonly known as toluene, $C_6H_5CH_3$ (**Figure 5**).



toluene

Figure 5 Toluene (methylbenzene) is a substituted benzene compound with one methyl group substituted for a hydrogen atom.

Reactions of Aromatic Compounds

Its unusual bonding makes the benzene ring behave quite differently from an unsaturated hydrocarbon. Unsaturated hydrocarbons easily undergo addition reactions. However, benzene does not because its bonds are not really alternating double and single bonds. Each bond in benzene is identical and they are much more stable than a carbon–carbon double bond. Bond strength is between that of a single and that of a double bond. In general, therefore, aromatic compounds are much less reactive than alkenes. The hydrogenation of benzene to form cyclohexane requires high temperatures and a catalyst. Benzene does undergo substitution reactions in which hydrogen atoms are replaced by other atoms, such as halogens (**Figure 6**).

Substitution reactions are characteristic of saturated hydrocarbons, and addition reactions are characteristic of unsaturated ones. Benzene reacts more like a saturated hydrocarbon because of the specialized bonding in the benzene ring (**Figure 7**).

UNIT TASK **BOOKMARK**

Aromatic compounds tend to be quite volatile, which means that they easily evaporate and disperse in the air. You may consider the properties of aromatic compounds as you work on the Unit Task, described on page 116.

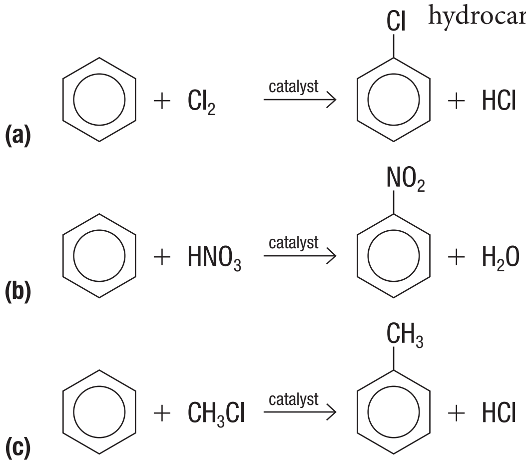


Figure 6 Substitution reactions of benzene. (a) Reaction with chlorine, Cl_2, produces chlorobenzene (an aromatic halide) and hydrogen chloride. (b) Reaction with nitric acid, HNO_3, produces nitrobenzene and water. (c) Reaction with chloromethane, CH_3Cl, produces toluene and hydrogen chloride.

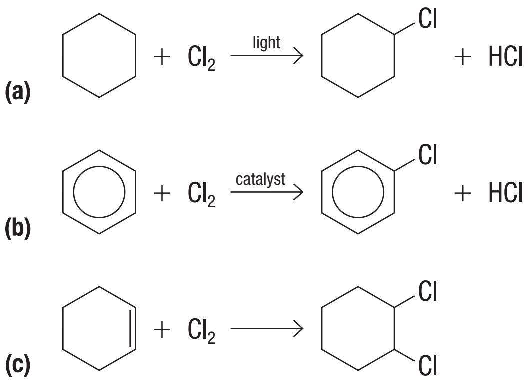


Figure 7 Reactions of cyclohexane, benzene, and cyclohexene with chlorine. (a) Cyclohexane reacts with chlorine in a substitution reaction. A hydrogen atom is lost as the chlorine atom is gained. (b) Benzene reacts with chlorine in a substitution reaction, like cyclohexane. (c) Cyclohexene reacts with chlorine in an addition reaction: no atoms are lost from the organic compound.

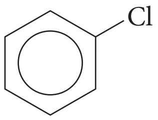
1.3 Review

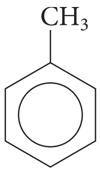
Summary

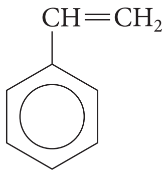
- Aromatic hydrocarbons are a class of cyclic unsaturated hydrocarbons that have a ring structure and bonding that causes them to be chemically stable.
- Measurements show that the bonds in a benzene ring are all equal in length.
- Naming aromatic compounds with one or more simple substituents requires just the addition of the substituent group name. Naming aromatic compounds with a more complex substituent requires treating the benzene ring, named “phenyl,” as a substituent on a carbon chain.
- Benzene is less reactive than alkenes. Since it participates in substitution reactions, benzene behaves more like an alkane.

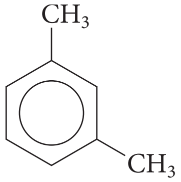
Questions

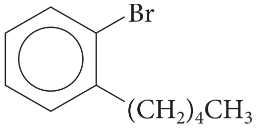
1. Name the compounds represented by the following structural formulas: K/U

   (a) 

   (b) 

   (c) 

   (d) 

   (e) 

2. Draw the structural formula for each of the following compounds: K/U C
   (a) 1,3-dichloro-4-ethylbenzene
   (b) 1-bromo-3-phenylhept-5-yne
3. (a) Draw the chemical equation for the reaction between benzene and bromine, Br_2. Is this reaction likely to occur? Explain why or why not.
   (b) How would your answer to (a) be different if the organic reactant were cyclohexene instead of benzene? T/I
4. Draw structural formulas representing the reaction that produces iodobenzene. Label the reactants and classify the reaction as addition or substitution. K/U T/I C
5. Mothballs are small lumps of pesticide that discourage moths from damaging woollen clothing. The main component of mothballs is paradichlorobenzene. T/I C A
   (a) What is the proper IUPAC name for this compound? (See the Learning Tip on page 29.)
   (b) Draw the structure of paradichlorobenzene.
   (c) When you order this chemical from a company, the label says “paradichlorobenzene” even though that is not the correct IUPAC name. Why do you think the compound is labelled this way? Do you think it is a good idea, or should all products be labelled with their IUPAC name? Explain your reasoning.
6. (a) Predict the products of reactions involving the following reactants:
      (i) cyclohexene and hydrogen bromide
      (ii) benzene and chloroethane
   (b) Explain how these two reactions are different, and the reason for the differences. K/U T/I
7. One aromatic compound that has been the subject of many studies is bisphenol-A. This chemical was used as a hardener in many plastics, but studies have uncovered a possible link to adverse health effects. As a result, Canada has now banned some products, including baby bottles, containing bisphenol-A. Find out more about this substance and the decision to restrict its use. Create a graphic organizer showing the pros and cons of banning products containing bisphenol-A. T/I C A
8. Benzene has, in the past, been used as a solvent in the dry-cleaning industry. Research this use, discover why its use is being phased out, and find out what “greener” alternatives are now used for dry cleaning. Present your findings in an attention-grabbing format for your stated target audience. T/I C A

WEB LINK

1.3

Aromatic Hydrocarbons

Michael Faraday (1791–1867) was the first person to isolate and identify benzene from a mixture of oils in 1825 (**Figure 1**). Since then, benzene has been used in many commercial products. One of its first uses was as an aftershave in the nineteenth and early twentieth centuries. In 1903, benzene was used to decaffeinate coffee. It was also used as an anti-knock additive in gasoline to control the ignition of the fuel until the 1950s, when it was replaced by tetraethyl lead. Benzene is also widely used in industry as a solvent in chemical reactions. Testing has identified benzene as a carcinogen and implicated it in other health problems. As the hazards of benzene have become known, many of its commercial uses have been discontinued.

Figure 1 Michael Faraday (left) working in his chemistry lab

What Is an Aromatic Hydrocarbon?

An **aromatic hydrocarbon** is an unsaturated hydrocarbon that has a ring structure and a bonding arrangement that causes it to be chemically stable. Benzene, C_6H_6, is a flat 6-carbon ring with a hydrogen atom bonded to each carbon atom (**Figure 2**). It is the simplest aromatic hydrocarbon. The structural diagram often shows benzene as having three double bonds alternating with three single bonds. Measurements of the bond length between carbon atoms, however, have shown that all six bond lengths are equal. If benzene actually had three double bonds, then those bonds would be shorter than the other three. To indicate that all six bonds are identical, the structure is shown as alternating between two arrangements of double bonds (Figure 2(b)) or as a hexagon with a circle inside (Figure 2(c)). The hexagon with the circle indicates that the electrons in the bonds are shared equally between all 6 carbon atoms.

aromatic hydrocarbon an unsaturated cyclic hydrocarbon with a pattern of bonding that makes it chemically stable

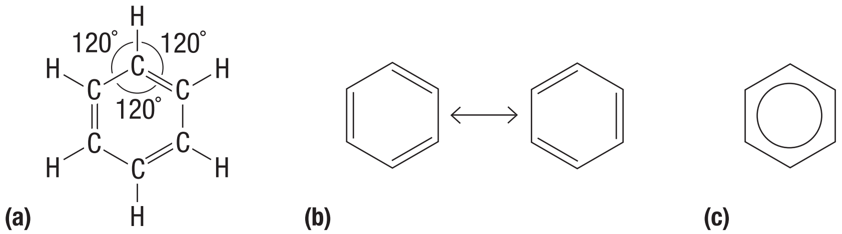


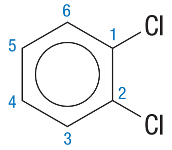
Figure 2 (a) The structure of benzene, a planar ring system in which all bond angles are 120° (b) Two structural formulas implying that the structure of benzene is a combination of them both together (c) The common representation of benzene

Naming Aromatic Compounds

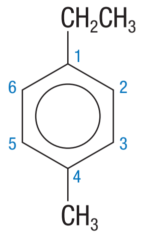
There are two conventions for naming compounds that include a benzene ring. Which one we use depends on the structure of the other part of the compound.

We use the first convention when naming aromatic compounds that have non-carbon substituents or a small alkyl group. In this case, the benzene ring is generally considered to be the parent molecule. The attached functional groups are named as substituents to benzene. If a single group is attached to a benzene ring, we put the name of the group before the root *-benzene*. For example, chlorobenzene, C_6H_5Cl, has one chlorine atom replacing a hydrogen atom on the benzene ring. Compounds made up of a benzene ring with one or more halogen atoms attached are called aromatic halides.

If two or more substituents are bonded to the benzene ring, we number the carbon atoms of the benzene ring starting with the first substituent (alphabetically) and continue numbering in the direction of the next closest substituent. **Figure 3** shows some examples.



1,2-dichlorobenzene



1-ethyl-4-methylbenzene

Figure 3 Substituted benzenes

In the second naming convention, the benzene ring is considered to be a substituent on a hydrocarbon chain. A benzene ring that has lost 1 hydrogen atom is called a **phenyl group**, just as a methyl group is like a methane molecule that has lost 1 hydrogen atom. The compound is named using "phenyl" as the substituent (**Figure 4**). WEB LINK

phenyl group a benzene ring (minus 1 hydrogen atom) that behaves as a substituent in an organic compound

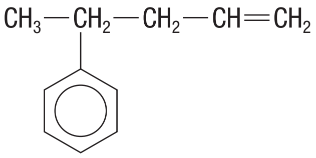


Figure 4 Benzene as a substituent group in 4-phenylpent-1-ene

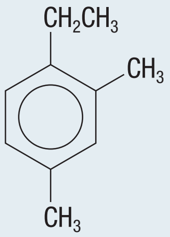
Tutorial 1 Naming and Drawing Aromatic Compounds

Aromatic hydrocarbons with one or more simple substituents are named by adding the substituent name(s) to the root "benzene." If the substituent is complex, such as a hydrocarbon chain with a multiple bond, consider this the parent group and the benzene ring the substituent. In this tutorial, you will recognize when to use each convention, and practise naming and drawing compounds using both conventions.

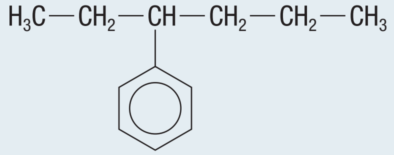
Sample Problem 1: Naming Aromatic Compounds

Name the compounds represented by the following structural formulas:

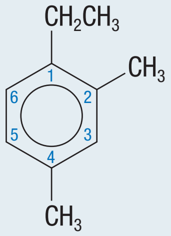
(a)



(b)



Solution (a)



The structure has three simple substituents, so can be named as a substituted benzene. Number the carbon atoms to give the substituents the lowest numbers.

This compound is 1-ethyl-2,4-dimethylbenzene.

Solution (b)

Treat the benzene ring as the substituent. The alkane chain is a hexane and the benzene ring is bonded to the third carbon atom in the chain. Therefore, this compound is 3-phenylhexane.

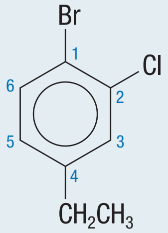
Sample Problem 2: Drawing Aromatic Compounds

Draw the structural formula for each of the following compounds:

(a) 1-bromo-2-chloro-4-ethylbenzene

(b) 4,6-diphenyloct-2-ene

Solution (a)

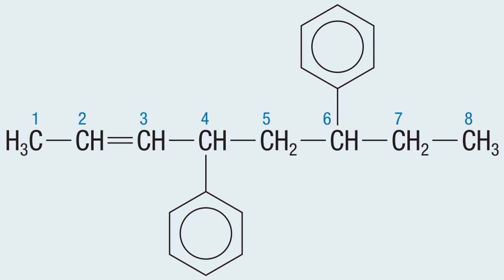


First, draw the benzene ring and number the carbon atoms.

Next, add the substituents as indicated in the name: a bromine atom on carbon 1, a chlorine atom on carbon 2, and an ethyl group on carbon 4.

Solution (b)

First, draw the parent alkene, oct-2-ene. Next, add the benzene rings to the fourth and sixth carbon atoms.



LEARNING **TIP**

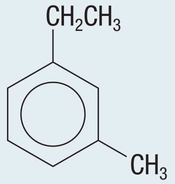
Traditional Names for Aromatic Hydrocarbons

An older naming convention for substituted aromatic compounds used the Greek prefixes *ortho*-, *meta*-, and *para*- to indicate the positions of substituents. Ortho substituents are on adjacent carbon atoms in 1,2 positions. Meta substituents are separated by 1 carbon atom in 1,3 positions. Para substituents are located on opposite sides of the 6-carbon ring in 1,4 positions.

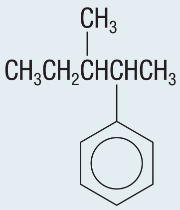
Practice

1. Name each of the following compounds: K/U

(a)



(b)



2. Draw the structural formulas of the following compounds: T/I C
   (a) 1-fluoro-3-methylbenzene
   (b) 2-phenylbut-2-ene

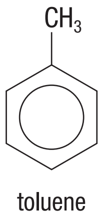


Figure 5 Toluene (methylbenzene) is a substituted benzene compound with one methyl group substituted for a hydrogen atom.

UNIT TASK BOOKMARK

Aromatic compounds tend to be quite volatile, which means that they easily evaporate and disperse in the air. You may consider the properties of aromatic compounds as you work on the Unit Task, described on page 116.

Properties of Aromatic Hydrocarbons

Many aromatic hydrocarbons are liquids at room temperature, while others are crystalline solids. Their symmetrical structure causes them to be non-polar unless they contain an electronegative substituent, so they are generally insoluble in water. From its discovery and well into the second half of the twentieth century, benzene was widely used as a solvent in industrial processes and for dry cleaning clothes. Since the discovery that benzene is carcinogenic, other chemicals have replaced benzene in the workplace. One replacement compound is methylbenzene, commonly known as toluene, $C_6H_5CH_3$ (**Figure 5**).

Reactions of Aromatic Compounds

Its unusual bonding makes the benzene ring behave quite differently from an unsaturated hydrocarbon. Unsaturated hydrocarbons easily undergo addition reactions. However, benzene does not because its bonds are not really alternating double and single bonds. Each bond in benzene is identical and they are much more stable than a carbon–carbon double bond. Bond strength is between that of a single and that of a double bond. In general, therefore, aromatic compounds are much less reactive than alkenes. The hydrogenation of benzene to form cyclohexane requires high temperatures and a catalyst. Benzene does undergo substitution reactions in which hydrogen atoms are replaced by other atoms, such as halogens (**Figure 6**).

Substitution reactions are characteristic of saturated hydrocarbons, and addition reactions are characteristic of unsaturated ones. Benzene reacts more like a saturated hydrocarbon because of the specialized bonding in the benzene ring (**Figure 7**).

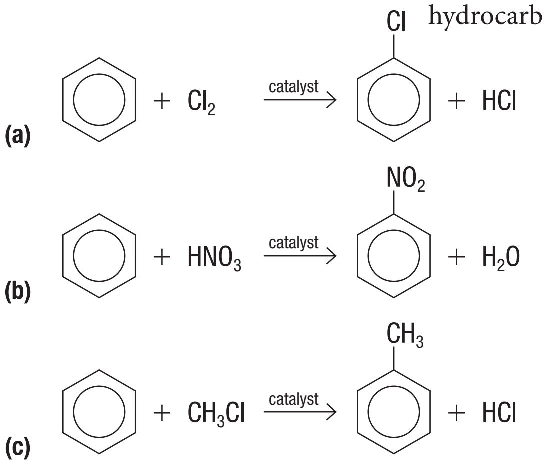


Figure 6 Substitution reactions of benzene. (a) Reaction with chlorine, Cl_2, produces chlorobenzene (an aromatic halide) and hydrogen chloride. (b) Reaction with nitric acid, HNO_3, produces nitrobenzene and water. (c) Reaction with chloromethane, CH_3Cl, produces toluene and hydrogen chloride.

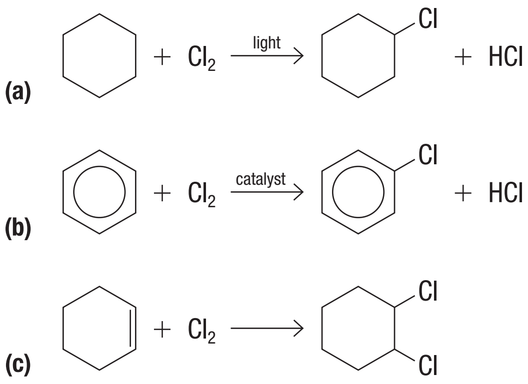


Figure 7 Reactions of cyclohexane, benzene, and cyclohexene with chlorine. (a) Cyclohexane reacts with chlorine in a substitution reaction. A hydrogen atom is lost as the chlorine atom is gained. (b) Benzene reacts with chlorine in a substitution reaction, like cyclohexane. (c) Cyclohexene reacts with chlorine in an addition reaction: no atoms are lost from the organic compound.

1.3 Review

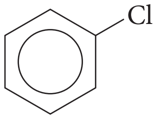
Summary

- Aromatic hydrocarbons are a class of cyclic unsaturated hydrocarbons that have a ring structure and bonding that causes them to be chemically stable.
- Measurements show that the bonds in a benzene ring are all equal in length.
- Naming aromatic compounds with one or more simple substituents requires just the addition of the substituent group name. Naming aromatic compounds with a more complex substituent requires treating the benzene ring, named “phenyl,” as a substituent on a carbon chain.
- Benzene is less reactive than alkenes. Since it participates in substitution reactions, benzene behaves more like an alkane.

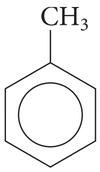
Questions

1. Name the compounds represented by the following structural formulas: K/U

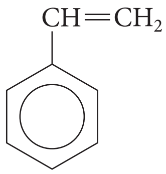
   (a)



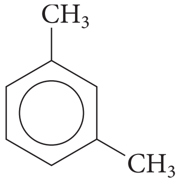
   (b)



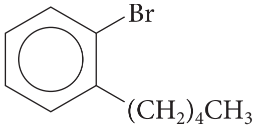
   (c)



   (d)



   (e)



2. Draw the structural formula for each of the following compounds: K/U C
   (a) 1,3-dichloro-4-ethylbenzene
   (b) 1-bromo-3-phenylhept-5-yne
3. (a) Draw the chemical equation for the reaction between benzene and bromine, Br_2. Is this reaction likely to occur? Explain why or why not.
   (b) How would your answer to (a) be different if the organic reactant were cyclohexene instead of benzene? T/I
4. Draw structural formulas representing the reaction that produces iodobenzene. Label the reactants and classify the reaction as addition or substitution. K/U T/I C
5. Mothballs are small lumps of pesticide that discourage moths from damaging woollen clothing. The main component of mothballs is paradichlorobenzene. T/I C A
   (a) What is the proper IUPAC name for this compound? (See the Learning Tip on page 29.)
   (b) Draw the structure of paradichlorobenzene.
   (c) When you order this chemical from a company, the label says “paradichlorobenzene” even though that is not the correct IUPAC name. Why do you think the compound is labelled this way? Do you think it is a good idea, or should all products be labelled with their IUPAC name? Explain your reasoning.
6. (a) Predict the products of reactions involving the following reactants:
      (i) cyclohexene and hydrogen bromide
      (ii) benzene and chloroethane
   (b) Explain how these two reactions are different, and the reason for the differences. K/U T/I
7. One aromatic compound that has been the subject of many studies is bisphenol-A. This chemical was used as a hardener in many plastics, but studies have uncovered a possible link to adverse health effects. As a result, Canada has now banned some products, including baby bottles, containing bisphenol-A. Find out more about this substance and the decision to restrict its use. Create a graphic organizer showing the pros and cons of banning products containing bisphenol-A. T/I C A
8. Benzene has, in the past, been used as a solvent in the dry-cleaning industry. Research this use, discover why its use is being phased out, and find out what “greener” alternatives are now used for dry cleaning. Present your findings in an attention-grabbing format for your stated target audience. T/I C A

WEB LINK

1.4

Alcohols, Ethers, and Thiols

Figure 1 Flambé is a cooking technique in which alcohol is added to food and heated until the alcohol ignites.

The flammability of alcohol was used in the past to determine whether producers of distilled alcoholic beverages were watering down their product. Ethanol, which contains 2 carbon atoms, is the alcohol in alcoholic beverages. To determine whether a beverage contained a certain concentration of ethanol, a small quantity of gunpowder was mixed with the beverage. If a spark ignited the gunpowder, the liquid contained at least 57 % alcohol by volume and the beverage was considered to be full strength: not watered down. Beverages that passed this test were labelled "100 percent proof." If the gunpowder did not ignite, the alcohol concentration was under proof and the water concentration too high. Most modern alcoholic-beverage containers still list the proof of the contents, but today the numerical value is typically based on the percentage of ethanol by volume. The mention of proof on the label of alcoholic drinks is for historical reasons. These days, the flammability of ethanol is more often used in the cooking technique known as flambé (**Figure 1**).

Although there are many important alcohols, the two simplest, methanol and ethanol, have the greatest commercial value. Methanol, also known as *wood alcohol* because it was originally obtained by heating wood in the absence of air, is now generally manufactured from methane. Ethanol can be manufactured by an addition reaction of ethene, although most ethanol, including beverage alcohol, is produced by fermentation of sugars from plants. Although ethanol is legally consumed in Canada, it has serious health effects and is toxic in large quantities.

Alcohols

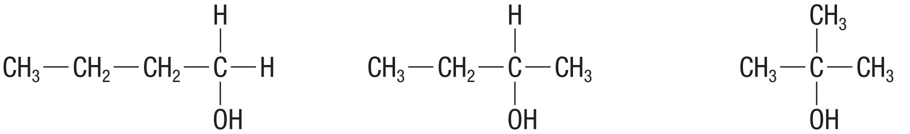
alcohol organic compound that contains the hydroxyl (–OH) functional group

primary alcohol an alcohol in which the hydroxyl group is bonded to a terminal carbon atom

secondary alcohol an alcohol in which the hydroxyl group is bonded to a carbon atom with two alkyl groups bonded to it

tertiary alcohol an alcohol in which the hydroxyl group is bonded to a carbon atom with three alkyl groups bonded to it

An **alcohol** is an organic compound that contains the hydroxyl group (–OH). Alcohols are classified according to the number of other carbon atoms that are directly bonded to the carbon atom attached to the hydroxyl group. For example, the 4-carbon alcohol, butanol, has three different isomers. Their properties depend on the arrangement of the carbon atoms within the molecule. Butan-1-ol (**Figure 2(a)**) is a **primary alcohol** because the –OH group is attached to the carbon atom at the end of the carbon chain, which has only 1 carbon atom attached to it. Butan-2-ol (**Figure 2(b)**) is a **secondary alcohol** because the –OH group is bonded to a carbon atom that is attached to 2 other carbon atoms. In a **tertiary alcohol**, such as 2-methylpropan-2-ol (**Figure 2(c)**), the carbon atom is bonded to the –OH group and 3 carbon atoms from alkyl groups.



(a) butan-1-ol
a primary alcohol (1°)

(b) butan-2-ol
a secondary alcohol (2°)

(c) 2-methyl-propan-2-ol
a tertiary alcohol (3°)

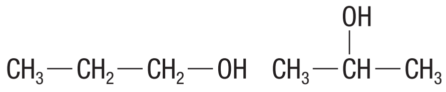
Figure 2 Examples of the three classes of alcohols

The presence of the electronegative oxygen atom in the –OH group affects the polarity of the molecule. The C–O bond is significantly more polar than the C–H bond based on the electronegativity difference between carbon and oxygen compared to that between carbon and hydrogen. The bond between oxygen and hydrogen is also polar. Therefore, alcohols (unlike hydrocarbons) are polar molecules.

Naming and Drawing Alcohols

IUPAC conventions for naming alcohols are similar to those for naming alkenes. We name an alcohol by replacing the final *-e* of the parent hydrocarbon with *-ol*. The name includes the number of the carbon atom to which the hydroxyl group is attached. If the chain also has hydrocarbon or halide constituents, we assign the lowest number to the carbon atom with the hydroxyl group.

The isomers of alcohols have different properties. For example, there are two isomers of propanol (**Figure 3**). Propan-1-ol is used as a solvent for lacquers and waxes, and as brake fluid. The other isomer, propan-2-ol (isopropyl alcohol), is also known as rubbing alcohol. It is used as an antiseptic to clean the skin before injections and in the manufacture of oils, gums, and propanone (also known as acetone). Both isomers of propanol are toxic to humans and many other animals if ingested.

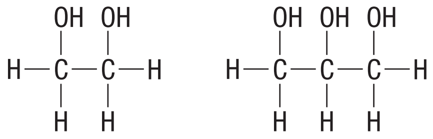


$CH_3-CH_2-CH_2-OH$ $\quad$ $CH_3-\overset{OH}{\overset{|}{C}H}-CH_3$

propan-1-ol propan-2-ol

Figure 3 The two isomers of propanol

Alcohols containing more than one –OH group are referred to as polyalcohols. The suffix *-diol* (for two –OH groups) or *-triol* (for three –OH groups) is added to the alkane name instead of *-ol*. A common example of a polyalcohol is ethane-1,2-diol (**Figure 4(a)**), commonly known as ethylene glycol. This compound is widely used as antifreeze in automobile engines. Another common polyalcohol is propane-1,2,3-triol, commonly called glycerol or glycerine (**Figure 4(b)**). Since glycerine has a low toxicity and is soluble in water, it is frequently used in pharmaceutical preparations to help dissolve less polar compounds. The solubility in water is due to the three –OH groups, which increase the polarity.



(a) ethane-1,2-diol **(b)** propane-1,2,3-triol

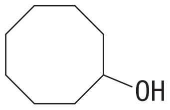
Figure 4 Two commonly used polyalcohols

Cyclic hydrocarbons may also form alcohols. The naming conventions for cyclic alcohols are the same as for straight-chain alcohols: Use the root name of the cyclic hydrocarbon, drop the ending, and add the suffix *-ol*. For example, the addition of an –OH group to cyclooctane results in cyclooctanol (**Figure 5(a)**).

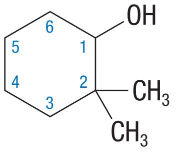
When numbering the atoms in a cyclic hydrocarbon, the –OH functional group takes precedence over other substituents in naming. An example is 2,2-dimethylcyclohexanol. Even though there are two methyl groups, the number starts with the hydroxyl group (**Figure 5(b)**).

An aromatic hydrocarbon can have a bonded –OH group added, forming an aromatic alcohol. The simplest aromatic alcohol is a benzene ring with one hydroxyl group bonded to it. The IUPAC name for this compound is phenol (**Figure 5(c)**). If the benzene ring has two –OH groups, the name is based on benzene and includes the numbers for the –OH groups. An example is benzene-1,2-diol (**Figure 5(d)**).

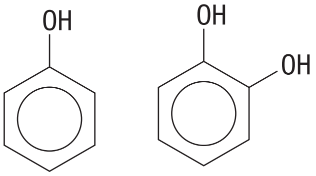
In some cases, a different functional group takes precedence over the alcohol in naming. In this case, the –OH group is treated as a substituent, called *hydroxyl*. This convention applies to carboxylic acids, aldehydes, and ketones, which will be discussed later. When there is a multiple bond in the chain, the –OH group takes precedence (for example: pent-4-ene-1-ol).



(a) cyclooctanol



(b) 2,2-dimethylcyclohexanol



(c) phenol **(d)** benzene-1,2-diol

Figure 5 Four cyclic alcohols

Tutorial 1 Naming and Drawing Alcohols

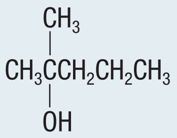
In this tutorial, you will first practise using the structure of an alcohol to determine its name. Then, you will practise drawing the structure of an alcohol from its name.

Naming alcohols follows many of the same steps that you have already learned:

1. Identify the longest carbon chain or ring.
2. If there is only one –OH group, the compound has the suffix *-ol*. If more than one group, use the suffixes *-diol* or *-triol*.
3. Number the parent chain from the end so that the –OH group is attached to the carbon atom with the lowest possible number.
4. Identify any other substituents and their locations.
5. If you are required to identify the type of alcohol, count the number of carbon atoms bonded to the atom to which the –OH group is attached.

Sample Problem 1: Naming Alcohols from Structural Formulas

Name the following alcohol and identify it as a primary, secondary, or tertiary alcohol:



$$\begin{array}{c} \quad CH_3 \\ \quad | \\ CH_3CCH_2CH_2CH_3 \\ \quad | \\ \quad OH \end{array}$$

Solution

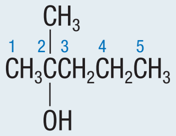
Step 1. Identify the longest carbon chain or ring.

In this compound, the longest chain has 5 carbon atoms: pentane.

Step 2. If there is only one –OH group, the compound has the suffix *-ol*. If more than one group, use the suffixes *-diol* or *-triol*.

There is one –OH group, so this compound is a pentanol.

Step 3. Number the parent chain from the end so that the –OH group is attached to the carbon atom with the lowest possible number.



$$\begin{array}{c} \quad CH_3 \\ 1 \;\; 2 | 3 \;\; 4 \;\; 5 \\ CH_3CCH_2CH_2CH_3 \\ \quad | \\ \quad OH \end{array}$$

The –OH group is attached to the second carbon atom: pentan-2-ol.

Step 4. Identify any other substituents and their locations.

There is also a methyl group attached to the second carbon atom.

This compound is 2-methylpentan-2-ol.

Step 5. Count the number of carbon atoms bonded to the atom to which the –OH group is attached.

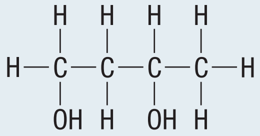
The carbon atom to which the hydroxyl group is attached is also bonded to 3 other carbon atoms, so this is a tertiary alcohol.

Sample Problem 2: Drawing Alcohols

Draw the structure of butane-1,3-diol.

Solution

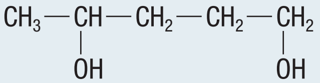
The name "butanediol" indicates that this alcohol consists of a 4-carbon chain with two hydroxyl groups attached to it. The hydroxyl groups are attached to the first and third carbon atoms. Therefore, the structure of this alcohol is



Practice

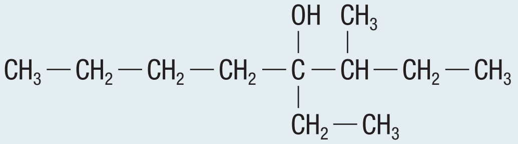
1. Write the name for each of the following compounds: K/U

(a)



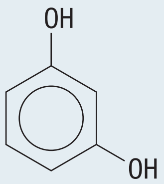
$$\begin{array}{l} CH_3-CH-CH_2-CH_2-CH_2 \\ \qquad\;\; | \qquad\qquad\qquad\quad | \\ \qquad OH \qquad\qquad\quad OH \end{array}$$

(b)



$$\begin{array}{c} \qquad\qquad\qquad\qquad\qquad OH \;\; CH_3 \\ \qquad\qquad\qquad\qquad\qquad | \qquad | \\ CH_3-CH_2-CH_2-CH_2-C-CH-CH_2-CH_3 \\ \qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad\quad CH_2-CH_3 \end{array}$$

(c)



2. Draw the structural formula for each of the following alcohols: K/U C

(a) 2-chloro-2,5-dimethylheptan-3-ol

(b) propane-1,3-diol

(c) phenol

(d) pent-2-ene-1,4-diol

Properties of Alcohols

Alcohols typically have much higher boiling points than the corresponding unsubstituted alkanes. For example, the boiling point of methanol is 65 °C while the boiling point of methane is −162 °C. Consider the intermolecular forces that occur in the compounds in order to understand the differences in properties.

Methane molecules are non-polar and exhibit only weak van der Waals forces. The polarity of methanol molecules, however, results in very strong dipole–dipole forces. These dipole interactions allow hydrogen bonding between the hydroxyl groups of adjacent molecules. As you may recall, **hydrogen bonding** is a type of dipole interaction in which the hydrogen atom attached to a highly electronegative atom on one molecule is strongly attracted to an electronegative atom on another molecule. In methanol, a hydroxyl hydrogen atom on one molecule forms a hydrogen bond with the oxygen atom of a neighbouring molecule (**Figure 6**). Hydrogen bonding between alcohol molecules means that more energy is needed in order to separate molecules from one another. This additional energy must be added to change the liquid into vapour, so the boiling point is higher.

Simple alcohols with short carbon chains are more soluble in water than those with longer carbon chains. The addition of the –OH group increases the polarity of the alcohol molecule and, therefore, its solubility in water. However, as the size of the carbon chain grows, alcohols are less soluble in water. Because the hydrocarbon region of an alcohol molecule is non-polar, alcohols tend to be able to dissolve both polar and non-polar substances. This makes alcohols very useful as solvents.

UNIT TASK **BOOKMARK**

Alcohols are relatively environmentally benign solvents for non-polar solutes. For the Unit Task (page 116), consider whether alcohols would be suitable alternatives to more toxic solvents.

hydrogen bonding a strong dipole–dipole force between a hydrogen atom attached to a highly electronegative atom (N, O, or F) in one molecule and a highly electronegative atom in another molecule

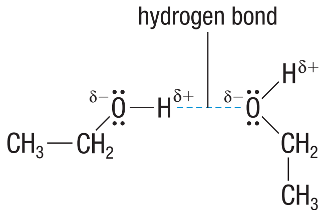


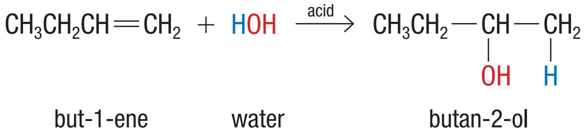
Figure 6 Hydrogen bonds form between the hydroxyl groups of adjacent alcohol molecules.

Investigation **1.4.1**

Properties of Alcohols (page 63)
In this controlled experiment you will make and test predictions about the properties of alcohols.

Reactions Involving Alcohols

Recall from Section 1.2 that an alkene may react with water to produce an alcohol. This hydration reaction is a form of addition reaction. Many alcohols are manufactured commercially by the addition reaction of an alkene and water. An example is the formation of an alcohol from but-1-ene and water, using sulfuric acid as a catalyst. There are two possible products of this reaction: butan-1-ol and butan-2-ol. The reaction follows Markovnikov's rule, however: the hydrogen atom tends to bond to the carbon atom at the end of the butene chain, leaving the –OH group to attach to the second carbon atom. The production of butan-2-ol is therefore favoured. (**Figure 7**).



$$CH_3CH_2CH{=}CH_2 + HOH \xrightarrow{acid} CH_3CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle H}{\underset{|}{CH_2}}$$

Figure 7 The reaction of but-1-ene with water produces butan-2-ol.

The modern method for production of methanol, CH_3OH, combines carbon monoxide with hydrogen gas at high temperature and pressure, using a catalyst. The chemical equation for this reaction is

$$CO(g) + 2\,H_2(g) \xrightarrow{catalyst} CH_3OH(l)$$

Ethanol or beverage alcohol, CH_3CH_2OH, is traditionally prepared by fermenting an aqueous sugar solution, usually from fruit or grains. This reaction requires the presence of yeast and the absence of oxygen. The chemical equation for this reaction is shown below.

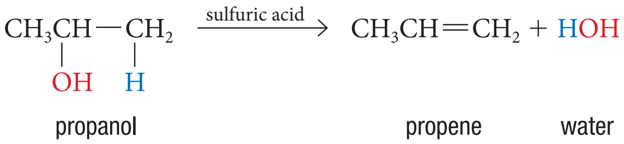
$$C_6H_{12}O_6(aq) \rightarrow 2\,CO_2(g) + 2\,C_2H_5OH(aq)$$

Like many organic compounds, alcohols undergo combustion with oxygen. This reaction, similar to the combustion of hydrocarbons, produces carbon dioxide and water. For example, the following equation represents the combustion of propanol:

$$2\,CH_3CH_2CH_2OH(l) + 9\,O_2(g) \rightarrow 8\,H_2O(g) + 6\,CO_2(g)$$

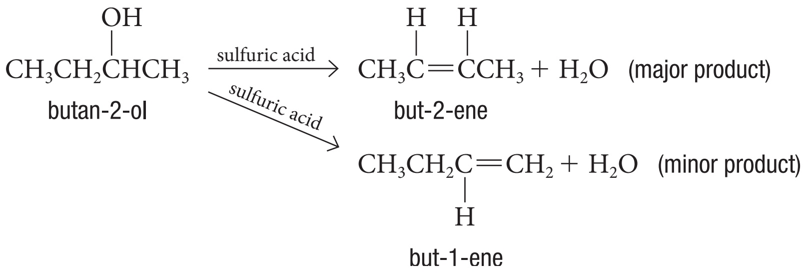
The reverse of the addition reaction that produces an alcohol is a **dehydration reaction** to form an alkene and water. The reaction is catalyzed by sulfuric acid, which removes

dehydration reaction a reaction that involves the removal of a hydrogen atom and a hydroxyl group from the reactant, producing a slightly smaller molecule and water the hydrogen atom and hydroxyl group. The two adjacent carbon atoms form a double bond. An example of a dehydration reaction is the dehydration of propanol.



$$\underset{\text{propanol}}{CH_3\underset{OH}{\underset{|}{C}}H-\underset{H}{\underset{|}{C}}H_2} \xrightarrow{\text{sulfuric acid}} \underset{\text{propene}}{CH_3CH=CH_2} + \underset{\text{water}}{HOH}$$

In dehydration reactions of secondary or tertiary alcohols containing more than 3 carbon atoms, more than one alkene may potentially be produced. Predicting the major product is beyond the scope of this course.



$$\underset{\text{butan-2-ol}}{CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3} \xrightarrow{\text{sulfuric acid}} \underset{\text{but-2-ene}}{CH_3\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}CH_3} + H_2O \quad \text{(major product)}$$

$$\xrightarrow{\text{sulfuric acid}} \underset{\text{but-1-ene}}{CH_3CH_2\underset{H}{\underset{|}{C}}=CH_2} + H_2O \quad \text{(minor product)}$$

In the following tutorial, you will study examples of reactions involving alcohols: addition and dehydration. Addition reactions will be familiar, as you encountered them in Section 1.2.

Tutorial 2 Predicting Reactions Involving Alcohols

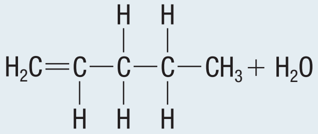
In this tutorial, you will learn to predict the products of two different reactions involving alcohols.

Sample Problem 1: Addition Reaction to Form an Alcohol

Write the chemical equation for the addition reaction of pent-1-ene and water.

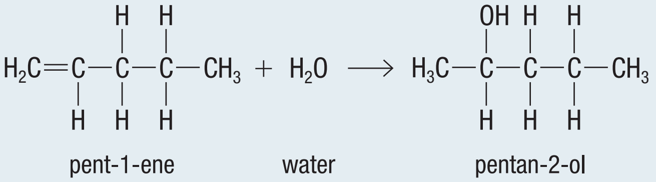
Solution

First, draw the reactants, pent-1-ene and water.



$$H_2C=\underset{H}{\underset{|}{C}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-CH_3 + H_2O$$

As the molecule being added is water, this is a hydration reaction. During the hydration reaction, the double bond will break. According to Markovnikov's rule, a hydrogen atom from the water molecule will tend to bond to the carbon atom that is already bonded to the greatest number of hydrogen atoms. In pent-1-ene, that is the first carbon atom.



$$\underset{\text{pent-1-ene}}{H_2C=\underset{H}{\underset{|}{C}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-CH_3} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{pentan-2-ol}}{H_3C-\overset{OH}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-CH_3}$$

Therefore, the main product of the reaction is pentan-2-ol.

Sample Problem 2: Dehydration Reaction of an Alcohol

Write the chemical equation for the dehydration of ethanol.

Solution

During a dehydration reaction, a water molecule is removed from an alcohol to form an alkene. Ethanol contains only 2 carbon atoms, so there is only one possibility for the position of the double bond; the resulting alkene is ethene. The chemical reaction is

$$C_2H_5OH(l) \xrightarrow{H_2SO_4} C_2H_4(g) + H_2O(g)$$

Practice

1. Draw the chemical equation, showing structural formulas, for the addition reaction that forms butan-2-ol. T/I
2. Write the chemical equation for the dehydration of pentanol. T/I

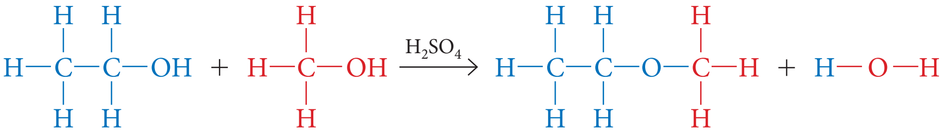
Ethers

Physicians and chemists have long searched for substances that would eliminate pain during medical procedures. A Boston dentist demonstrated the use of dinitrogen monoxide as an anesthetic in 1844. Around the same time, another organic compound was being tested. The compound ethoxyethane (also named diethyl ether or, at that time, simply "ether") is an effective anesthetic. Although ethoxyethane has been used successfully for decades, it is very volatile and flammable. Because of this hazard, ethoxyethane has largely been replaced by safer compounds. Currently, its major use is as a solvent for fats and oils.

An **ether** is an organic compound that contains a functional group in which an oxygen atom is bonded between 2 carbon atoms within a chain. Ethers can be synthesized from the reaction of alcohols. When the alcohols react, a molecule of water is produced in a **condensation reaction**:

ether an organic compound containing an oxygen atom between 2 carbon atoms in a chain

condensation reaction a chemical reaction in which two molecules combine to form a larger molecule and a small molecule, such as water



$$H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}OH + H{-}\overset{H}{\underset{H}{C}}{-}OH \xrightarrow{H_2SO_4} H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}\overset{H}{\underset{H}{C}}{-}H + H{-}O{-}H$$

$$\underset{\text{ethanol}}{CH_3CH_2OH} + \underset{\text{methanol}}{CH_3OH} \xrightarrow{H_2SO_4} \underset{\text{methoxyethane}}{CH_3CH_2OCH_3} + \underset{\text{water}}{HOH}$$

Experimental evidence shows that the boiling points of ethers tend to be slightly higher than those of similar-sized alkanes but lower than the boiling points of similar-sized alcohols. We can explain this by comparing the intermolecular forces in each type of compound. Ethers do not contain hydroxyl groups and they cannot form hydrogen bonds as alcohols do. However, the C–O bond is polar. Furthermore, unbonded electron pairs on the oxygen atom give the molecule a V shape. As a result, we can conclude that ether molecules are somewhat polar. The intermolecular forces in ethers are stronger than those in hydrocarbons but weaker than those in alcohols.

Ethers are useful solvents. The C–O bond allows them to dissolve highly polar substances, while the alkyl group allows them to dissolve less polar substances.

UNIT TASK **BOOKMARK**

Could we use ethers as solvents, to reduce toxic VOCs? Consider this question as you work on the Unit Task, described on page 116.

Naming Ethers

The IUPAC method to name an ether is to add the suffix *-oxy* to the smaller hydrocarbon group that is bonded to the larger alkane group. For example, an ether made up of a methyl group and an ethyl group joined by an oxygen molecule is called methoxyethane. A commonly used alternative nomenclature uses the names of the two hydrocarbon groups followed by the word "ether:" methylethyl ether. If the two alkane groups are the same size, the prefix *di-* is used. Thus, methoxymethane would be called dimethyl ether.

Tutorial 3 Naming and Drawing Ethers

In this tutorial, you will first practise naming ethers according to the IUPAC convention. Then, you will practise drawing structural formulas of ethers.

When naming ethers, follow these steps:

1. Identify the two alkyl groups.
2. Write the name of the shorter alkyl group, then the suffix -*oxy*, then the name of the longer alkyl group as if it were an alkane.

Sample Problem 1: Naming an Ether Given the Structural Formula

Write the name of the ether shown below.

$$H_3C—CH_2—CH_2—O—CH_3$$

Solution

Step 1. Identify the two alkyl groups.

This ether has a propyl group on one side of the oxygen atom and a methyl group on the other.

Step 2. Write the name of the shorter alkyl group, then the suffix -*oxy*, then the name of the longer alkyl group as if it were an alkane. In this case, a number is required to indicate the carbon atom in the propyl group to which the methoxy group is attached.

This ether is 1-methoxypropane.

Sample Problem 2: Drawing an Ether from Its Name

Draw the structural formula for 1-ethoxybutane.

Solution

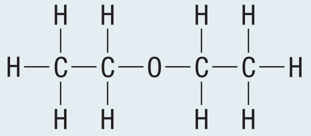
The longer carbon chain is butane, which has 4 carbon atoms. The shorter chain is ethyl, which has 2 carbon atoms. Therefore, 1-ethoxybutane has the following structure:

$$H_3C—CH_2—O—CH_2—CH_2—CH_2—CH_3$$

Practice

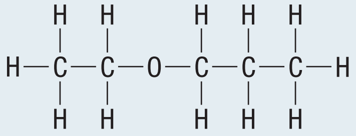
1. Name each of the following ethers: K/U

(a)



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & — & C & — & C & —O— & C & — & C & — & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

(b)



$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & — & C & — & C & —O— & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

2. Draw the structural formula of each of the following ethers: K/U C

(a) 2-methoxypropane

(b) 3-ethoxypentane

Thiols

thiol an organic compound that contains the sulfhydryl (–SH) group

A **thiol** is an organic compound that includes the sulfhydryl functional group, –SH. The sulfhydryl group is similar to the hydroxy group, –OH. Thiols generally have strong odours. For example, a thiol gives garlic its strong odour. The smell associated with the spray of a skunk is also caused by a thiol. Since sulfur is present in the products of digested proteins, thiols are also responsible for the strong stench of sewage.

Gas delivery companies add thiols to natural gas to make leaks easier to detect, since natural gas itself (mostly methane) has no odour.

Hydrogen peroxide reacts with thiols to form odourless disulfide compounds. Hence, hydrogen peroxide is sometimes used to neutralize the odours of many thiols.

To name thiols, the suffix -*thiol* is added to the end of the alkane name. For example, $HSCH_3$ is methanethiol.

1.4 Review

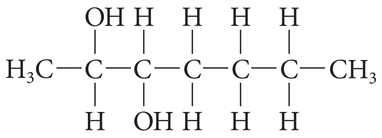
Summary

- Alcohols contain a hydroxyl group, —OH. The hydroxyl group allows alcohols to form hydrogen bonds. Alcohols can be further classified as primary, secondary, and tertiary.
- Alcohols can be produced by hydration reactions of alkenes. Dehydration reactions use a catalyst and acid to change the alcohol back to an alkene and water. In a combustion reaction an alcohol reacts with oxygen, producing carbon dioxide and water.
- Ethers can be produced from the condensation reaction of alcohols. Ethers are widely used as solvents because of their ability to dissolve both polar and non-polar substances.
- Thiols contain the sulfhydryl functional group —SH. They typically have strong odours.

Questions

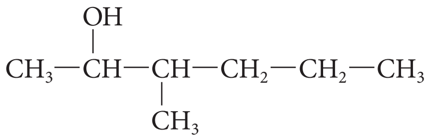
1. Write the name of each of the following compounds: K/U

(a)



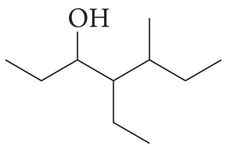
$$\begin{array}{ccccccccccccc} & & \text{OH} & & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \\ & & | & & | & & | & & | & & | & & \\ \text{H}_3\text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{CH}_3 \\ & & | & & | & & | & & | & & | & & \\ & & \text{H} & & \text{OH} & & \text{H} & & \text{H} & & \text{H} & & \end{array}$$

(b)

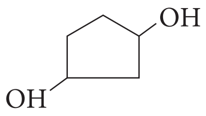


$$\begin{array}{ccccccccccc} & & \text{OH} & & & & & & & & \\ & & | & & & & & & & & \\ \text{CH}_3 & - & \text{CH} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_3 \\ & & & & | & & & & & & \\ & & & & \text{CH}_3 & & & & & & \end{array}$$

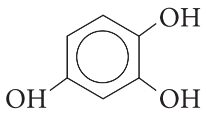
(c)



(d)

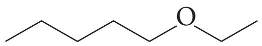


(e)



(f) $H_3C—CH_2—CH_2—CH_2—O—CH_2—CH_2—CH_3$

(g)



(h) $H_3C—CH_2—SH$

2. Draw the structural formula for each of the following compounds: K/U C
   - (a) 5-bromohexan-3-ol
   - (b) 2-methylpentan-3-ol
   - (c) 3,5-dichloropentan-2-ol
   - (d) cyclobutane-1,2-dithiol
   - (e) 2-methoxyheptane
   - (f) cyclohex-4-ene-1,3-diol
3. If you were given two samples and told that one was ethanol and one was heptan-2-ol, describe two tests that you could run on the samples to identify them. T/I
4. Predict the product(s) of each of the following chemical reactions: T/I
   - (a) hept-1-ene + water
   - (b) butan-1-ol with sulfuric acid catalyst
   - (c) propan-1-ol + ethanol
5. Write the chemical equation for the complete combustion of methanol. T/I
6. A chemist needs to synthesize 1-ethoxypentane. She has the following substances available: ethene, pent-1-ene, and water. Describe how the chemist could synthesize 1-ethoxypentane. (Assume that the chemist can use reaction conditions that allow her to overcome Markovnikov's rule.) T/I A
7. Rotten eggs have a distinct odour. Based on your reading in this section, what type(s) of compounds do you think are present in rotten eggs? Conduct research to check your reasoning. A

WEB LINK

1.5 Aldehydes and Ketones

Saffron, produced from the stamens of the crocus flower, is the most expensive spice on Earth (**Figure 1**). The cost per gram of saffron is approximately equal to that of silver. An organic compound, safranal, is responsible for its characteristic aroma. The compounds responsible for the scents of saffron and many other spices, including cumin, vanilla, cinnamon, and ginger, all have a similar functional group: carbonyl. Not surprisingly, scents and perfumes contain many compounds with carbonyl groups. The solvents in some paint and fingernail polish removers, lacquers, and glues also have carbonyl groups. WEB LINK

Figure 1 The stamens of crocus flowers are removed and dried for use as the spice saffron.

carbonyl group a carbon atom double-bonded to an oxygen atom, found in organic compounds such as aldehydes and ketones

The Carbonyl Group

Aldehydes and ketones both contain the carbonyl group. A **carbonyl group** is an atom of carbon double-bonded to an atom of oxygen (**Figure 2**). The carbonyl group is the functional group responsible for the properties of ketones and aldehydes. The difference between the two classes of compound is the location of the carbonyl group within the molecule.

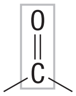
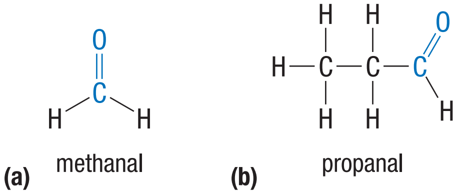


Figure 2 A carbonyl group

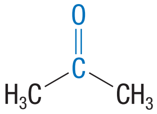
aldehyde an organic molecule containing a carbonyl group that is bonded to at least 1 hydrogen atom

In an **aldehyde**, the carbonyl group is bonded to at least 1 hydrogen atom, which means that it is located at the end of the parent chain of the molecule. In the simplest aldehyde, methanal (also called formaldehyde), the carbon of the carbonyl group is the only carbon atom in the molecule (**Figure 3**). In longer molecules, such as butanal, the carbonyl group is at the end.



(a) methanal (b) propanal

Figure 3 The carbonyl group is always at the end of the carbon chain in an aldehyde molecule.



propanone; a ketone

Figure 4 The carbonyl group is always attached to 2 other carbon atoms in the carbon chain in a ketone molecule.

A **ketone** is an organic compound whose molecules have a carbonyl group bonded to 2 carbon atoms in the carbon chain. The simplest ketone is propanone (also known as acetone), which has 3 carbon atoms including the one in the carbonyl group. Compare the structure of propanone (**Figure 4**) with the structure of propanal (Figure 3(b)).

ketone an organic compound that contains a carbonyl group bonded to 2 carbon atoms

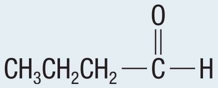
Naming Aldehydes and Ketones

The naming of aldehydes and ketones follows conventions similar to those of the compounds discussed in earlier sections. For an aldehyde, replace the final *-e* from the name of the parent alkane with the suffix *-al*. As Figure 3(a) shows, the simplest aldehyde contains only the carbonyl group bonded to 2 hydrogen atoms. Its parent alkane is methane, so the aldehyde is called methanal. Position numbers are not used in naming aldehydes because the carbonyl group is always designated as carbon number 1 in the chain.

Tutorial 1 Naming and Drawing Aldehydes

Sample Problem 1: Naming Aldehydes from Structural Formulas

Name the following compound:



$$CH_3CH_2CH_2-\overset{\overset{\large O}{\|}}{C}-H$$

Solution

First, determine the name of the base alkane. This compound has a 4-carbon parent chain, so it is based on the alkane butane. The name of the corresponding aldehyde is butanal.

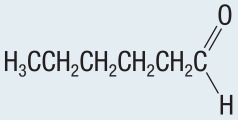
Sample Problem 2: Drawing Aldehydes

Draw the structure of each of the following molecules:

(a) hexanal (b) 7-hydroxyoctanal

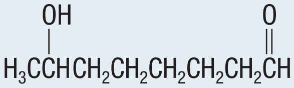
Solution (a)

Hexanal is based on hexane. The suffix *-al* tells us that the compound is an aldehyde, so it has a carbonyl group at one end (carbon atom number 1) of the carbon chain.



Solution (b)

7-hydroxyoctanal is based on octane. The carbonyl group is located on carbon atom number 1 and a hydroxyl group is located on carbon atom number 7.



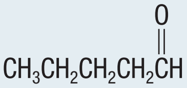
$$H_3C\overset{\overset{\large OH}{|}}{C}HCH_2CH_2CH_2CH_2CH_2\overset{\overset{\large O}{\|}}{C}H$$

When representing molecules that have several carbon atoms, chemists sometimes use a convention called line diagrams. These are a "shorthand" form of structural diagrams in which the carbon atoms and their attached hydrogen atoms are not shown. Instead, you assume that there is a carbon atom at the end of each line and at every bend in the line, and that each carbon atom is surrounded by the maximum possible number of hydrogen atoms. The following Practice questions include an example of a line diagram.

Practice

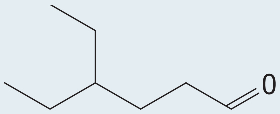
1. Name each of the following aldehydes: K/U

(a)

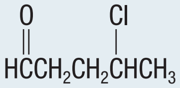


$$CH_3CH_2CH_2CH_2\overset{\overset{\large O}{\|}}{C}H$$

(b)



(c)



$$H\overset{\overset{\large O}{\|}}{C}CH_2CH_2\overset{\overset{\large Cl}{|}}{C}HCH_3$$

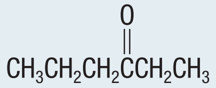
2. Draw the structure of each of the following aldehydes: K/U C
    (a) butanal
    (b) 4-methylpentanal
    (c) 2-hydroxybutanal

To name a ketone, the *-e* of the parent alkane is replaced with the suffix *-one*. The simplest ketone, shown in Figure 4, has 3 carbon atoms. Its name, derived from propane, is propanone. For ketones with 5 or more carbon atoms, the position of the carbonyl is designated by the number of the carbon atom of the carbonyl group. As usual, we assign the lowest possible number.

Tutorial 2 Naming and Drawing Ketones

Sample Problem 1: Naming Ketones from Structural Formulas

Name the ketone shown below.



$$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3$$

Solution

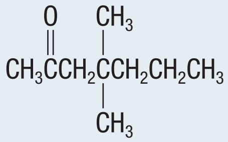
First, identify the parent alkane: hexane. Then, number the carbon atoms to give the carbonyl group the lowest possible number. This compound is hexan-3-one.

Sample Problem 2: Drawing Ketones

Draw the structural formula for 4,4-dimethyl-heptan-2-one.

Solution

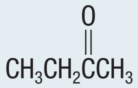
First, draw the carbon chain for the parent alkane: heptane. Then, draw the carbonyl group attached to the appropriate carbon atom. Next, add the other substituent groups—two methyl groups—to their carbon atoms. Finally, add hydrogen atoms to the remaining carbon atoms so that each carbon has four bonds.



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_2CH_2CH_3$$

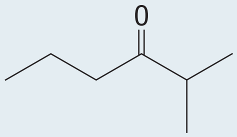
Practice

1. Name the following ketones: K/U
    (a)

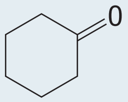


$$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

    (b)



    (c)



2. Draw the structures for the following ketones: K/U C
   (a) 4-methylheptan-3-one
   (b) 1,3-dichlorobutan-2-one
   (c) heptane-3,5-dione
   (d) cyclobutanone
   (e) 4-hydroxypentan-2-one

Properties of Aldehydes and Ketones

The chemical and physical properties of aldehydes and ketones are affected by the carbonyl group. Because oxygen has a much higher electronegativity than carbon, electrons from the double bond are attracted to the oxygen atom. As a result, the molecules are polar. They have dipole–dipole attractions but, since the molecules do not contain a hydroxyl group, they do not form hydrogen bonds with one another. Therefore, their boiling points are lower than similar alcohols. The presence of the carbonyl oxygen does allow aldehydes and ketones to form attractions with water molecules, so these molecules are more soluble in water than are alkanes, but less soluble than are similarly sized alcohol molecules. Small aldehydes and ketones are completely soluble in water, but the solubility decreases as additional carbons are added to the chain. Aldehydes and ketones are often used as solvents in industrial processes.

UNIT TASK BOOKMARK

Propanone (acetone) is a VOC that is widely used as a solvent. Consider its pros and cons as you work on the Unit Task, described on page 116.

Reactions Involving Aldehydes and Ketones

Historically, reactions in which oxygen is a reactant were referred to as oxidation reactions. The term has since come to have a broader meaning, including those reactions in which a substance loses electrons. The chemistry of these reactions will be discussed in Unit 5.

Formation of Aldehydes and Ketones: Controlled Oxidation

Aldehydes and ketones are synthesized by the controlled oxidation of alcohol. In a complete oxidation reaction (combustion reaction) of alcohol, the products are carbon dioxide and water. Thermal energy is also released.

In the controlled oxidation of an alcohol, the reactant is not completely oxidized. If there is only a limited quantity of oxygen present, an aldehyde or ketone is produced. In these types of reactions, oxygen atoms can be supplied by air or by compounds known as oxidizing agents. The balanced chemical equation for the reaction of ethanol with oxygen from the air is

$$2\ C_2H_5OH(l) + O_2(g) \rightarrow 2\ C_2H_4O(l) + 2\ H_2O(l)$$

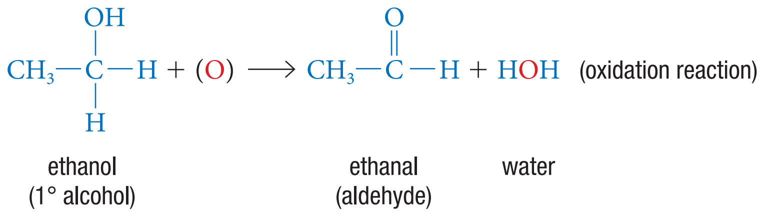
Oxidizing agents are oxygen-rich compounds such as potassium dichromate, K_2Cr_2O hydrogen peroxide, H_2O_2, and potassium permanganate, $KMnO_4$. To keep the equations simple, we often use (O) to represent the oxidizing agent in an oxidation reaction.

Investigation 1.5.1

Reactions of Three Isomers of Butanol (page 64)

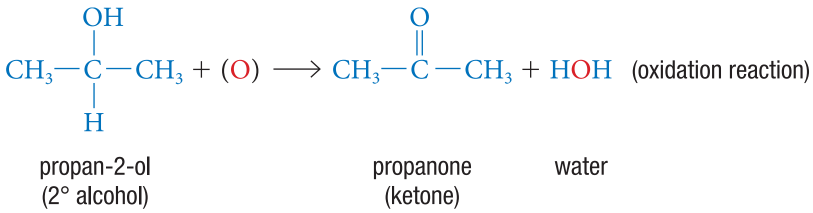
Now that you have studied the reactions of various alcohol isomers, you have an opportunity to investigate how the structures of alcohol molecules affect their chemical characteristics.

When a primary alcohol is oxidized, the oxygen atom and one of the hydrogen atoms remain on the carbon atom, resulting in a carbonyl group on the terminal carbon atom, an aldehyde. The 2 hydrogen atoms that were removed bond with oxygen from the oxidizing agent. For example, the controlled oxidation of ethanol (a primary alcohol) produces ethanal and water:



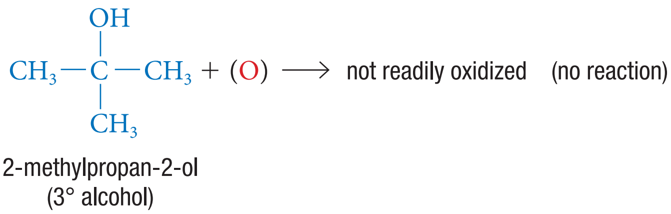
$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-H + (O) \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-H + HOH$$

A secondary alcohol will also form a carbonyl group, producing a ketone rather than aldehyde. One hydrogen atom is removed from the hydroxyl group and the second comes from the carbon atom to which the hydroxyl group is bonded. The controlled oxidation of propan-2-ol produces propanone and water:



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_3 + (O) \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + HOH \quad \text{(oxidation reaction)}$$

Tertiary alcohols do not react in the same way because no hydrogen atom is available on an adjacent carbon atom. An example is the attempted oxidation of 2-methylpropan-2-ol:

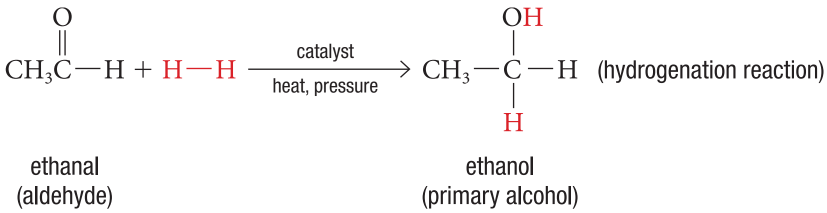


$$CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3 + (O) \longrightarrow \text{not readily oxidized} \quad \text{(no reaction)}$$

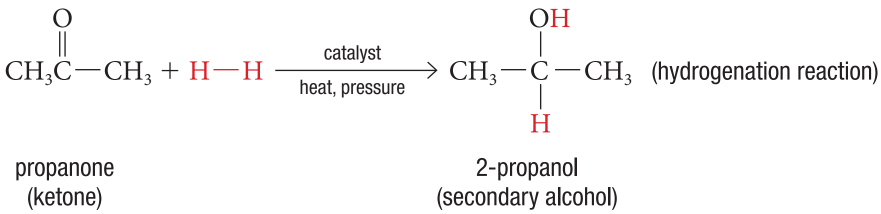
To summarize the controlled oxidation reactions of alcohols, a primary alcohol produces an aldehyde, a secondary alcohol produces a ketone, and a tertiary alcohol does not easily oxidize.

Hydrogenation of Aldehydes and Ketones

Recall from Section 1.2 that a hydrogenation reaction involves the addition of hydrogen to another molecule. In the hydrogenation reaction of an aldehyde or a ketone, the net result is that a double bond is broken. One hydrogen atom is added to the oxygen atom and another is added to the carbon atom to which the oxygen is bonded. Hydrogenation of aldehydes or ketones occurs only under conditions of high temperature and pressure, and the presence of a catalyst. The product of this reaction is an alcohol. For example, hydrogenation of ethanal forms ethanol, and hydrogenation of propanone forms propan-2-ol. These are the reverse of the oxidation of alcohols. The hydrogenation of the aldehyde produces a primary alcohol, and the hydrogenation of a ketone produces a secondary alcohol:



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-H + H-H \xrightarrow[\text{heat, pressure}]{\text{catalyst}} CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \quad \text{(hydrogenation reaction)}$$



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H-H \xrightarrow[\text{heat, pressure}]{\text{catalyst}} CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_3 \quad \text{(hydrogenation reaction)}$$

Tutorial 3 Reactions Involving Aldehydes and Ketones

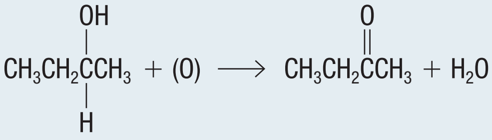
In this tutorial you will explore reactions involving aldehydes and ketones as both reactants and products.

Sample Problem 1: Preparing Aldehydes and Ketones from Alcohols

Draw the structural formula equations for the reactions that produce butanone and butanal.

Solution

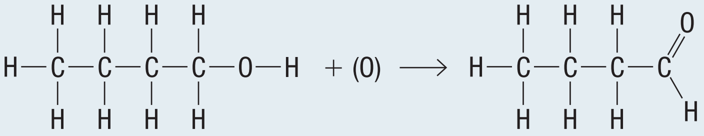
Butanone and butanal both have 4-carbon backbones. Both can be formed by the controlled oxidation of a 4-carbon alcohol. Ketones form from a secondary alcohol, so butanone will form during the controlled oxidation of butan-2-ol:



$$CH_3CH_2\underset{H}{\overset{OH}{C}}CH_3 + (O) \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3 + H_2O$$

butan-2-ol butanone

Aldehydes form during the oxidation of primary alcohols, so to form butanal, butan-1-ol needs to react with oxygen:



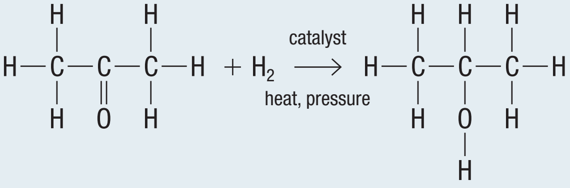
butan-1-ol butanal

Sample Problem 2: Producing an Alcohol from a Ketone

Draw the structural formula equation representing the hydrogenation of propanone.

Solution

The hydrogenation of a ketone produces a secondary alcohol. Therefore, the hydrogenation of propanone will form propan-2-ol:



propanone propan-2-ol

Practice

1. Name the reactants required to produce each of the following compounds, then illustrate the reactions using structural formulas. K/U C
   (a) pentanone
   (b) pentanal
2. Name the products resulting from the hydrogenation of each of the following compounds, then illustrate the reactions using structural formulas. K/U C
   (a) ethanal
   (b) butanone
3. Predict the products of the controlled oxidation of the following isomers: K/U
   (a) hexan-1-ol
   (b) hexan-2-ol
   (c) 2-methylpentan-2-ol

1.5 Review

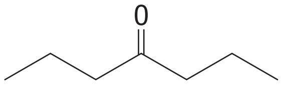
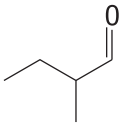
Summary

- If a carbonyl group is attached to at least 1 hydrogen atom, the molecule is an aldehyde. It is named using the suffix *-al*.
- If a carbonyl group is attached to 2 carbon atoms, the molecule is a ketone. It is named using the suffix *-one*.
- The carbonyl group (C=O) makes organic molecules polar, giving them higher boiling points and greater water solubility than the corresponding alkanes.
- The controlled oxidation of a primary alcohol produces an aldehyde. The controlled oxidation of a secondary alcohol produces a ketone. Tertiary alcohols do not readily undergo controlled oxidation.
- The hydrogenation of an aldehyde produces a primary alcohol. The hydrogenation of a ketone produces a secondary alcohol.

Questions

1. Copy and complete **Table 1** in your notebook. T/I C
2. Using the condensed structural formulas, write a chemical equation for the controlled oxidation of the following alcohols. Write the IUPAC name for each product. T/I
   (a) pentan-2-ol
   (b) hexan-1-ol
3. (a) Design a procedure to prepare an alcohol from propanone. Describe the main steps in the procedure and the conditions needed.
   (b) Write a chemical equation to represent the reaction. T/I C
4. You have been asked to prepare a sample of ethanal from an alcohol. K/U T/I
   (a) What alcohol will you use as your reactant? Explain.
   (b) Describe the main steps in the procedure and the conditions needed to prepare ethanal.
   (c) Draw or write a chemical equation to represent the reaction.
5. Design an experimental procedure that you could carry out to allow you to distinguish a tertiary alcohol from a primary or secondary alcohol. T/I A

Table 1

Name	Condensed structure	Line diagram or structural formula	Type of compound
	$CH_3CH_2CH_2CH_2CH_2CH_2CHO$		
			
	$CH_3CH_2COCH_2CH_3$		
1-chlorobutan-2-one			
3-methylpentanal			
			

Carboxylic Acids, Esters, and Fats

1.6

Oranges, lemons, and tomatoes are all foods that naturally contain citric acid. Sour candies get their sour taste from ascorbic acid. Compounds with functional groups that make them acidic give foods a tart flavour.

Carboxylic Acids

A **carboxylic acid** is an organic compound that contains a **carboxyl group**, –COOH (**Figure 1**). When a carboxylic acid is in aqueous solution, a hydrogen ion may be removed from the carboxyl group relatively easily. As you know, a solution that contains hydrogen ions is acidic. These compounds are therefore weak acids. Citrus fruits, crabapples, rhubarb, and other foods that contain carboxylic acids have a sour, tangy taste. Police routinely use tracking dogs to aid in their police work. The dogs, with their acute sense of smell, are able to pick up and follow the trail of a scent. One scent that the dogs can track is the carboxylic acid in the molecules of a person's sweat.

carboxylic acid a weak organic acid containing at least one carboxyl group

carboxyl group a carbon atom that is double-bonded to 1 oxygen atom and single-bonded to a hydroxyl group

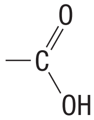


Figure 1 A carboxyl group

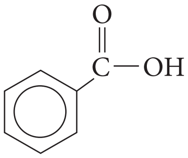
Naming Carboxylic Acids

The functional group of carboxylic acids, –COOH, combines two smaller groups: a hydroxyl group and a carbonyl group. To name organic compounds containing a carboxylic group, start with the alkane name for the longest chain, including the carbon atom in the carboxyl group. Drop the *-e* suffix of the root compound and replace it with the suffix *-oic*, followed by the word *acid*. For example, a carboxylic acid with 3 carbon atoms is propanoic acid (**Figure 2**(**a**)).

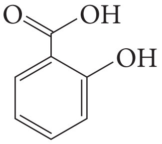
The simplest carboxylic acid is methanoic acid (formic acid) (**Figure 2**(**b**)). The molecule has 1 carbon atom that is also part of the carboxylic group. Methanoic acid is used to remove hair from hides and in rubber-recycling processes. It is also the compound that causes a burning sensation when ants bite.

The next carboxylic acid, with 2 carbon atoms, is ethanoic acid (**Figure 2**(**c**)). Vinegar is typically 5 % ethanoic acid by volume, so it has the sour taste that is characteristic of carboxylic acids. Ethanoic acid is used as a preservative in the food industry, and is also used extensively in the textile-dyeing industry.

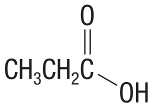
The simplest aromatic carboxylic acid is benzoic acid, an acid whose common name is the same as its IUPAC name. The sodium salt of benzoic acid, sodium benzoate, is used as a preservative in foods and beverages. Note that, in a compound that combines an alcohol and a carboxylic acid, the alcohol is indicated as a substituent group: *hydroxy.*



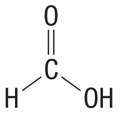
benzoic acid



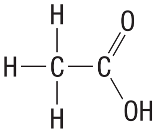
2-hydroxybenzoic acid



(a) propanoic acid



(b) methanoic acid (formic acid)

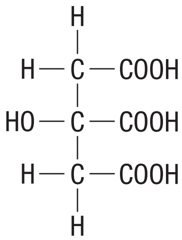


(c) ethanoic acid (acetic acid)

Figure 2 Three common carboxylic acids

Some carboxylic acids have more than one carboxyl group. When naming an acid with two carboxyl groups, use the suffix *dicarboxylic acid*. Citric acid is an example of a compound with three carboxylic groups (**Figure 3**).

Formic acid, acetic acid, and benzoic acid are acceptable IUPAC names that do not follow the systematic rules for naming acids. In the following tutorial, you will practise naming and drawing carboxylic acids according to the systematic IUPAC rules.



2-hydroxypropane-1,2,3-tricarboxylic acid
(citric acid)

Figure 3 A tricarboxylic acid

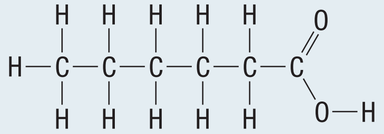
Tutorial 1 Naming and Drawing Carboxylic Acids

Naming and drawing carboxylic acids requires first identifying the part of the compound that includes the carboxyl group, then accounting for any substituents.

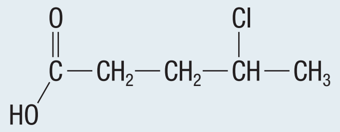
Sample Problem 1: Naming Carboxylic Acids from Structural Formulas

Write the name of each of the following carboxylic acids:

(a)



(b)



Solution (a)

First, identify the compound that forms the root of the acid. This compound contains a 6-carbon chain (including the carboxylic acid carbon), so its root is hexane. There is one carboxyl group in the compound, so its name is hexanoic acid.

Solution (b)

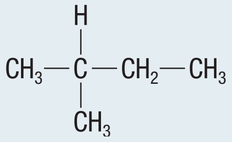
This compound contains a 5-carbon chain: pentane. There is one carboxyl group in the compound, so it is a pentanoic acid. The chlorine substituent is on the fourth carbon, numbering from the carboxyl group, so the compound is 4-chloropentanoic acid.

Sample Problem 2: Drawing Carboxylic Acids

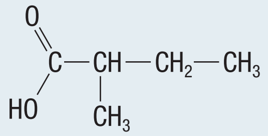
Draw the structure of 2-methylbutanoic acid.

Solution

First, draw the root structure, methylbutane.

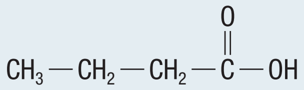


Next, change a terminal carbon to a carboxyl group. The *2-* prefix indicates that the methyl group is on the second carbon from the carboxyl group, so the carboxyl group must be on the end closest to the methyl group. Therefore, the correct structure is as shown at right:



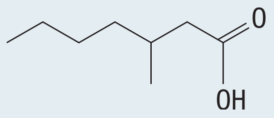
Practice

1. Name each of the following carboxylic acids: K/U
   (a) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$
   (b)



$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$

   (c)



2. Draw the structure of each of the following carboxylic acids: K/U C
   (a) octanoic acid
   (b) 3-methylpentanoic acid
   (c) ethanedioic acid

LEARNING **TIP**

IUPAC and Common Names
You have probably realized that many compounds have both common names and systematic IUPAC names. This textbook mostly uses the systematic names as they help with visualizing the structure of the compound. However, some common names are so familiar that they are also recognized by IUPAC. Acetic acid and formic acid are two such names. You should be familiar with the common names as well as the systematic names of these compounds.

Properties of Carboxylic Acids

Since carboxylic acids have two polar groups—a carbonyl and a hydroxyl—located close together, their molecules are very polar. The carboxyl groups form hydrogen bonds with one another and with polar solvents such as water. Due to this hydrogen bonding, carboxylic acids with 5 or fewer carbon atoms are very soluble in water. Larger carboxylic acids have decreasing solubility due to the large non-polar hydrocarbon group. They are, however, soluble in polar organic solvents, such as alcohols.

Carboxylic acids share many properties with other acids. They affect acid–base indicators, so litmus paper can be used to indicate the presence of carboxylic acids in a mixture of hydrocarbons. Carboxylic acids also react with bases to form ionic compounds and water. Soap is a compound made up of cations of sodium or potassium and anions based on carboxylic acids with multi-carbon alkyl chains.

The melting points of carboxylic acids are higher than their hydrocarbon counterparts because of dipole interactions of the polar carboxyl groups (**Table 1**).

Investigation **1.6.1**

Properties of Carboxylic Acids (page 65)

Now that you have learned about the structures and properties of carboxylic acids, you are ready to explore their properties in the lab.

Table 1 Comparison of the Melting Points of Carboxylic Acids and Alkanes

Number of carbon atoms	Number of –COOH groups	Compound	Melting point (°C)
1	0	methane	−182
1	1	methanoic acid (formic acid)	8
2	0	ethane	−183
2	1	ethanoic acid (acetic acid)	17
2	2	ethanedioic acid (oxalic acid)	189
4	0	butane	−138
4	1	butanoic acid	−8
4	2	2,3-dihydroxybutanedioic acid (tartaric acid)	206
6	0	hexane	−95
6	1	hexanoic acid	13
6	3	2-hydroxypropane-1,2,3-tricarboxylic acid (citric acid)	153

Esters

Many plants naturally produce esters, which are responsible for many of the odours of fruits, flowers, and perfumes. Synthetic esters are often used as flavourings in processed foods, and as scents in cosmetics and perfumes. An **ester** is characterized by a functional group that is similar to a carboxyl group except that the hydrogen atom is replaced with an alkyl group (**Figure 4**). The letters R and R′ in the formula represent alkyl groups in which a carbon atom attaches to the functional group. CAREER LINK

ester an organic compound that contains a carbonyl group bonded to a second oxygen atom which is bonded to another carbon atom

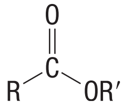
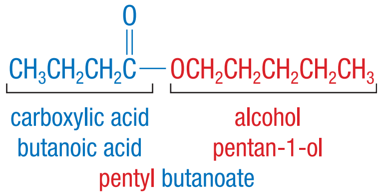


Figure 4 An ester functional group

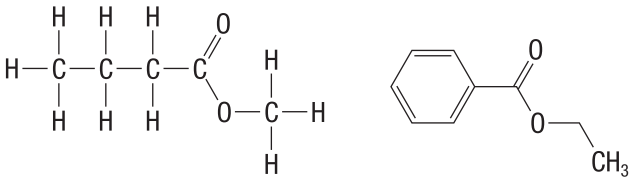
Naming Esters

Esters are formed by the condensation reaction of a carboxylic acid and an alcohol. To name the resulting ester, determine which part of the molecule was contributed by the alcohol. This is the part that does not include the carbonyl group. In **Figure 5** the alcohol portion of the ester comes from pentan-1-ol. This gives the ester the first part of its name: *pentyl*. The second part of the name comes from the carboxylic acid, butanoic acid. The *-oic acid* part of the name is dropped and replaced with *-oate*: *butanoate*. Therefore, the name of the compound is pentyl butanoate, the ester that gives apricots their aroma. Other esters have different distinctive aromas (**Figure 6**).



$$\underbrace{\mathrm{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}}}_{}{-}\underbrace{\mathrm{OCH_2CH_2CH_2CH_2CH_3}}_{}$$

Figure 5 The ester pentyl butanoate is formed by combining a carboxylic acid with an alcohol in a condensation reaction.



(a) methyl butanoate **(b)** ethyl benzoate

Figure 6 These esters have the aromas of (a) pineapple and (b) cherries.

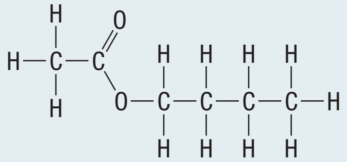
Tutorial 2 Naming and Drawing Esters

When naming esters, follow these steps:

1. Identify the two alkyl groups.
2. Determine which group originated from the carboxylic acid and which originated from the alcohol.
3. Write the name with the alcohol part first and the carboxylic acid part second.

Sample Problem 1: Naming an Ester from Its Structural Formula

Name this ester:



Solution

Step 1. Identify the two alkyl groups.

There is a 2-carbon ethyl group and a 4-carbon butyl group.

Step 2. Determine which group originated from the carboxylic acid and which originated from the alcohol.

The group that includes the carbonyl group originated from the carboxylic acid; in this case, ethanoic acid. The other group originated from the alcohol: butan-1-ol.

Step 3. Write the name with the alcohol part first and the carboxylic acid part second.

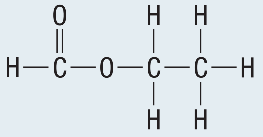
This ester is butyl ethanoate.

Sample Problem 2: Drawing an Ester

Draw the structural formula of ethyl methanoate.

Solution

The first part of the name is ethyl, which indicates a 2-carbon alkyl group. The second part of the name, methanoate, indicates a 1-carbon carboxyl part. Therefore, the structure is

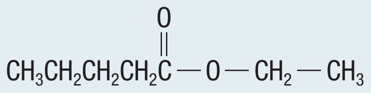


$$\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}$$

Practice

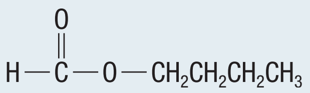
1. Name each of the following esters: K/U

(a)



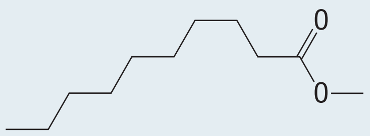
$\mathrm{CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3}$

(c)

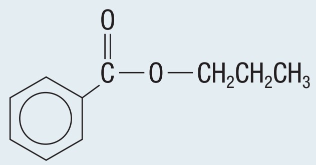


$\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_2CH_2CH_3}$

(b)



(d)



2. Draw the structure of each of the following esters: K/U C

(a) methyl hexanoate (b) methyl benzoate

Properties of Esters

The functional group of an ester is similar to the carboxyl group of an acid, but without the hydroxyl group. As a result, esters are less polar than carboxylic acids and do not form hydrogen bonds. Small esters are soluble in water due to the polarity of their carbon–oxygen bonds. Esters are less soluble in water than carboxylic acids and have lower boiling points. Since their polarities are similar to those of aldehydes and ketones, the melting and boiling points of esters are similar to those of the corresponding aldehydes and ketones. Smaller, low–molecular mass esters are gases at room temperature, but the larger, heavier esters are waxy solids.

Reactions Involving Carboxylic Acids and Esters

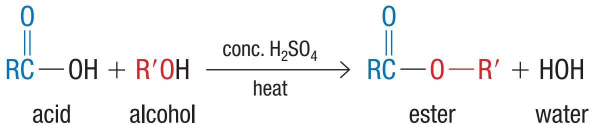
Formation of Carboxylic Acids

Carboxylic acids can be formed by the oxidation of aldehydes in the presence of an oxidizing agent. The roadside Breathalyzer test relies on just such a reaction, in which the oxidizing agent changes colour. The dichromate ion, $Cr_2O_7^{2-}$, is the oxidizing agent. It is orange in colour. When a person exhales air containing ethanol into the Breathalyzer tube, the ethanol is oxidized to ethanal, which is then further oxidized to ethanoic acid. The dichromate ion is changed to a different ion, which has a green colour. The extent of the colour change indicates the concentration of alcohol in the exhaled air.

Formation of Esters: Esterification

Esterification is a condensation reaction in which an alcohol and carboxylic acid react to form an ester and water. **Figure 7** shows the general reaction. You have already seen some specific examples of these reactions earlier in this section.

esterification the reaction of a carboxylic acid and alcohol to form an ester and water



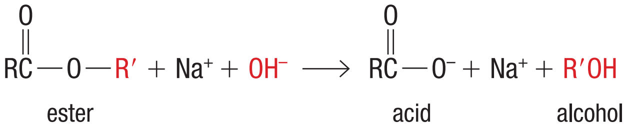
$$\mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{OH} + \mathrm{R'OH} \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} \mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{R'} + \mathrm{HOH}$$

Figure 7 The general esterification reaction

Reaction of Esters: Hydrolysis

When esters are treated with an acid or a base, the esterification process can be reversed. The ester splits into the carboxylic acid and alcohol components with the addition of a molecule of water. This reaction is called **hydrolysis**. The general example, shown in **Figure 8**, is carried out in a basic solution. One of the products is the sodium salt of the carboxylic acid and the other is an alcohol.

hydrolysis the breaking of a covalent bond in a molecule by the addition of the elements of water (hydrogen and oxygen); the splitting of an ester into carboxylic acid and alcohol components



$$\mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{R'} + \mathrm{Na^+} + \mathrm{OH^-} \longrightarrow \mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O^-} + \mathrm{Na^+} + \mathrm{R'OH}$$

Figure 8 The general hydrolysis reaction of an ester

Fats and oils are esters of long-chain acids. When these long-chain esters are heated with a strong base, such as sodium hydroxide, the hydrolysis reaction occurs. The sodium salts of this reaction are commonly known as soaps. The reaction is known as saponification. You will learn more about this reaction later in the section.

Tutorial 3 Predicting Reactions Involving Carboxylic Acids

This tutorial reviews some reactions that involve carboxylic acids.

Sample Problem 1: Carboxylic Acid Production

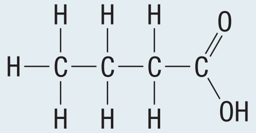
Write equations representing the two chemical reactions that result in the formation of butanoic acid from an alcohol.

Solution

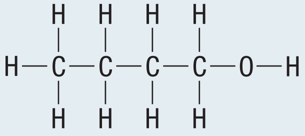
First, consider the reactions that must take place for an alcohol to be converted into butanoic acid. Butanoic acid can be formed from an aldehyde. The first reaction must therefore be the reaction of the alcohol to form an aldehyde; the second must be the reaction of the aldehyde to form the carboxylic acid.

Next, draw the structural formulas of the three compounds.

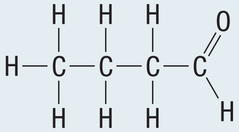
The product is butanoic acid:



To form butanoic acid, start with a primary alcohol with 4 carbon atoms: butan-1-ol.

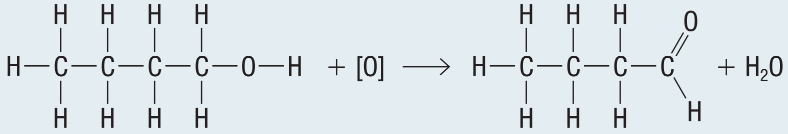


The alcohol reacts with an oxidizing agent to form an aldehyde, butanal.



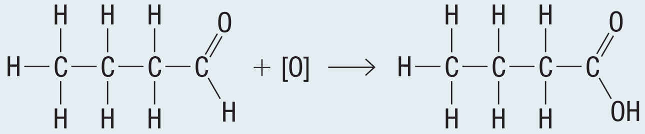
Butanal is oxidized further to form the carboxylic acid, butanoic acid.

Finally, write the equations in the order in which they occur.



butan-1-ol

butanal



butanal

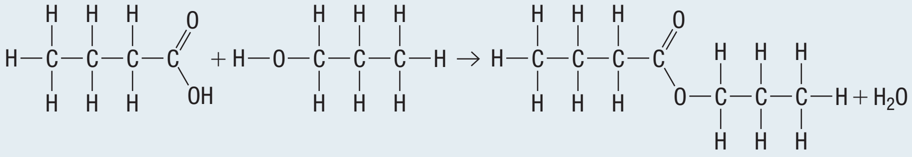
butanoic acid

Sample Problem 2: Esterification

Draw the structural formula equation representing the reaction that forms propyl butanoate. Also write the names of the compounds involved.

Solution

First, determine the compounds that react to produce the ester. Esters are formed from a carboxylic acid and an alcohol. The last part of the ester name tells you that the carboxylic acid is butanoic acid. The first part of the ester name tells you that the alcohol is propan-1-ol. Esterification reactions are usually written with the carboxylic acid first, followed by the alcohol.



butanoic acid

propan-1-ol

propyl butanoate

water

Investigation **1.6.2**

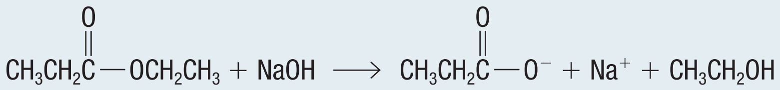
Synthesizing Esters (page 66)
In this investigation you will synthesize specific esters from their component carboxylic acids and alcohols.

Sample Problem 3: Hydrolysis of Esters

Write the structural formula equation for the hydrolysis of ethyl propanoate by sodium hydroxide solution.

Solution

The hydrolysis of an ester produces a carboxylic acid and an alcohol. In this case, the carboxylic acid is propanoic acid and the alcohol is ethanol. Draw the part of the compound that includes the carboxyl group on the left side of the reactant molecule.



$$\mathrm{CH_3CH_2\overset{\overset{O}{\|}}{C}-OCH_2CH_3 + NaOH \longrightarrow CH_3CH_2\overset{\overset{O}{\|}}{C}-O^- + Na^+ + CH_3CH_2OH}$$

Practice

1. Draw structural formula equations illustrating the following reactions. Give the IUPAC name for every compound involved. T/I
   - (a) the production of 2-methylpropanoic acid from an aldehyde
   - (b) the production of a carboxylic acid from ethanal
   - (c) the esterification reaction between propanol and hexanoic acid
   - (d) the hydrolysis of methyl butanoate in the presence of sodium hydroxide solution

Fats and Oils

Fats and oils are large ester molecules known as **lipids**. The long-chain carboxylic acid component is called a **fatty acid**. Common fatty acids are listed in **Table 2**. The alcohol component is glycerol. Glycerol is a 3-carbon alcohol with three hydroxyl groups, so it can bond with three fatty acids at once (**Figure 9**). The ester that is formed is called a **triglyceride**. So, fats and oils are triglycerides.

lipid a class of organic compound that includes fats and oils

fatty acid a long-chain carboxylic acid

triglyceride an ester formed from long-chain fatty acids and glycerol

Table 2 Common Fatty Acids

Name	Formula	Source
linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	vegetable oils (e.g., sunflower seed oil); soya bean oil
oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	most animal fats and vegetable oils (e.g., olive oil)
palmitic acid	$CH_3(CH_2)_{14}COOH$	lard, tallow, palm, and olive oils
stearic acid	$CH_3(CH_2)_{16}COOH$	most animal fats and vegetable oils

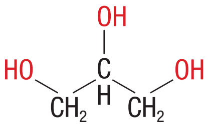


Figure 9 Glycerol

Although the general structure of fats and oils is the same, fats are usually solid at room temperature, while oils are usually liquid. The chain length and degree of unsaturation of the fatty acids generally determine whether a triglyceride is a fat or an oil.

Lipids contain long hydrocarbon chains that release a lot of energy when "burned" or oxidized. In this way lipids are similar to fossil fuels. Living cells can "burn" or metabolize lipids to release their stored energy.

Investigation **1.6.3**

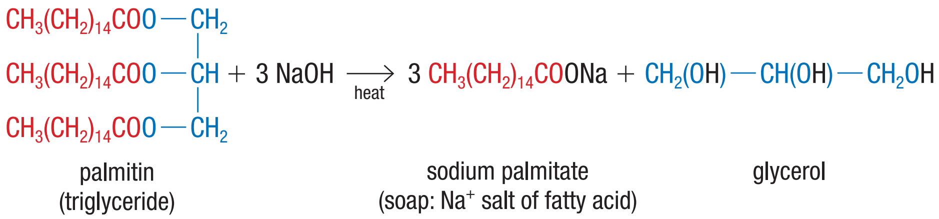
Making Soap (Teacher Demonstration) (page 67)
Making soap is a traditional skill. Here you will see soap emerge from the reactants.

Saponification

You have already seen how esters can be hydrolyzed into their component alcohols and acids in a reaction that is the reverse of esterification. In a similar way, a triglyceride can be split to produce glycerol and the sodium salt of the fatty acid when sodium hydroxide is added to the triglyceride. This resulting sodium salt is commonly

saponification the process of making soap by heating fats or oils with a strong base

called soap, so the reaction is called **saponification** (**Figure 10**). Palmitin and stearin from palm oil and olive oil are common triglycerides used for soap making.



$$\begin{array}{l} CH_3(CH_2)_{14}COO-CH_2 \\ \qquad\qquad\qquad\qquad\;\; | \\ CH_3(CH_2)_{14}COO-CH + 3\ NaOH \xrightarrow[\text{heat}]{} 3\ CH_3(CH_2)_{14}COONa + CH_2(OH)-CH(OH)-CH_2OH \\ \qquad\qquad\qquad\qquad\;\; | \\ CH_3(CH_2)_{14}COO-CH_2 \end{array}$$

Figure 10 Saponification reactions involve a triglyceride (fat or oil) and a base.

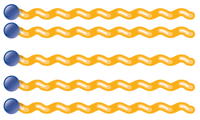
Structure and Properties of Fats and Oils

The best-known property of lipids is their insolubility in water. For example, salad dressing made of oil and vinegar needs to be shaken to mix the two liquids before using. Even so, the two components quickly separate again: oil does not dissolve in the aqueous vinegar. Lipids are not water soluble because of the non-polar nature of the long fatty acid chains in the triglyceride molecules. These long, non-polar chains overcome the polarity of the carbon–oxygen bonds in the ester groups.

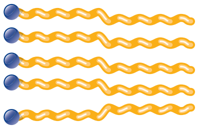
The hydrocarbon chains in fatty acids affect the physical state of the lipid. The shape of the fatty acids determines how tightly the lipid molecules can be packed together. This affects their melting point. Saturated hydrocarbon chains rotate freely around the single carbon–carbon bonds. Each long hydrocarbon chain is a flexible structure that allows the chains to find an optimal packing position. This maximizes the van der Waals interactions between molecules. More thermal energy is required to overcome the attractive forces and separate the molecules, which causes lipids made from saturated fatty acids to have a relatively high melting point. These triglycerides are solids at room temperature.

Unsaturated hydrocarbon chains contain double bonds. These double bonds limit the amount of rotation around the carbon–carbon bonds. Fatty acid chains that contain double bonds can have a *cis* formation or a *trans* formation. *Cis* formations produce kinks in the fatty acid chains and prevent them from packing together tightly (**Figure 11**). The van der Waals interactions are weaker, so it takes less thermal energy to separate the fatty acid chains. Therefore, the melting point of a given unsaturated compound is lower than that of its saturated counterpart. Triglycerides made from unsaturated fatty acid chains with *cis* double bonds are likely to be liquids at room temperature.

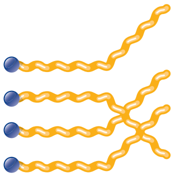
The *trans* form of the fatty acid has a much smaller bend in the chain, so its melting point is closer to that of the unsaturated fat. *Trans* fats are widely manufactured and used because they have properties that increase stability and enhance flavours in some foods. In addition, they allow the manufacture of solid margarine from liquid oils. Unfortunately, these fats are not digested by the digestive system in the same way as saturated fats. This can lead to health problems due to buildup of fats and their by-products in blood vessels and internal organs. Health Canada advises us to choose foods that contain little or no *trans* fat.



(a) saturated lipid



(b) unsaturated lipid with *trans* double bonds



(c) unsaturated lipid with *cis* double bonds

Figure 11 (a) Saturated lipids and (b) those that are unsaturated with *trans* double bonds are able to pack tightly together. Their intermolecular forces are quite strong, so these lipids are solid at room temperature. (c) Unsaturated lipids with *cis* double bonds cannot pack tightly together so tend to be liquid at room temperature.

Research This

Banning *Trans* Fat

Skills: Questioning, Researching, Communicating, Defending a Decision

SKILLS HANDBOOK A5.1

To help increase the shelf life of processed food, manufacturers sometimes add hydrogen to oil, creating *trans* fat. Health risks associated with the consumption of *trans* fats have raised the issue of banning *trans* fats from processed foods.

1. Write a list of information that you would like to know in order to make a decision about the banning of *trans* fats.
2. Once you have made a list, conduct research to find the required information.

A. Should *trans* fats be banned from processed foods? Answer this question in a format of your choice, providing specific information from your research that supports your conclusion. C A

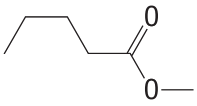
WEB LINK

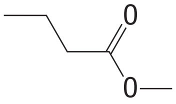
1.6 Review

Summary

- A carboxyl group is a combination of a carbonyl group, C=O, and a hydroxyl group, O–H. Carboxylic acids are named by replacing the *-e* ending of the alkane with *-oic acid*.
- Carboxylic acids are formed by the controlled oxidation of aldehydes.
- An ester's name is derived from the name of the alkyl group of alcohol followed by the name of the alkyl group of the carboxylic acid with the ending *-oate*.
- Esterification is the formation of an ester from a carboxylic acid and an alcohol. Hydrolysis of esters is the breaking down of the ester by a strong base to form the carboxylic acid and alcohol.
- Fats and oils are triglycerides. They are esters made from long chains of fatty acids.
- Saponification is the process by which a fatty acid reacts with a strong base to form a salt of the fatty acid: soap. Saponification is a type of esterification.

Questions

1. Draw the condensed structure or structural formula of the following compounds: K/U C
   (a) 3-methylhexanoic acid
   (b) propyl pentanoate
2. Name the following compounds: K/U C
   (a)
   

   (b)
   

3. Octyl ethanoate is used in artificial orange flavouring. What molecules could be used to synthesize this ester? Write condensed structural formulas for all the organic molecules in this reaction. K/U C
4. Carboxylic acids, like other organic molecules, are flammable. Write a balanced chemical equation for the combustion of ethanoic acid. K/U
5. Compare the solubility and melting points of ethane, ethanol, and ethanoic acid. Explain. K/U T/I
6. The fatty acid in corn oil is oleic acid: $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
   Draw the structure of oleic acid, using this condensed formula. K/U C
7. Given the physical properties of olive oil, would you expect the fatty acid components to be saturated or unsaturated? What process may be necessary to convert olive oil into margarine? T/I
8. Use structural formulas to describe the synthesis of a carboxylic acid using methanol. Name all reactants and products. T/I C
9. Create a flow chart showing the steps needed to transform but-1-ene to butanoic acid. T/I C
10. Table 1 (page 49) lists the melting points of several alkanes and their related carboxylic acids. T/I A
    (a) Predict how the melting point of methanol compares to the melting points of compounds in the table.
    (b) Research the melting point of methanol.
    (c) Give a theoretical explanation for the melting point of methanol, compared to those of the other compounds.
11. Sour milk and yogurt contain a common carboxylic acid. Research the identity of this compound, its structure, and how it is produced industrially. Prepare a poster of your findings. T/I C A
12. Research at least two examples of saponification reactions taking place in the environment. Do you think that these reactions are, on balance, beneficial or damaging to the environment? Explain. T/I A

WEB LINK

1.7

Amines and Amides

During a severe allergic reaction, the body's immune system overreacts to the presence of a foreign substance. The allergic reaction causes the tissues of the airway to swell and the lungs to fill with fluid. If not treated quickly, this severe reaction can cause death. The most common treatment for severe allergic reactions is epinephrine, also known as adrenaline. Epinephrine is a hormone produced naturally by the adrenal glands. The hormone molecules contain a functional group called an amino group, –NH (**Figure 1**). Most people who have severe allergies to common substances, such as bee venom or peanuts, carry auto-injection syringes filled with epinephrine with them at all times (**Figure 2**). Amines are one class of organic compounds that contain nitrogen.

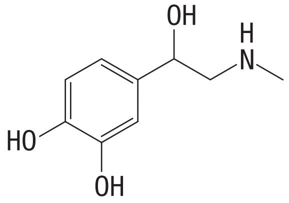


Figure 1 The epinephrine (adrenaline) molecule. The –NH group on the right of the molecule is bonded to 2 carbon atoms, making this compound a secondary amine.

Figure 2 Epinephrine auto-injection syringes can be lifesavers for people who are susceptible to severe allergic reactions.

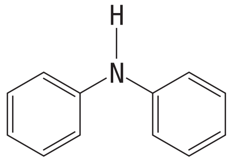
Amines

An **amine** is a derivative of ammonia in which one or more of the hydrogen atoms are replaced with alkyl groups. Amines are classified as primary (1°) if one alkyl group is attached to the nitrogen atom, secondary (2°) if two alkyl groups are present, and tertiary (3°) if all three hydrogen atoms in ammonia have been replaced by alkyl groups. **Table 1** lists some common amines.

Amines generally have strong, often unpleasant, odours, sometimes described as "fishy." Many amine odours resemble ammonia. For example, urine contains amines that come from the breakdown of proteins. The odours associated with decaying animal and human tissues are caused by amines such as putrescine, $H_2N(CH_2)_4NH_2$, and cadaverine, $H_2N(CH_2)_5NH_2$. Notice that these compounds have an amino group at either end of each molecule. Aromatic amines are used to make dyes. Since many of them are carcinogenic, they must be handled with great care. CAREER LINK

amine an organic compound, related to ammonia, that contains a nitrogen atom bonded to one or more alkyl groups on each molecule

Table 1 Some Common Amines

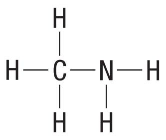
Formula	Systematic IUPAC name	Common name	Type
CH_3NH_2	methanamine	methylamine	primary
$CH_3CH_2NH_2$	ethanamine	ethylamine	primary
$(CH_3)_2NH$	*N*-methylmethanamine	dimethylamine	secondary
$(CH_3)_3N$	*N*,*N*-dimethylmethanamine	trimethylamine	tertiary
$C_6H_5NH_2$	aniline	aniline	primary
	*N*-phenylaniline	diphenylamine	secondary

Naming Amines

Consider the primary amine with the structure CH_3NH_2. Using the IUPAC naming system, this molecule would be named by adding the *-amine* suffix to the name of the chain or ring to which it is attached. The *-e* is removed from this name, giving the name methanamine (**Figure 3**).

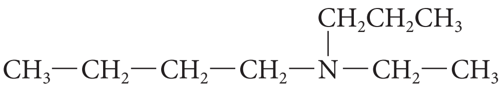
Note that, in Table 1, the IUPAC name for an aromatic amine consisting of an amine group attached to a benzene ring is aniline, rather than benzamine.

To name secondary and tertiary amines, begin with an amine name based on the name of the longest alkyl group. We use the locator, *N*, to indicate the attachment of additional chains to the nitrogen atom, just as we use a number to indicate a specific carbon atom. For example, an amine with an ethyl group, a propyl group, and a butyl group, each bonded to the nitrogen atom at carbon number 1, is named *N*-ethyl-*N*-propylbutan-1-amine.



methanamine

Figure 3 Alternative names for methanamine are methylamine and aminomethane.



$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2CH_2CH_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_3-CH_2-CH_2-CH_2-N-CH_2-CH_3 \end{array}$$

N-ethyl-*N*-propylbutan-1-amine

As you have already read, some compounds contain more than one amino group. A molecule of cadaverine, for example, is a 5-carbon chain with an amino group at each end: $NH_2(CH_2)_5NH_2$. This type of compound is called a diamine, so cadaverine's IUPAC name is pentane-1,5-diamine.

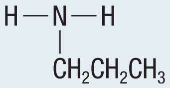
Tutorial 1 Naming and Drawing Amines

This tutorial will give you practice in drawing and naming amines.

Sample Problem 1: Naming Amines from Their Structures

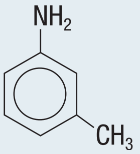
Name each of the following amines according to the IUPAC system:

(a)

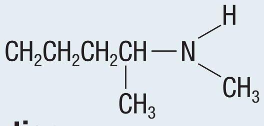


$$\begin{array}{l} H-N-H \\ \quad\ | \\ \quad CH_2CH_2CH_3 \end{array}$$

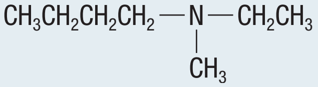
(c)



(b)



(d)



$$\begin{array}{l} CH_3CH_2CH_2CH_2-N-CH_2CH_3 \\ \qquad\qquad\qquad\qquad\ \ | \\ \qquad\qquad\qquad\qquad CH_3 \end{array}$$

Solution

(a) The longest carbon chain is a propyl group, whose terminal carbon atom is bonded to the nitrogen atom. This is the only alkyl group attached to the nitrogen atom, so the compound is a primary amine. The compound's name is propan-1-amine.

(b) This compound is a secondary amine with a pentyl group attached at its second carbon atom and a methyl group. The amine's name is based on the longer group: the pentyl group. The name of the compound is *N*-methylpentan-2-amine.

(c) The root name for an amine attached to a benzene ring is aniline. There is also a substituent methyl group on the third carbon atom. The name of the compound is 3-methylaniline.

(d) This is a tertiary amine whose longest carbon chain has 4 carbon atoms: butanamine. The two substituents are a methyl group and an ethyl group. The compound is named *N*-ethyl-*N*-methylbutan-1-amine.

Sample Problem 2: Drawing Amines

Draw the structural formula and write the name of each of the following amines, with ethyl as the attached alkyl group(s):

(a) a primary amine

(b) a secondary amine

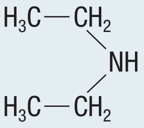
(c) a tertiary amine

Solution

(a) A primary amine has one alkyl group attached to the nitrogen atom.

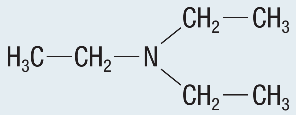
$CH_3CH_2-NH_2$ ethanamine

(b) A secondary amine has two alkyl groups and one hydrogen atom bonded to the nitrogen atom.



N-ethylethanamine

(c) A tertiary amine has three alkyl groups but no hydrogen atoms bonded to the nitrogen atom.

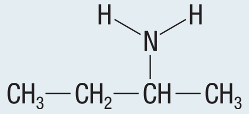


N,*N*-diethylethanamine

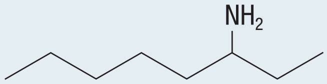
Practice

1. Name each of the following compounds: K/U

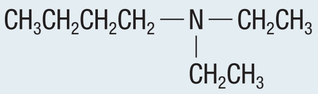
(a)



(d)

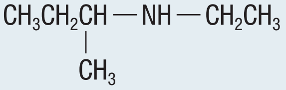


(b)



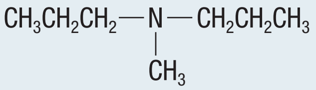
$CH_3CH_2CH_2CH_2-\underset{\substack{|\\ CH_2CH_3}}{N}-CH_2CH_3$

(e)



$CH_3CH_2\underset{\substack{|\\ CH_3}}{CH}-NH-CH_2CH_3$

(c)

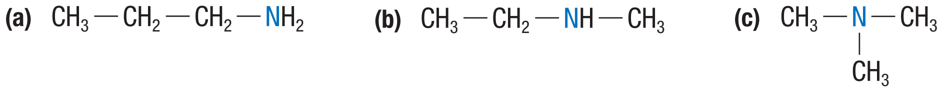


$CH_3CH_2CH_2-\underset{\substack{|\\ CH_3}}{N}-CH_2CH_2CH_3$

2. Draw the structure of each of the following compounds: K/U C
   - (a) 2-methylpropan-1-amine
   - (b) a primary amine with a 2-carbon alkyl group

Properties of Amines

Small amines are soluble in water. Since nitrogen is more electronegative than either carbon or hydrogen, the N–C bonds and any N–H bonds are polar. This polarity increases the strength of the van der Waals forces between molecules so more energy is needed to separate them. That means that amines have higher melting points and higher boiling points than corresponding hydrocarbon compounds. The series of amines in **Figure 4** explains the effect that reducing the number of –NH groups has on the boiling points of amines of similar size.



(a) $CH_3-CH_2-CH_2-NH_2$ **(b)** $CH_3-CH_2-NH-CH_3$ **(c)** $CH_3-\underset{\substack{|\\ CH_3}}{N}-CH_3$

primary amine
b.p. 49 °C

secondary amine
b.p. 37 °C

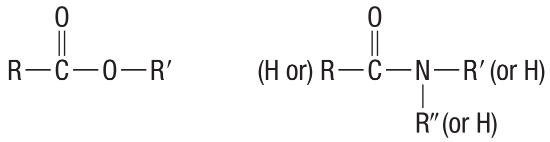
tertiary amine
b.p. 3 °C

Figure 4 Boiling points (b.p.) for three possible CH isomers of an amine, each with 3 carbon atoms. The primary amine, (a), can form two hydrogen bonds and hence has the highest boiling point. The tertiary amine, (c), cannot form hydrogen bonds at all and hence has the lowest boiling point.

Amides

Amides are structurally similar to esters, except the two chains are joined by a nitrogen atom next to a carbonyl group rather than by an oxygen atom (**Figure 5**). The amide functional group consists of a carbonyl group bonded to a nitrogen atom.

amide an organic compound that contains a carbonyl group bonded to a nitrogen atom



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'$$

$$\text{(H or) }R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle R''\text{ (or H)}}{|}}{N}-R'\text{ (or H)}$$

ester

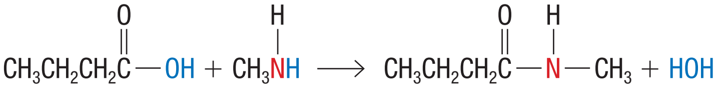
amide

Figure 5 General structures of esters and amides illustrate that the compounds include one or more alkyl groups. These groups, which might be the same or different, are represented in the diagrams by the symbols R, R′, and R″.

Carboxylic acids react with alcohols to produce esters. Carboxylic acids react in a similar way with ammonia, primary amines, and secondary amines to produce amides. You will learn more about these reactions a little later in this section.

Naming Amides

Naming amides is similar to naming esters. The name of an amide has three parts: the first part from the amine; the second part from the acid; and the ending, which is always the suffix *-amide*. For example, the reaction of methanamine and butanoic acid will produce an amide: *N*-methylbutanamide (**Figure 6**).



$$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-OH + CH_3\overset{\overset{\displaystyle H}{|}}{N}H \longrightarrow CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-CH_3 + HOH$$

butanoic acid
acid

methanamine
amine

N-methylbutanamide
amide

water

Figure 6 Note how to derive the name of the amide from the names of the amine and the carboxylic acid.

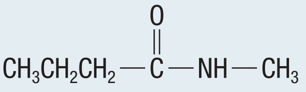
Tutorial 2 Naming and Drawing Amides

This tutorial will give you practice in naming and drawing amides.

Sample Problem 1: Naming Amides from Their Structures

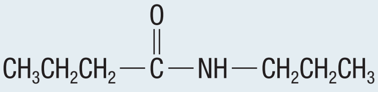
Name each of the following amides:

(a)



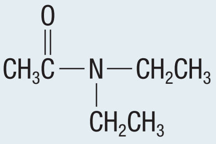
$$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_3$$

(b)



$$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2CH_2CH_3$$

(c)



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CH_2CH_3}{|}}{N}-CH_2CH_3$$

Solution (a)

The first part of the compound came from a carboxylic acid, with 4 carbon atoms: butanoic acid. The second part of the compound came from a primary amine with 1 carbon atom: methanamine. The name of the amide is *N*-methylbutanamide.

Solution (b)

The carboxylic acid had a chain with 4 carbon atoms: butanoic acid. The amine was a primary amine with 3 carbon atoms: propanamine. The name of the amide is *N*-propylbutanamide.

Solution (c)

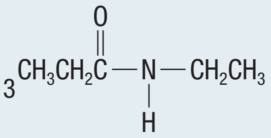
The carboxylic acid had 2 carbon atoms: ethanoic acid. The amine was a secondary amine: *N*-ethylethanamine. The name of the amide is *N,N*-diethylethanamide.

Sample Problem 2: Drawing Amides

Draw the structure of *N*-ethylpropanamide.

Solution

The alkyl group bonded to the nitrogen atom (from the amine) is ethyl. It therefore has 2 carbon atoms. The carbonyl group from the carboxylic acid is attached to a propan- chain, so has 3 carbon atoms. Therefore, the structure is as shown at right:

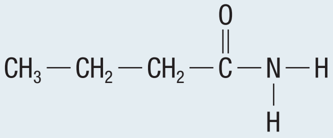


$$\mathrm{CH_3CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{CH_2CH_3}$$

Practice

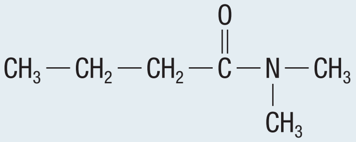
1. Name each of the following amides: K/U

(a)



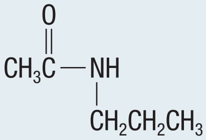
$$\mathrm{CH_3}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{H}$$

(c)



$$\mathrm{CH_3}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{N}}-\mathrm{CH_3}$$

(b)



$$\mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{CH_2CH_2CH_3}}{|}}{\mathrm{NH}}$$

2. Draw the structure of each of the following amides: K/U C

(a) *N,N*-diethylethanamide

(b) *N*-methylbutanamide

Investigation 1.7.1

Building Organic Molecular Models (page 69)

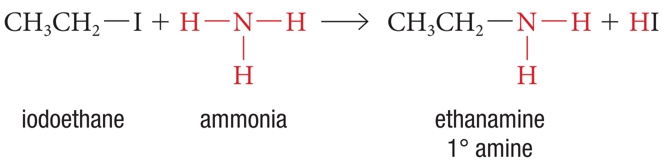
This investigation gives you an opportunity to put into practice your knowledge of the names and properties of amines and amides. You will have the opportunity to build and explore models of these compounds.

Properties of Amides

The smaller amides are somewhat soluble in water. This can be explained by the molecules' structure: the –NH groups form hydrogen bonds with water molecules. As the length of the carbon chain increases, solubility decreases. Primary amides, with their nitrogen atoms each bonded to 2 hydrogen atoms, have higher melting points and boiling points than similar amides. This is likely due to more hydrogen bonding between primary amide molecules.

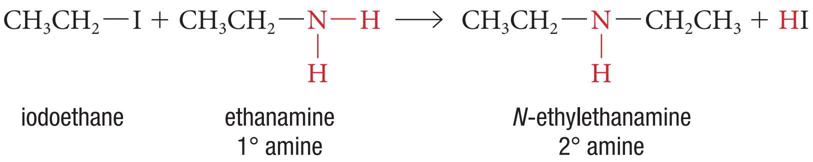
Reactions Involving Amines and Amides

An amine can generally be synthesized from an alkyl halide and ammonia. For example,



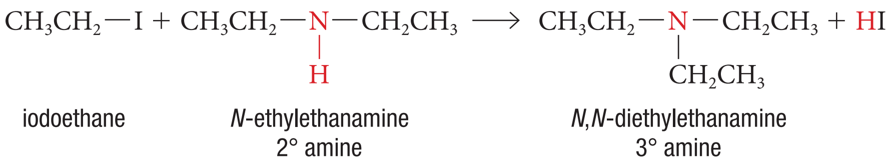
$$\mathrm{CH_3CH_2}-\mathrm{I} + \mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{H} \longrightarrow \mathrm{CH_3CH_2}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{H} + \mathrm{HI}$$

Ethanamine is a primary amine. It reacts with additional iodoethane to form a secondary amine, *N*-ethylethanamine, and hydrogen iodide:



$$\mathrm{CH_3CH_2}-\mathrm{I} + \mathrm{CH_3CH_2}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{H} \longrightarrow \mathrm{CH_3CH_2}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{CH_2CH_3} + \mathrm{HI}$$

N-ethylethanamine also reacts with iodoethane, this time forming a tertiary amine, *N*,*N*-diethylethanamine, along with hydrogen iodide.



$$CH_3CH_2{-}I + CH_3CH_2{-}\underset{\displaystyle H}{\underset{|}{N}}{-}CH_2CH_3 \longrightarrow CH_3CH_2{-}\underset{\displaystyle CH_2CH_3}{\underset{|}{N}}{-}CH_2CH_3 + HI$$

Amides can be synthesized by the condensation reaction of a carboxylic acid with ammonia or primary or secondary amines (**Figure** 7).

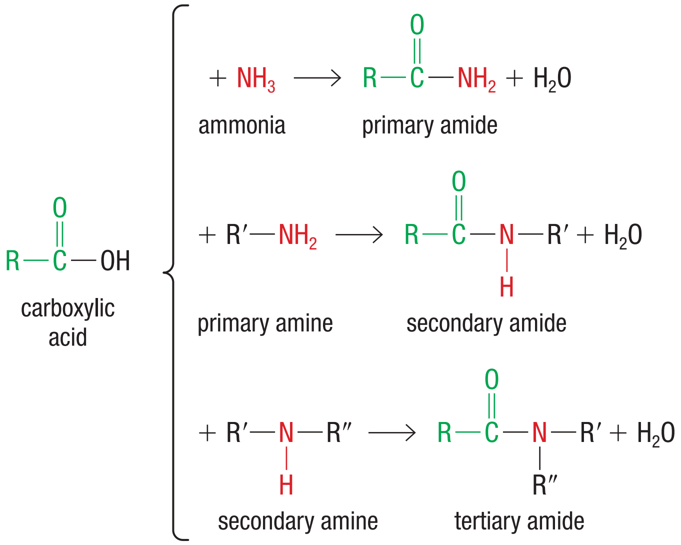


Figure 7 The structure of the amide product depends on whether the carboxylic acid reacts with ammonia, a primary amine, or a secondary amine.

An example of the synthesis of an amide is the reaction of butanoic acid with methanamine to produce *N*-methylbutanamide plus water.

The reactions above are reversible: Amides can be hydrolyzed in acidic or basic conditions to produce the carboxylic acid and the amine.

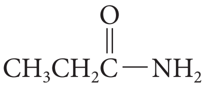
1.7 Review

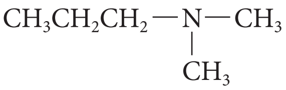
Summary

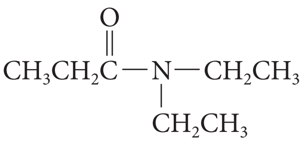
- Amines can be viewed as alkyl groups bonded to a nitrogen atom or an amino group bonded to an alkane. Primary amines have one alkyl group attached to the nitrogen atom; secondary amines have two; tertiary amines have three.
- Amines are named by adding the suffix -*amine* to the root of the name of the longest alkyl group attached to the nitrogen atom. The prefix *N*- indicates that a second (and third) alkyl group is also attached to the nitrogen atom.
- Amides are formed from the reaction of carboxylic acid and amines. Amides can be hydrolyzed to re-form the amine and carboxylic acid.
- Amides are named with the root of the name of the carboxylic acid first, followed by the root of the name of the amine, and ending with -*amide*.

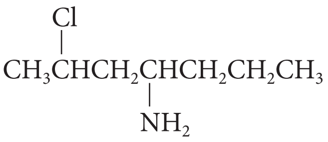
Questions

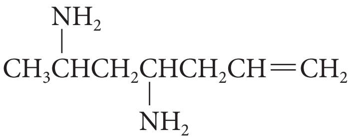
1. Name each of the following compounds: K/U

   (a)
   
   $CH_3CH_2\overset{O}{\overset{\|}{C}}-NH_2$

   (b)
   
   $CH_3CH_2CH_2-\underset{\underset{CH_3}{|}}{N}-CH_3$

   (c)
   
   $CH_3CH_2\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_2CH_3}{|}}{N}-CH_2CH_3$

   (d)
   
   $CH_3\overset{Cl}{\overset{|}{C}}HCH_2\underset{\underset{NH_2}{|}}{C}HCH_2CH_2CH_3$

   (e)
   
   $CH_3\overset{NH_2}{\overset{|}{C}}HCH_2\underset{\underset{NH_2}{|}}{C}HCH_2CH=CH_2$

2. Copy and complete **Table 2** in your notebook. K/U C

3. Draw the structural formulas for the isomers of C_3H_9N. Show at least one primary, one secondary, and one tertiary amine. K/U C

4. Write a structural formula equation that represents the formation of *N*,*N*-diethylpropanamide. K/U

5. Identify the reaction type and write the structures and names for the products you would expect for each of the following reactions: K/U C

   (a) $H_3C-CH_2-Br \quad + \quad H_3N-CH_2-CH_3$

   (b) $H_3C-CH_2-Br \quad + \quad H_3C-NH-CH_2-CH_3$

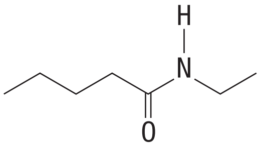
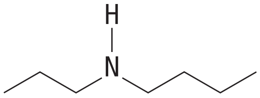
   (c) ethanoic acid and propan-1-amine

6. Create a flow chart showing how you would synthesize *N*,*N*-dimethylethanamide from an alkane, an alkene, a halogen, and ammonia. Draw and name each compound. T/I C

7. Several amines are used in natural gas processing. Research how these amines reduce air pollution. Create a storyboard or diagram to communicate your findings. T/I C A

WEB LINK

Table 2

Name	Condensed structure	Line diagram or structural formula	Type of compound
N,*N*-dimethylbutanamide			
	$CH_3CH_2CH_2NH_2$		
			
	$CH_3CH_2CH_2CH_2CH_2NHCH_3$		
N-methylbutan-1-amine			
			

Investigation 1.4.1 CONTROLLED EXPERIMENT

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Properties of Alcohols

Chemical properties within a group of alcohols may follow a trend. In this investigation, you will use your knowledge of intermolecular forces and the structure of alcohol molecules to predict trends in the properties of alcohols. You will test one of your predictions experimentally.

Testable Question

What is the trend in melting points, boiling points, and solubility of the primary alcohols butan-1-ol, propan-1-ol, and ethanol?

Hypothesis

Use your understanding of the structures of alcohols to predict the trend of the melting points, boiling points, and solubility of primary alcohols. Give reasons for your predictions.

Variables

Identify all the major variables that will be measured and/or controlled in this experiment. Also identify the independent variable and the dependent variable.

Experimental Design

Use reference sources to determine the melting points and boiling points of three alcohols. The solubility of each alcohol is determined by mixing the alcohol with a non-polar solvent, cyclohexane, and with a polar solvent, water.

Equipment and Materials

- chemical safety goggles
- lab apron
- MSDS for each chemical used
- 3 test tubes
- test-tube rack
- wax pencil
- 3 mL calibrated disposable pipette (or similar pipetting device)
- small stoppered bottles containing
  - butan-1-ol
  - ethanol
  - propan-1-ol
  - cyclohexane
- wash bottle containing distilled water

Alcohols and cyclohexane are flammable. They should be used only in a well-ventilated area. There should be no open flames or other sources of ignition in the laboratory.

Procedure

SKILLS HANDBOOK A1, A2.2, A3.3

1. Read through the MSDS and list the hazards of the chemicals you will be using. Include this information, and how to minimize the hazards, in your report.
2. Put on your safety goggles and apron.
3. Use the wax pencil to label the 3 test tubes. Using the pipette, place about 1 mL of ethanol in one test tube, 1 mL of propan-1-ol in the second test tube, and 1 mL of butan-1-ol in the third test tube.
4. To each test tube, add 1 mL of cyclohexane. Record your observations.
5. Follow your teacher's instructions for the disposal of the liquids and for cleaning the test tubes.
6. Set up the test tubes as described in Step 3. Follow Step 4 but use distilled water in place of cyclohexane.

Observations

Prepare a table in which to record your observations. In addition, record the melting point and boiling point data. C

Analyze and Evaluate

(a) What variables were measured/recorded and/or manipulated in this investigation? What type of relationship was being tested? T/I

(b) Did the evidence that you collected allow you to answer the testable question? If so, answer the question. If not, explain why not. T/I

(c) Compare your answer in (b) to your hypothesis. Did the evidence support your hypothesis? Explain. T/I

(d) Evaluate your hypothesis. T/I

Apply and Extend

(e) Predict, in a qualitative way, the melting points, boiling points, and solubilities of larger primary alcohols. Include an explanation for your prediction, referring to the forces of attraction between molecules. T/I

Investigation 1.5.1 OBSERVATIONAL STUDY

Reactions of Three Isomers of Butanol

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Alcohols that have different structures form different products. The location of the hydroxyl bond is particularly important. In this investigation, isomers of butanol are used as examples of primary (1°), secondary (2°), and tertiary (3°) alcohols. You will examine the relationship between structure and product formed.

First, you will mix each of the three isomers of butanol with concentrated hydrochloric acid. The presence of an alkyl halide will be indicated by the cloudiness of the mixture because alkyl halides are only slightly soluble in water.

Next, you will mix each alcohol with dilute potassium permanganate solution. This provides the conditions for controlled oxidation. Any colour change of the potassium permanganate solution is an indication that an oxidation reaction has taken place.

Purpose

To test the reactions of primary, secondary, and tertiary alcohols with acid and with an oxidizing agent

Equipment and Materials

- chemical safety goggles
- lab apron
- protective gloves
- 3 test tubes
- test-tube rack
- eyedropper
- dropper bottles containing
  - butan-1-ol
  - butan-2-ol
  - 2-methylpropan-2-ol
  - potassium permanganate solution, $KMnO_4(aq)$ (0.01 mol/L)
  - concentrated hydrochloric acid, HCl(aq) (12 mol/L) (for teacher use only)

Alcohols are flammable. They should be used only in a well-ventilated area. There should be no open flames or other sources of ignition in the laboratory.

Concentrated hydrochloric acid is very corrosive. It should only be handled by the teacher in a fume hood or fume cupboard.

Potassium permanganate solution is corrosive and may stain the skin. If you spill potassium permanganate on your skin, wash the affected area with lots of cool water and inform your teacher.

Procedure

SKILLS HANDBOOK A1, A2.3, A5.1

1. Put on your safety goggles, apron, and protective gloves.
2. Put 3 test tubes in a test-tube rack. From the dropper bottles, place 2 drops of butan-1-ol in the first test tube, 2 drops of butan-2-ol in the second test tube, and 2 drops of 2-methylpropan-2-ol in the third test tube.
3. Under the fume hood, your teacher will add 10 drops of concentrated hydrochloric acid to each of your 3 test tubes. Gently shake the mixtures very carefully. Return to your lab bench with the test-tube rack and test tubes. Allow the tubes to stand for 1 min and observe for evidence of cloudiness. Record your observations.
4. Follow your teacher's instructions for the disposal of the contents of the test tubes and for cleaning the test tubes.
5. Set up the 3 test tubes again, as described in the setup part of Step 2. This time, use 4 drops of each alcohol.
6. To each test tube, carefully add about 20 drops of potassium permanganate solution. Shake the mixture carefully.
7. Allow the tubes to stand for 5 min with occasional gentle shaking. Observe and record the colour of the solution in each tube.

Analyze and Evaluate

(a) What evidence of reactions did you observe? T/I

(b) Write structural formula equations to represent each of the reactions that occurred. If there was no reaction, write NR. T/I C

(c) Does the evidence collected allow you to achieve the Purpose? Explain. T/I

(d) Summarize in a few sentences the halogenation and controlled oxidation reactions of primary, secondary, and tertiary alcohols. T/I

Apply and Extend

(e) Research to find an application for at least two of the reactions that you observed. How does this reaction benefit society? Does it have any drawbacks? Combine your findings with those of four or five classmates and create a graphic organizer summarizing your findings. T/I C A

WEB LINK

Investigation 1.6.1 CONTROLLED EXPERIMENT

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Properties of Carboxylic Acids

Carboxylic acids are characterized by the presence of a carboxyl group. The physical properties and reactivity of a carboxylic acid depend on the combination of its polar functional group and its non-polar hydrocarbon tail. In this investigation, you will compare the melting point, boiling point, solubility, acidity, and reaction with sodium hydrogen carbonate solution, $NaHCO_3(aq)$, of two carboxylic acids. The acids you will investigate are ethanoic acid and octadecanoic acid.

Testable Question

Do the chemical and physical properties such as the melting and boiling points, solubility, acidity, and reaction with sodium hydrogen carbonate depend on the molecular mass of the carboxylic acid?

Hypothesis

Predict the trend you expect to observe in the melting points, boiling points, solubility, acidity, and reaction with sodium hydrogen carbonate as the mass of the carboxylic acid increases. Give reasons for your prediction.

Variables

Identify all the major variables that will be measured and/or controlled in this experiment. Also, identify the independent variable and the dependent variable(s).

Experimental Design

The melting points of ethanoic acid and octadecanoic acid are obtained from reference resources. The solubility of each carboxylic acid is determined by mixing it first with water and then with vegetable oil. The reactivity of the acids is assessed by combining each acid with sodium hydrogen carbonate.

Equipment and Materials

- chemical safety goggles
- lab apron
- MSDS for the chemicals used
- 10 mL graduated cylinder
- 2 test tubes
- test-tube holder
- test-tube rack
- test-tube brush
- pH meter or universal indicator paper
- wash bottle containing distilled water
- vegetable oil in a beaker
- dropper bottles containing
  - concentrated ethanoic acid (glacial acetic acid) (for teacher use only)
  - dilute ethanoic acid (vinegar)
  - sodium hydrogen carbonate solution, $NaHCO_3(aq)$ (saturated)
- octadecanoic acid (stearic acid, solid)

Concentrated ethanoic acid (glacial acetic acid) is very corrosive. It should only be handled by the teacher in a fume hood or fume cupboard.

Procedure

SKILLS HANDBOOK A1, A2.2, A2.5

1. Read through the MSDS and list the hazards of the chemicals you will be using. Include this information, and what you should do to minimize the hazards, in your report.
2. Put on your safety goggles and lab apron.
3. Add 5 mL of water to one test tube and the same volume of oil to a second test tube. In the fume hood, your teacher will add one drop of glacial acetic acid to each tube. Gently shake each tube to mix. Record your observations on the solubility of concentrated ethanoic acid in each solvent.
4. Still working in the fume hood, use the pH meter or the universal indicator paper to determine the pH of each mixture. Record your observations.
5. Follow your teacher's instructions to dispose of the contents of each test tube and clean the test tubes.
6. Repeat Steps 3, 4, and 5, using a small quantity of solid octadecanoic acid (enough to cover the tip of a toothpick) in place of the concentrated ethanoic acid. You do not need to work in the fume hood from this step on.
7. Place 20 drops of sodium hydrogen carbonate solution from a dropper bottle into each of the 2 clean test tubes. Add 20 drops of dilute ethanoic acid to one test tube and a pea-sized piece of solid octadecanoic acid to the second test tube. Gently shake the test tubes to mix their contents. Watch for the formation of bubbles. Record all observations.

Observations

Prepare a table in which to record the observations made for each test. In addition, the data table needs a space for the melting point and boiling point data.

Analyze and Evaluate

(a) What variables were measured/recorded and/or manipulated in this investigation? What type of relationship was being tested? T/I

(b) Compare the solubilities of octadecanoic acid and ethanoic acid in vegetable oil and in water. Explain any differences in solubility. T/I

(c) Which acid, ethanoic or octadecanoic, seems to exhibit more acidic properties? Explain. T/I

(d) Answer the Testable Question using the evidence that you collected. T/I

(e) Compare your answer to (d) with your Prediction. Explain any differences. T/I A

(f) Did your previous knowledge about carboxylic acids allow you to correctly predict the chemical properties of these acids? Provide reasons. T/I C

Apply and Extend

(g) Write a balanced chemical equation for the reaction of ethanoic acid and sodium hydrogen carbonate. K/U

(h) Using what you discovered about trends in the properties of carboxylic acids, predict how methanoic acid and a carboxylic acid with 16 carbon atoms would compare to ethanoic acid and stearic acid. T/I A

(i) Why is decanoic acid effective at hardening soaps made with vegetable oil? Research your answer. Write an explanation for a website designed for people who create handmade soaps. Include a diagram with your explanation. T/I A

WEB LINK

Investigation 1.6.2

OBSERVATIONAL STUDY

Synthesizing Esters

Many esters are found in fruits. Esters typically have very pleasant odours. In the lab, esters can be synthesized from the condensation reaction between alcohols and carboxylic acids.

Purpose

To produce several esters and observe their odours

Equipment and Materials

- chemical safety goggles
- lab apron
- 500 mL beaker
- utility stand and ring clamp
- hot plate
- wax pencil
- 3 test tubes
- 3 test-tube holders
- test-tube rack
- Petri dish
- dropper bottles containing
  - ethanol
  - propan-2-ol
  - pentan-1-ol
  - concentrated ethanoic acid (glacial acetic acid), $CH_3COOH(l)$ (for teacher use only)
  - 2 mL concentrated sulfuric acid, $H_2SO_4(aq)$ (for teacher use only)
- wash bottle containing cold tap water

Alcohols are flammable. They should be used only in a well-ventilated area. There should be no open flames or other sources of ignition in the laboratory.

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

The acids are corrosive and flammable. Avoid skin and eye contact. If you spill these chemicals on your skin, wash the affected area with a lot of cool water.

Use caution around the hot plate. Avoid touching the heating surface with your hands. To unplug the hot plate, pull on the plug itself rather than the cord.

Procedure

SKILLS HANDBOOK A1, A2.3

1. Put on your safety goggles and lab apron.
2. Read through the MSDS and list the hazards of the chemicals you will be using. Include this information, and what you should do to minimize the hazards, in your report.
3. Prepare a water bath by filling a 500 mL beaker half-full with tap water. Dry the outside of the beaker and place it inside the ring that is secured to a utility stand so that the beaker rests on the hot plate. Heat the water until it comes to a boil. Turn the heat off when the water starts to boil.
4. Using the wax pencil, number the 3 test tubes in a test-tube rack. Add 10 drops of ethanol to the first test tube, 10 drops of propan-2-ol to the second test tube, and 10 drops of pentan-1-ol to the third test tube.
5. Under the fume hood, your teacher will carefully add 10 drops of concentrated ethanoic acid and 5 drops of concentrated sulfuric acid to each of your 3 test tubes. Gently shake each test tube to mix.

6. Return to your lab bench with the test tubes and carefully place them in the hot-water bath. Make certain that the test tubes do not point at anyone. Leave the test tubes in the hot-water bath for 5 min and then, using a test-tube holder, move the test tubes back to the test-tube rack.
7. Pour the contents of the first test tube into a Petri dish half-filled with cold water (approximately 10–20 mL). Smell the odour of the ester as instructed by your teacher. **Figure 1** illustrates proper technique for identifying the odour of the ester. Record your observations, paying close attention to the miscibility of the contents.
8. Repeat Step 7 for each ester.

Analyze and Evaluate

(a) Write a chemical equation to represent each reaction. K/U

(b) What is the odour of each ester produced? T/I

(c) Use your observations to write a statement about the solubility of esters in water. T/I

(d) What is the function of the concentrated sulfuric acid in the reactions? K/U

Figure 1 Use your hand to waft the smell of the ester toward you. Do not hold the substance directly under your face.

Apply and Extend

(e) Suggest a use for each of your products. A

(f) What must be done before the esters are used as you suggested in (e)? A

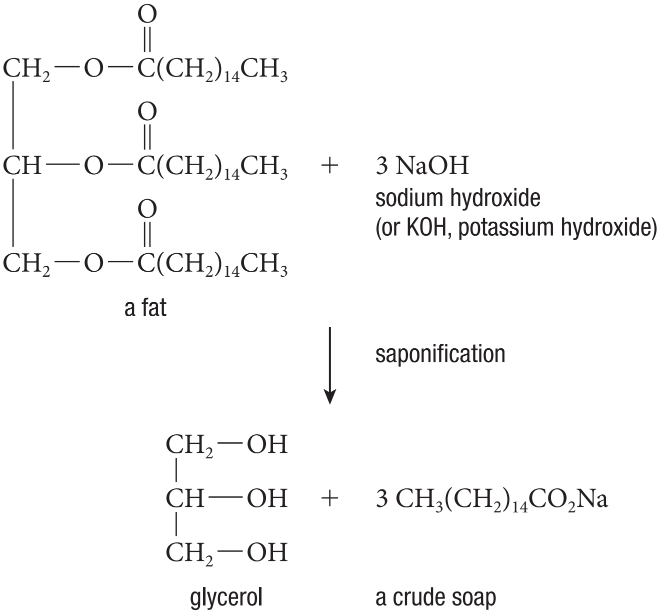
Investigation 1.6.3 OBSERVATIONAL STUDY

Making Soap (Teacher Demonstration)

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

To make soap, a reaction must occur between a strong base and a triglyceride (fat or oil).



Purpose

To produce soap from the saponification of lard, vegetable shortening, or oils

Equipment and Materials

- chemical safety goggles
- lab apron
- protective gloves
- wax pencil
- two 100 mL beakers
- 250 mL beaker
- forceps
- 50 mL graduated cylinder
- 2 glass stirring rods
- balance
- utility stand with ring clamp
- hot plate
- beaker tongs
- heat-resistant mat

- thermometer
- filter funnel and paper
- fats (lard or vegetable shortening)
- oils (cooking oils such as corn oil, canola oil, olive oil)
- sodium hydroxide pellets, NaOH(s) (for teacher use only)
- ethanol
- vinegar, $CH_3COOH(aq)$
- sodium chloride crystals, NaCl(s)
- wash bottle containing distilled water
- food colouring (optional)
- perfume (optional)
- paper towel

Sodium hydroxide pellets are extremely corrosive to eyes and skin. They must only be handled with forceps; gloves must be worn. If sodium hydroxide comes into contact with your skin, wash the affected area with a lot of cool water. If sodium hydroxide contacts the eyes, it can cause blindness. Flush the eyes with water at an eyewash station for at least 10 min and seek medical attention as soon as possible.

Ethanol is flammable. It should be used only in a well-ventilated area. There should be no open flames or other sources of ignition in the laboratory.

Procedure

SKILLS HANDBOOK **A1, A2.3, A3.2**

Note that this Procedure should be performed only by a qualified teacher.

1. Label a 100 mL beaker with the letter "A," a 250 mL beaker with the letter "B," and the second 100 mL beaker with the letter "C."
2. Measure about 10 mL of distilled water into beaker A.
3. Put on your safety goggles, lab apron, and protective gloves.
4. Using forceps, carefully add 18 pellets of solid sodium hydroxide, a few at a time, to beaker A. **Do not allow the pellets to touch your skin**. Carefully stir the sodium hydroxide pellets with a glass rod until they dissolve. The solution will get very hot as the sodium hydroxide dissolves. Set beaker A aside to cool.
5. Use the balance to measure about 15 g of fat, such as lard or shortening, or oil, such as corn oil or olive oil, into beaker "B." Add 15 mL of ethanol to the fat or oil.
6. Put the beaker, supported by the ring clamp, on the hot plate. Warm the mixture very gently. Stir with a glass rod until the fat and ethanol are melted and thoroughly mixed. Turn the hot plate off. Use beaker tongs to remove beaker B and place it on a heat-resistant mat on the bench.
7. Once the contents of beaker A have cooled, add them to beaker B.
8. Replace beaker B, inside the ring clamp, on the hot plate. Heat it again very gently for 20 min, stirring continuously. Keep the temperature between 40 and 45 °C for this time. If the mixture spatters or bubbles, it is too hot. Remove the beaker from the hot plate and let it cool to below 45 °C. Return it to the hot plate again. Record your observations.
9. Continue heating the mixture until it has a consistency similar to pudding, then turn off the hot plate. Use tongs to move the beaker to the heat-resistant mat. Allow the contents to cool. To colour the soap, add a drop or two of food colouring.
10. Use the balance to measure 4 g of sodium chloride crystals into beaker C. Add 20 mL of cold distilled water and stir until the salt is dissolved.
11. Add the contents of beaker C to beaker B. Stir.
12. Add 10 mL of vinegar. Record your observations.
13. Carefully pour any excess liquid into the sink. Wash any excess vinegar off the soap with about 10 mL of distilled water. Once again, pour off excess liquid in the sink.
14. Filter the soap mixture through a filter funnel and filter paper. Take care not to puncture the filter paper. A few drops of perfume or scent can be added.
15. Dry the soap on the filter paper or remove the soap, shape it, and dry it on a paper towel.

Do not use this soap on your skin. It may contain unreacted sodium hydroxide. Wear protective gloves when handling the soap.

Observations

Observe the colour and texture of the soap. Compare it to those of common commercial soaps, and record your observations.

Analyze and Evaluate

(a) Write a word equation describing the reaction taking place in Steps 8 and 9. Classify the reaction. T/I

(b) What was the purpose of adding vinegar in Step 12? Write a balanced chemical equation describing the reaction taking place. (Note that the molecular formula for ethanoic acid can be written as either $CH_3COOH(aq)$ or $HC_2H_3O_2(aq)$.) Classify the reaction. T/I

(c) What other substances may be in the filtrate after the soap was filtered out? K/U

Apply and Extend

(d) Describe how saponification and esterification are related. K/U

(e) Do you think soap molecules are polar or non-polar? How would this affect their ability to remove oils from greasy surfaces? T/I A

(f) Research how soap was made historically. How were the reactants obtained? What were the hazards of the process, and the benefits of the product? Present your findings in a format of your choice. T/I C A

WEB LINK

Investigation 1.7.1 ACTIVITY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Building Organic Molecular Models

Using molecular models of organic compounds, you will demonstrate a variety of chemical reactions.

Purpose

To help differentiate between the structures of the reactant and the product of a reaction using molecular models

Equipment and Materials

- molecular modelling kit

Procedure

SKILLS HANDBOOK A2.4, B.3

Part A

1. In **Table 1**, the columns specify the type of compound involved in the reaction, and the type of reaction. For example, for Reaction 1, the reactant is an alkane and it will undergo a substitution reaction. Copy Table 1 into your notebook, leaving space to write the names and structural formulas of reactant and product compounds.

Table 1 Organic Reactions

Reaction number	Reactant	Reaction type	Product
1	alkane	substitution	
2	alkene	addition	
3	alcohol		aldehyde
4			ether
5	aldehyde	controlled oxidation	
6			chlorobenzene
7		controlled oxidation	ketone
8		esterification	
9			amide
10	aromatic compound		aromatic halide

2. For each reaction listed, choose an appropriate reactant and make a model of this compound. Write its name and structural formula in your table.
3. Manipulate the model as indicated to create a model of the product. Add its name and structural formula to your table. Compare the models of the reactants and products for structural changes.
4. Supply the name of any missing reaction types in the table.

Part B

5. Draw a flow chart to show the synthesis of ethanoic acid from ethene.
6. Build a molecular model of ethene and make changes to the model following the flow chart you created.

Analyze and Evaluate

(a) Create a concept map to summarize the various reaction types. T/I C

(b) For which kinds of organic molecules are molecular modelling exercises most effective? Explain. T/I

CHAPTER 1 SUMMARY

Summary Questions

1. Create a study guide for this chapter based on the Key Concepts on page 6. For each point, create three or four sub-points that provide further information, relevant examples, explanatory diagrams, or general equations.
2. Look back at the Starting Points questions on page 6. Answer these questions using what you have learned in this chapter. Compare your latest answers with those that you wrote at the beginning of the chapter. Note how your answers have changed.

Vocabulary

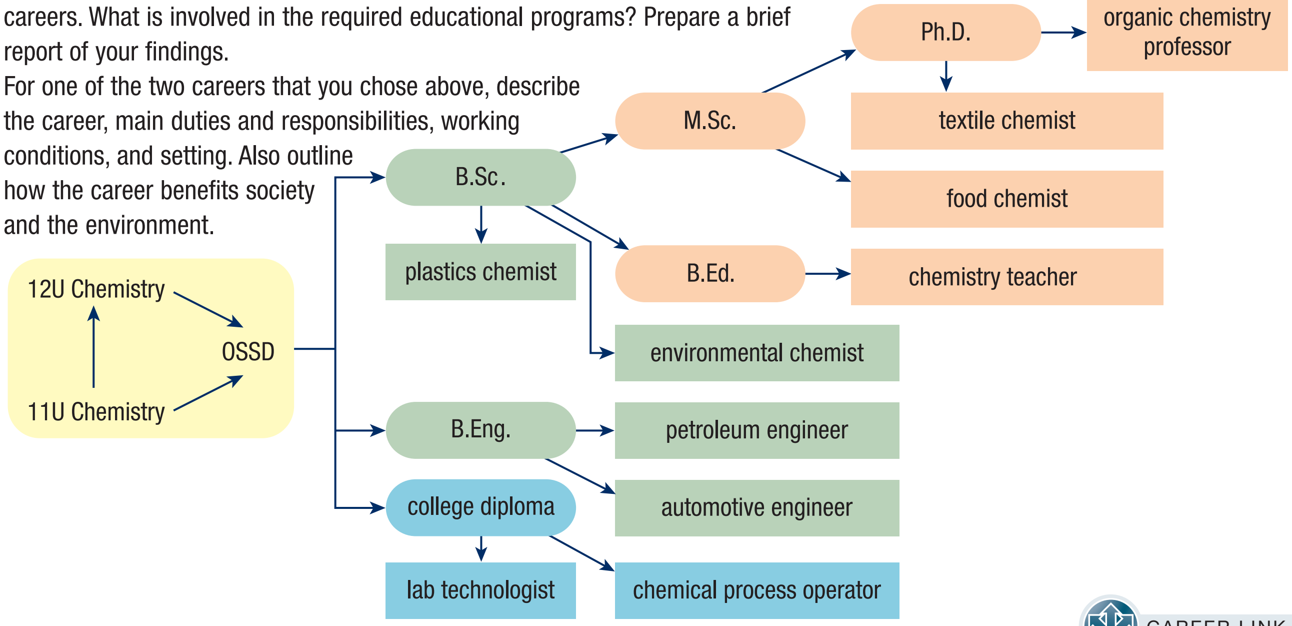
organic compound (p. 8)
hydrocarbon (p. 8)
saturated hydrocarbon (p. 8)
alkane (p. 8)
cyclic alkane (p. 9)
alkyl group (p. 10)
substituent group (p. 10)
structural isomer (p. 10)
complete combustion (p. 15)
alkyl halide (p. 16)
unsaturated hydrocarbon (p. 18)
alkene (p. 18)
alkyne (p. 18)
aliphatic hydrocarbon (p. 18)
stereoisomers (p. 22)
cis isomer (p. 22)
trans isomer (p. 22)
functional group (p. 23)
addition reaction (p. 23)
Markovnikov's rule (p. 25)
aromatic hydrocarbon (p. 28)
phenyl group (p. 28)
alcohol (p. 32)
primary alcohol (p. 32)
secondary alcohol (p. 32)
tertiary alcohol (p. 32)
hydrogen bonding (p. 35)
dehydration reaction (p. 35)
ether (p. 37)
condensation reaction (p. 37)
thiol (p. 38)
carbonyl group (p. 40)
aldehyde (p. 40)
ketone (p. 40)
carboxylic acid (p. 47)
carboxyl group (p. 47)
ester (p. 49)
esterification (p. 51)
hydrolysis (p. 51)
lipid (p. 53)
fatty acid (p. 53)
triglyceride (p. 53)
saponification (p. 54)
amine (p. 56)
amide (p. 59)

CAREER **PATHWAYS**

SKILLS HANDBOOK A7

Grade 12 Chemistry can lead to a wide range of careers. Some require a college diploma or a B.Sc. degree. Others require specialized or postgraduate degrees. This graphic organizer shows a few pathways to careers mentioned in this chapter.

1. Select two careers related to Organic Compounds that you find interesting. Research the educational pathways that you would need to follow to pursue these careers. What is involved in the required educational programs? Prepare a brief report of your findings.
2. For one of the two careers that you chose above, describe the career, main duties and responsibilities, working conditions, and setting. Also outline how the career benefits society and the environment.



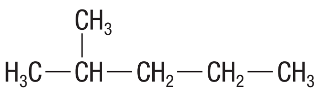
CAREER LINK

CHAPTER 1 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. What is the correct name for the compound in **Figure 1**? (1.1) K/U



$H_3C-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-CH_3$

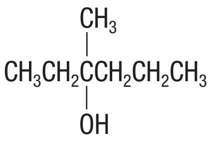
Figure 1

(a) 2-methylpentane
(b) 2-propylpropane
(c) 1,1-dimethylbutane
(d) 1-ethylbutane

2. What is the major product of the reaction between hex-1-ene and hydrochloric acid? (1.2) K/U
(a) 1-chlorohexane
(b) 2-chlorohexane
(c) 1,2-dichlorohexene
(d) 1-hexachlorine

3. Benzene, C_6H_6, and bromine, Br_2, react to form bromobenzene, C_6H_5Br. Which reaction type below best describes the reaction? (1.3) K/U
(a) addition
(b) elimination
(c) hydration
(d) substitution

4. What type of compound is shown in **Figure 2**? (1.1, 1.2, 1.4) K/U



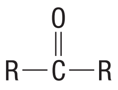
$CH_3CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH_2CH_2CH_3$

Figure 2

(a) alkane
(b) alkene
(c) secondary alcohol
(d) tertiary alcohol

5. Which of the following compounds is a structural isomer of butanone? (1.5) K/U
(a) $CH_3CH_2CH_2CH_2OH$
(b) $CH_3CH_2CH_2CHO$
(c) $CH_3CH_2OCH_2CH_3$
(d) $CH_3CH_2CH_2COOH$

6. The general formula in **Figure 3** represents which type of organic compound? (1.5) K/U

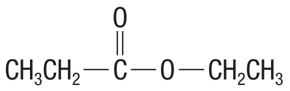


$R-\overset{\overset{O}{\|}}{C}-R$

Figure 3

(a) an aldehyde
(b) an amide
(c) an ester
(d) a ketone

7. Which of the following pairs of compounds may react to synthesize the ester shown in **Figure 4**? (1.6) K/U



$CH_3CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$

Figure 4

(a) ethanol and propanoic acid
(b) ethanol and ethanoic acid
(c) methanol and propanoic acid
(d) propanol and ethanoic acid

8. Which of the following elements differentiates an amine from an alkane? (1.7) K/U
(a) carbon
(b) hydrogen
(c) oxygen
(d) nitrogen

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

9. Alkanes are unsaturated hydrocarbons. (1.1) K/U
10. The names of alkenes include numbers to specify the location of the triple bond. (1.2) K/U
11. Benzene is less reactive than the alkenes. (1.3) K/U
12. Ethers may be synthesized by the addition reaction of two alcohols. (1.4) K/U
13. Thiols contain the group —OH. (1.4) K/U
14. Aldehydes and ketones each have a carbonyl group but different chemical properties. (1.5) K/U
15. An ester is formed by the condensation reaction of a carboxylic acid and alcohol. (1.6) K/U
16. Amine and amide compounds always include a nitrogen atom. (1.7) K/U

Go to Nelson Science for an online self-quiz.

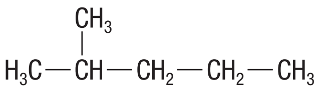
WEB LINK

CHAPTER 1 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. What is the correct name for the compound in **Figure 1**? (1.1) K/U



$$H_3C-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_3$$

Figure 1

(a) 2-methylpentane
(b) 2-propylpropane
(c) 1,1-dimethylbutane
(d) 1-ethylbutane

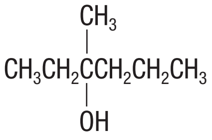
2. What is the major product of the reaction between hex-1-ene and hydrochloric acid? (1.2) K/U

(a) 1-chlorohexane
(b) 2-chlorohexane
(c) 1,2-dichlorohexene
(d) 1-hexachlorine

3. Benzene, C_6H_6, and bromine, Br_2, react to form bromobenzene, C_6H_5Br. Which reaction type below best describes the reaction? (1.3) K/U

(a) addition
(b) elimination
(c) hydration
(d) substitution

4. What type of compound is shown in **Figure 2**? (1.1, 1.2, 1.4) K/U



$$CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_2CH_2CH_3$$

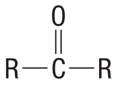
Figure 2

(a) alkane
(b) alkene
(c) secondary alcohol
(d) tertiary alcohol

5. Which of the following compounds is a structural isomer of butanone? (1.5) K/U

(a) $CH_3CH_2CH_2CH_2OH$
(b) $CH_3CH_2CH_2CHO$
(c) $CH_3CH_2OCH_2CH_3$
(d) $CH_3CH_2CH_2COOH$

6. The general formula in **Figure 3** represents which type of organic compound? (1.5) K/U

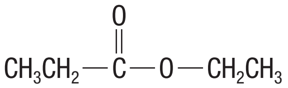


$$R-\overset{\displaystyle O}{\overset{\|}{C}}-R$$

Figure 3

(a) an aldehyde
(b) an amide
(c) an ester
(d) a ketone

7. Which of the following pairs of compounds may react to synthesize the ester shown in **Figure 4**? (1.6) K/U



$$CH_3CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_2CH_3$$

Figure 4

(a) ethanol and propanoic acid
(b) ethanol and ethanoic acid
(c) methanol and propanoic acid
(d) propanol and ethanoic acid

8. Which of the following elements differentiates an amine from an alkane? (1.7) K/U

(a) carbon
(b) hydrogen
(c) oxygen
(d) nitrogen

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

9. Alkanes are unsaturated hydrocarbons. (1.1) K/U
10. The names of alkenes include numbers to specify the location of the triple bond. (1.2) K/U
11. Benzene is less reactive than the alkenes. (1.3) K/U
12. Ethers may be synthesized by the addition reaction of two alcohols. (1.4) K/U
13. Thiols contain the group –OH. (1.4) K/U
14. Aldehydes and ketones each have a carbonyl group but different chemical properties. (1.5) K/U
15. An ester is formed by the condensation reaction of a carboxylic acid and alcohol. (1.6) K/U
16. Amine and amide compounds always include a nitrogen atom. (1.7) K/U

Go to Nelson Science for an online self-quiz.

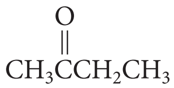
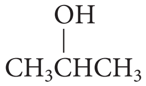
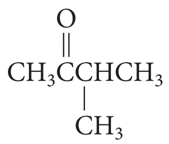
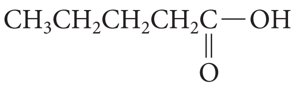
WEB LINK

CHAPTER 1 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Gasoline contains many structural isomers of octane. Which of the following is NOT a structural isomer of octane? (1.1) K/U
   (a) 3-methylheptane
   (b) 4-ethylheptane
   (c) 2,2,4-trimethylpentane
   (d) 2,2,3,3-tetramethylbutane
2. What is the major product of the hydration reaction of but-1-ene? (1.2) K/U
   (a) butan-1-al
   (b) butan-1-ol
   (c) butan-2-al
   (d) butan-2-ol
3. Which of the following statements best describes an aromatic organic compound? (1.3) K/U
   (a) an aldehyde or a ketone with a distinctive odour
   (b) an unsaturated compound containing a 6-carbon ring with 6 identical bonds
   (c) a compound containing a cyclic structure
   (d) a compound containing a cyclic structure with a double bond
4. Which of the following compounds is an ether? (1.4) K/U
   (a)
   
   $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$
   (b)
   
   $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H$
   (c)
   
   $CH_3\overset{\overset{OH}{|}}{C}HCH_3$
   (d) $CH_3CH_2CH_2OCH_3$
5. Which of the following formulas represents propanone? (1.5) K/U
   (a) CH_3CHO
   (b) CH_3OCH_3
   (c) CH_3COCH_3
   (d) CH_3COOCH_3
6. Which statement best describes the compound $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$? (1.6) K/U
   (a) It is a saturated fatty acid.
   (b) It is soluble in a polar solvent.
   (c) It is a long-chain alcohol.
   (d) It contains a carboxyl group.
7. Which of the following compounds has the highest solubility in water? (1.6) K/U
   (a) $CH_3CH_2CH{=}CHCH_3$
   (b)
   
   $CH_3\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{|}}{C}HCH_3$
   (c)
   
   $CH_3CH_2CH_2CH_2\underset{\underset{O}{\|}}{C}-OH$
   (d) $CH_3CH_2CH_2CH_2CH_2OH$
8. Choose the statement that best describes the compound in **Figure 1**. (1.6) K/U

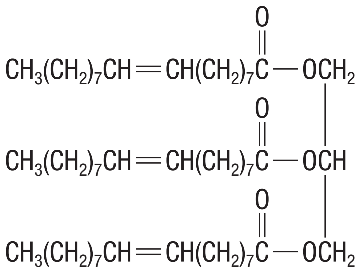
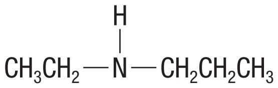


Figure 1

   (a) an amide
   (b) a product of a saponification reaction
   (c) a saturated fatty acid
   (d) a triglyceride
9. Predict which of the following compounds has the highest boiling point. (Assume that all have similar molecular masses.) (1.6) K/U
   (a) aldehyde
   (b) ketone
   (c) carboxylic acid
   (d) ester
10. Name the compound illustrated in **Figure 2**. (1.7) K/U

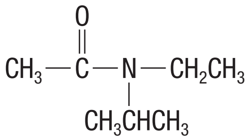


$CH_3CH_2-\overset{\overset{H}{|}}{N}-CH_2CH_2CH_3$

Figure 2

   (a) 2-aminopentane
   (b) 2-nitropentane
   (c) ethylpropylamide
   (d) *N*-ethylpropan-1-amine

11. Which two reactants could form the compound illustrated in **Figure 3**? (1.7) K/U



$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3CHCH_3}{|}}{N}-CH_2CH_3$

Figure 3

(a) ethanoic acid and a secondary amine
(b) ethanoic acid and a primary amine
(c) ethanoic acid and a tertiary amine
(d) methanoic acid and a secondary amine

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

12. Unsaturated hydrocarbons must contain at least one carbon–carbon double or triple bond. (1.1) K/U
13. But-1-ene and but-2-ene are structural isomers of each other (1.1, 1.2) K/U
14. Markovnikov's rule states that, in an addition reaction involving a hydrogen atom, the hydrogen atom will usually bond to the carbon atom with the fewest hydrogen atoms attached. (1.2) K/U
15. Aromatic compounds usually undergo addition reactions. (1.3) K/U
16. A compound that is a benzene ring with a hydroxyl group on one of the carbon atoms is called phenyl. (1.4) K/U
17. An ester is formed from the reaction of two alcohols. K/U
18. Aldehydes contain a carbonyl group on the terminal carbon atom. (1.5) K/U
19. A ketone can be oxidized to produce a primary alcohol. (1.5) K/U
20. Carboxylic acid molecules are much less polar than the corresponding alkane molecules. (1.6)

Match each condensed chemical formula on the left with the most appropriate term on the right.

21.

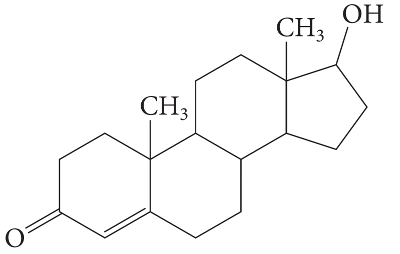
(a) $CH_3CH{=}CH_2$	(i) a ketone
(b) CH_3COOCH_3	(ii) an ester
(c) CH_3CH_2CHO	(iii) propan-2-ol
(d) CH_3CH_2COOH	(iv) propanal
(e) $CH_3CHOHCH_3$	(v) an ether
(f) $CH_3CH_2CH_2OH$	(vi) propan-1-ol
(g) CH_3COCH_3	(vii) propene
(h) $CH_3CH_2OCH_3$	(viii) propanoic acid

(1.2, 1.4, 1.5, 1.6) K/U

Write a short answer to each question.

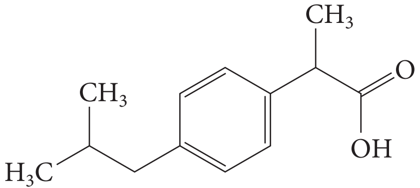
22. Write a balanced chemical equation to represent each of the following reactions. Use structural formulas or line diagrams in your equations. Classify each reaction as addition or substitution. (1.1, 1.2, 1.3) K/U
    (a) bromine reacting with pent-2-ene
    (b) bromine reacting with cyclopentene
    (c) bromine reacting with benzene
23. Draw a structural formula to represent each of the following organic compounds: (1.1, 1.3, 1.4, 1.5, 1.6) K/U C
    (a) ethan-1,2-diol
    (b) 1,3-dimethylbenzene
    (c) cyclohexanol
    (d) 1,2-dichloropropane
    (e) 2,2-dichloropropane
    (f) 2-methylbutanal
    (g) hexan-3-one
    (h) 2-ethoxypropane
    (i) aminoethanoic acid
    (j) 3,5-dimethylhexan-3-ol
24. List the non-alkyl functional groups in each of the compounds represented below. (1.1, 1.2, 1.3, 1.7) K/U

(a)



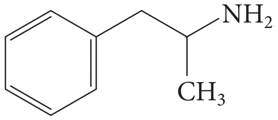
testosterone (hormone)

(b)



ibuprofen (pain reliever)

(c)

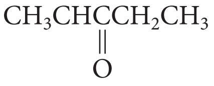


amphetamine (stimulant)

25. Organic compounds are classified by their functional groups. For each of the compounds listed below, identify the functional group(s), determine the type of compound, and write the correct IUPAC name. (1.4, 1.5, 1.6, 1.7) K/U C
    (a) $CH_3CH_2CH_2OH$
    (b) CH_3CH_2COOH
    (c) $CH_3CH_2CH_2CH_2CH_2CHO$
    (d) $CH_3CH_2OCH_2CH_2CH_3$
    (e) CH_3NH_2
    (f) $CH_3COCH_2CH_2CH_3$
    (g)

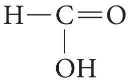
$CH_3\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_2CH_3$

    (h) $CH_3CH_2CONHCH_3$
    (i)



$CH_3CH\underset{\underset{\displaystyle O}{\|}}{C}CH_2CH_3$

    (j)



$H-\underset{\underset{\displaystyle OH}{|}}{C}=O$

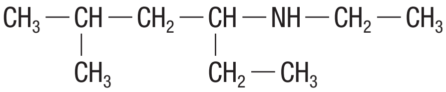
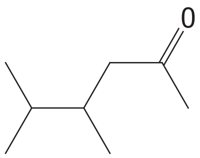
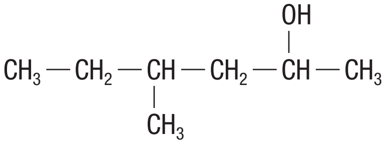
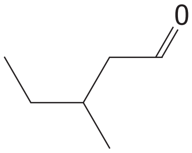
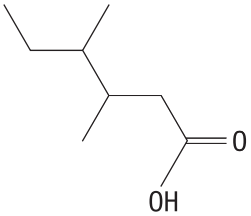
26. Draw structural formulas for each of the following organic compounds. Circle the non-alkyl functional group(s). (1.4, 1.5, 1.6, 1.7) K/U C
    (a) hexan-2-one
    (b) 2-methylpentanal
    (c) pentane-1,3-diol
    (d) buta-1,3-diene
    (e) 1-propoxybutane
    (f) 2-propoxybutane
    (g) ethyl ethanoate
27. Draw structural formulas (or line diagrams) and write names for the following isomers: (1.5, 1.6, 1.7) K/U C
    (a) three ketones with the molecular formula $C_5H_{10}O$
    (b) two esters with the formula $C_3H_6O_2$
    (c) a primary, a secondary, and a tertiary amine, with the formula $C_5H_{13}N$

Understanding

28. Can CH_2CF_2 exhibit hydrogen bonding? Explain. (1.1) K/U
29. If you were presented with the structural formulas for a variety of hydrocarbons, what features of the molecules would you look at to rank the hydrocarbons in order of increasing boiling point? Explain your answer. (1.1, 1.2) K/U
30. Draw a chemical equation to represent a reaction that could produce each of the following types of compounds. Use condensed structures in your equations. Name all reactants and products. (1.1, 1.2, 1.3) K/U
    (a) alkane
    (b) monohalogenated alkane
    (c) dihalogenated alkane
    (d) tetrahalogenated alkane
    (e) halogenated benzene
    (f) alkene
31. Starting with propane, list the sequence of reactions needed to produce propanone. (1.5) K/U
32. The following compounds all have similar molecular masses: ethanoic acid; ethanol; ethanal; ethane
    Order the compounds by increasing boiling point. Explain your decision. (1.1, 1.4, 1.5, 1.6) A
33. Explain why the following compounds do not exist: (1.2, 1.3, 1.4, 1.5, 1.6) K/U T/I
    (a) 2-chloro-2-butyne
    (b) 2-methyl-2-propanone
    (c) 1,1-dimethylbenzene
    (d) 2-pentanal
    (e) 3-hexanoic acid
    (f) 5,5-dibromo-1-cyclobutanol
34. Name and draw the structural formula for each of the following compounds: (1.2, 1.3, 1.4, 1.5, 1.6) K/U C
    (a) a secondary alcohol with the formula $C_4H_{10}O$
    (b) a tertiary alcohol with the formula $C_4H_{10}O$
    (c) an ether with the formula $C_4H_{10}O$
    (d) a ketone with the formula C_4H_8O
    (e) an aromatic compound with the formula C_7H_8
    (f) an alkene with the formula C_6H_{10}
    (g) an aldehyde with the formula C_4H_8O
    (h) a carboxylic acid with the formula $C_2H_4O_2$
    (i) an ester with the formula $C_2H_4O_2$
35. Write a chemical equation for each of the following reactions. Use condensed formulas. Classify each reaction by type. (1.2, 1.4, 1.5, 1.6) K/U
    (a) ethene from ethanol
    (b) ethoxyethane from ethanol
    (c) propanal from an alcohol
    (d) a secondary pentanol from an alkene
    (e) ethanoic acid from an alcohol
    (f) ethyl methanoate from an acid and an alcohol

36. Copy and complete **Table 1** in your notebook. (1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7) T/I C

Table 1

Name	Condensed structure	Line diagram or structural formula	Type of compound
1-methoxybutane			
methanal			
1,4-dichloropent-2-ene			
		 $CH_3-\underset{\substack{\vert\\ CH_3}}{CH}-CH_2-\underset{\substack{\vert\\ CH_2-CH_3}}{CH}-NH-CH_2-CH_3$	
propanamide			
	$CH_3CH_2CH_2CH_2CH(OH)CH_2CH_3$		
			
3-methylhexanoic acid			
		 $CH_3-CH_2-\underset{\substack{\vert\\ CH_3}}{CH}-CH_2-\overset{\substack{OH\\ \vert}}{CH}-CH_3$	
2-methylbutane			
	$CH_3CH_2CH(CH_3)CH_2CH_3$		
			
			
methyl pentanoate			

37. Predict which of the following pairs of compounds is more soluble in water. Give reasons for your answers. (1.3, 1.4, 1.5, 1.6) K/U T/I

(a)

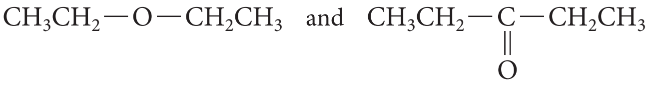
(b) CH_3COOH and CH_3COOCH_3

(c) ethanol and decanol

(d) 2-butanol and butanone

38. Predict which compound in each of the following pairs has the higher boiling point. Provide a reason for each answer. (1.4, 1.5, 1.6) K/U

(a)



$$CH_3CH_2{-}O{-}CH_2CH_3 \quad \text{and} \quad CH_3CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_2CH_3$$

(b)

$$\overset{\overset{O}{\|}}{CH_3CH} \quad \text{and} \quad \overset{\overset{O}{\|}}{CH_3COH}$$

(c) CH_3CH_2OH and $CH_3CH_2CH_2CH_2CH_2OH$

39. Give an example of a reaction that would yield the following products. For each reaction, name the organic reactant(s) and product(s). Remember to use (O) for oxidation reactions. (1.4, 1.5, 1.6) T/I

(a) primary alcohol

(b) secondary alcohol

(c) tertiary alcohol

(d) aldehyde

(e) ketone

(f) carboxylic acid

(g) ester

40. Classify each reaction and name all the reactants and products. (Note that the equations are not balanced.) (1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7) K/U

(a) $CH_3CH_3 + Br_2 \xrightarrow{\text{light}} CH_3CH_2Br + HBr$

(b) $CH_3CHCH_2 + Cl_2 \longrightarrow CH_3CHClCH_2Cl$

(c) $C_6H_6 + I_2 \xrightarrow{\text{catalyst}} C_6H_5I + HI$

(d) $CH_3CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Cl^-$

(e) $CH_3CH_2COOH + CH_3OH \rightarrow C_2H_5COOCH_3 + H_2O$

(f) $CH_3CH_2OH \rightarrow CH_2CH_2 + H_2O$

(g) $C_6H_5CH_3 + O_2 \rightarrow CO_2 + H_2O$

(h) $CH_3CHO + [O] \rightarrow CH_3COOH$

(i) $NH_3 + C_4H_9COOH \rightarrow C_4H_9CONH_2 + H_2O$

(j) $CH_3I + NH_3 \rightarrow CH_3NH_2 + HI$

41. For each of the descriptions, write a balanced chemical equation using condensed formulas. (1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7) K/U

(a) a substitution reaction of propane involving chlorine

(b) a halogenation reaction of benzene involving fluorine

(c) the complete combustion of ethanol

(d) a dehydration reaction of butan-2-ol

(e) the controlled oxidation of butanal

(f) the preparation of pentan-2-one from an alcohol

(g) the preparation of hexyl ethanoate from an acid and an alcohol

(h) the hydrolysis of methyl pentanoate

(i) the controlled oxidation of propan-1-ol

(j) an addition reaction of an alkene to produce an alcohol

(k) a condensation reaction of an amine

Analysis and Application

42. Describe a procedure that could be used to separate a mixture of alcohols containing methanol, ethanol, and hexan-1-ol? Explain why this procedure would work. (1.4) A

43. Analysis of an unknown organic compound gives the empirical formula $C_5H_{12}O$. It is only slightly soluble in water. When this compound is oxidized in a controlled way with potassium permanganate, $KMnO_4(aq)$, it is converted into a compound that has the empirical formula $C_5H_{10}O$. This second compound has the properties of a ketone. Based on the information provided, write the condensed formulas and names for all possible isomers of the unknown compound. If possible, give reasons why one or more of the isomers is more or less likely to be the unknown organic compound. (1.5) C A

44. Draw a flow chart outlining a procedure to synthesize the ester ethyl ethanoate, starting from ethene. (1.6) T/I C A

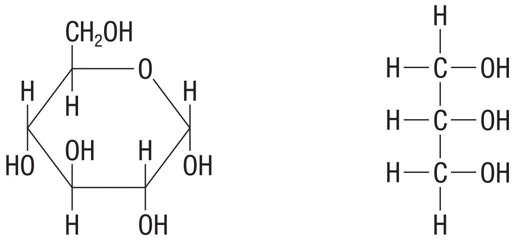
45. Create a table with the following headings: Type of organic compound; Functional group; Physical properties; Chemical reactions; Important uses.

Complete your table summarizing all you have learned about the organic compounds discussed in this chapter. (1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7) K/U C A

46. Create a graphic organizer to show how organic compounds are related and what reactions convert one to another. (1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7) K/U C A

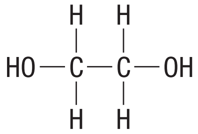
Evaluation

47. **Figure 4** shows the structural formulas of glucose, propane-1,2,3-triol (glycerol), and ethane-1,2-diol (ethylene glycol). All three compounds have a sweet taste. (1.4) A



glucose

propane-1,2,3-triol (glycerol)



ethane-1,2-diol (ethylene glycol)

Figure 4

(a) Predict their relative melting points and boiling points. Give reasons for your answer.

(b) Predict the solubility of each of these compounds in water and in gasoline. Give reasons for your answer.

(c) Ethane-1,2-diol (ethylene glycol) is toxic and is used as antifreeze in automobile radiators. Suggest an explanation for the toxicity of antifreeze.

(d) A hypothesis has been proposed that taste receptors respond to functional groups in the compounds that make up our food. Do the structures of these three compounds support that hypothesis? Explain.

48. Natural products are made by the cells of living organisms. Synthetic products are made by a laboratory process. The product may be exactly the same compound, but a distinction is made based on the source. For example, when bananas are dissolved in a solvent and the flavouring extracted, the pentyl ethanoate obtained is labelled "natural flavour." When pentyl ethanoate is synthesized by esterification of ethanoic acid and pentanol, it is labelled "artificial flavour." (1.6) T/I A

(a) Are substances such as artificial vanilla flavouring and vanilla extracted from a vanilla bean identical? Why or why not?

(b) In your opinion, should food companies be required to distinguish between a "natural" flavouring and an "artificial" flavouring on a food product label? Explain your position.

(c) Design a method for determining whether people can tell the difference between synthetic vanilla and natural vanilla and, if they can, which they prefer.

Reflect on Your Learning

49. Write a summary of what you have learned about organic chemistry in Chapter 1. K/U A

50. What are some typical errors made when naming organic compounds? How can you avoid those errors? K/U A

51. What concepts in this chapter did you struggle the most with? Describe three ways you can help improve your understanding of these concepts. K/U T/I

52. How would you explain to a friend why it is important to understand organic chemistry to make informed decisions in everyday life? A

Research

WEB LINK

53. Acetylsalicylic acid (ASA), better known as Aspirin, is a common pain reliever. Research the following topics and summarize your findings into a short paper, a concept map, or some other method of communication: T/I C A
    - Explore the chemical reactions associated with the synthesis of ASA. Determine the type of reaction that occurs, and the class of organic compounds involved.
    - Research the historical connection between willow bark and ASA. What advantages does ASA have over the compound extracted from willow bark? How were these advantages achieved?

54. Organic compounds are present in a huge variety of everyday substances. Examine the ingredient lists for some foods, beverages, or other products you use daily. Identify at least five examples of compounds whose names indicate that they are organic compounds. Research the chemical structures of these compounds, how they are produced, and what their functions are in the products you chose. Share your findings in a poster or electronic slide show. T/I C A

55. Gasoline is a mixture of many organic compounds. Research the structures of at least 4 of these compounds. Find out what the "octane rating" of gasoline means. Why do car manufacturers recommend using fuel with different octane ratings for different vehicles? What might happen if you use the wrong kind? Summarize your findings into an infomercial or poster to be displayed at a gas station. T/I C A

CHAPTER

2 Polymers

KEY CONCEPTS

After completing this chapter you will be able to

- assess the impact of natural and synthetic polymers on human health, society, and the environment
- propose a personal course of action to reduce the use of polymers that are harmful to human health and the environment
- use appropriate terminology related to polymer chemistry
- relate the properties of polymers to their structures
- explain the difference between addition polymerization reactions and condensation polymerization reactions, and analyze and predict the products of these reactions
- safely perform laboratory investigations, including analyzing polymerization reactions
- demonstrate an understanding of the processes by which synthetic polymers are developed

How Do We Use Polymers in Our Daily Lives?

A hockey puck travelling at 150 km/h can be dangerous if it strays into the stands. Fortunately, stray pucks are rare thanks to a clear “glass” safety wall that surrounds the ice and shields the spectators. This wall is usually not glass. More often it is constructed of very strong, thin, transparent, glass-like panels. They are made of a polymer known by the trade names Plexiglas, Lucite, or Perspex. This material is as clear as a glass window but is far less likely to shatter when a player collides with it. Much of the gear used during a hockey game—pucks, helmets, skates, pads, jerseys, gloves, and sticks—is made of various polymers.

Consider the objects that you have used today. How many of these items are made of plastic, at least in part? Alarm clocks, phones, TVs, bicycles, computers, shoes, clothes, toothbrushes, and milk bags all contain plastic. Could we use other materials to make a product, for example a food container? Glass, cardboard, or metal could be used. However, glass is heavy and breakable, and cardboard does not keep air out or moisture in. Metal is heavy and cannot be used in a microwave oven. Plastics make things lighter, stronger, more flexible, and cheaper. It is no surprise that plastics are used to manufacture so many things, from medical devices to parts of the International Space Station.

Along with the benefits of plastics, however, there are some major drawbacks. Most plastics are made from petrochemicals—a non-renewable resource. The process of extracting petrochemicals from the ground consumes energy, generates waste, and damages local ecosystems. The manufacturing process has similar problems.

One of the major benefits of plastics is that they tend to be very stable. They can be used for years without deteriorating. Unfortunately, this property can also cause problems. Plastic objects that have been discarded do not break down naturally. Instead, they remain in a landfill, along the roadside, or in the ocean for years, centuries, or even longer.

To reduce the environmental impacts, we need to cut back on our non-essential use of plastics. Recycling plastic products is an important step in reducing disposal problems, but many types of plastic cannot be recycled. We need to develop plastics that degrade naturally and find alternative products that are less harmful to the environment.

Plastics are synthetic polymers. Other polymers occur naturally. Silk, spiderwebs, hair, muscle, cotton, and wood are all composed of polymers made by living organisms. Polymer chemists have designed many synthetic polymers that have similar properties to natural polymers.

STARTING **POINTS**

Answer the following questions using your current knowledge. You will have a chance to revisit these questions later, applying concepts and skills from the chapter.

1. What is the difference between polymers and plastics?
2. What advantages do products made with polymers offer over products made with other materials?
3. Why are natural polymers put into the same category as plastics?
4. How are polymers made, and what are they made from?
5. What are some potential issues related to society’s use of plastics?

Mini Investigation

Making Polymer Worms

Skills: Predicting, Performing, Observing, Evaluating, Communicating

SKILLS HANDBOOK A1

Alginate is a natural polymer that is extracted from seaweed. Food manufacturers use alginate to thicken many food products, including ice cream. In this investigation, you will convert a solution of a soluble sodium alginate into an insoluble substance. Only when it is insoluble will you be able to see it. Squirting the dissolved sodium alginate into a solution of calcium chloride results in a chemical reaction that produces insoluble calcium alginate. The calcium alginate precipitates, forming long "worms."

Equipment and Materials: chemical safety goggles; lab apron; beaker or small bowl; tongs or spoon; approximately 250 mL of 1 % solution of calcium chloride; dropper bottle containing 5–10 mL of 2 % solution of sodium alginate; paper towel

1. Put on your safety goggles and lab apron.
2. Pour the calcium chloride into the beaker or bowl.
3. Squeeze about 5 mL of the sodium alginate solution into the calcium chloride solution as two or three continuous strands, and then squeeze several drops into the solution.
4. Remove the "worms" and drops from the solution and place them on the paper towel. Record your observations.
5. Place one of the "worms" and one of the drops back into the solution, leave them for 5 min, and remove them again. Observe the differences between the group left longer in the solution and the group left out of the solution. Record your observations.
6. Follow your teacher's instructions for safe disposal of the material.

A. Describe the "worms" that you removed from the solution in Step 4. T/I

B. Describe the differences between the group left longer in the solution and the group left out of the solution. T/I

2.1

Introducing Polymers

For thousands of years, people have prized silk fabric for its luxurious qualities. Silk is made of fibres produced by silkworms (**Figure 1**). For many centuries, the Chinese royal family kept secret the process of producing silk. During that time, silk was the foundation of the Chinese export economy, bringing great wealth from Asia and Europe.

Each silkworm (which is actually a caterpillar) produces a cocoon made of a single fibre hundreds of metres long. A silk fibre is thinner than a human hair, but much stronger and lighter in weight than a similar-sized steel wire. The silk workers get hold of a fibre from each of several cocoons and reel these fibres together to make a thread. This thread can then be woven into fabric or used for sewing or embroidery. Silk fabric is desirable because of its unique combination of properties, such as strength, light weight, soft texture, shiny appearance, and flexibility or "drape." Among other uses, silk's applications include packaging, medical devices, parachutes, and clothing. Silk fibres are examples of a remarkable group of compounds—polymers.

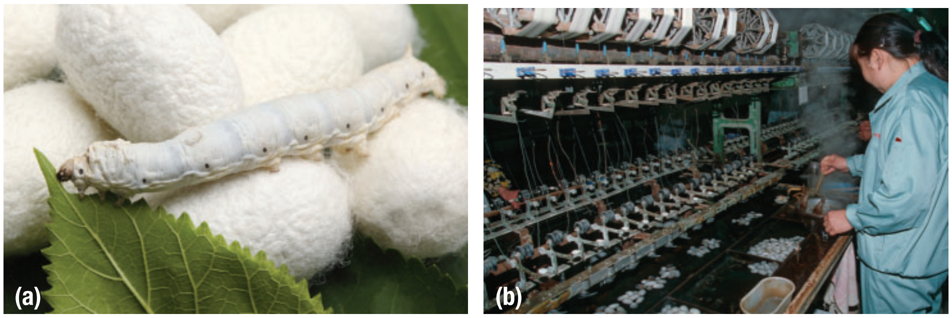


Figure 1 (a) Silk is a natural fibre produced when caterpillars of *Bombyx mori* moths make their cocoons. (b) Many countries now produce silk, harvesting the silk fibres from the cocoons.

The General Structure of Polymers

polymer a large, usually chain-like molecule that is built from small molecules

monomer one of the repeating small molecules that make up polymers

homopolymer a polymer of a single type of monomer

A **polymer** is a very large molecule that is built from monomers. A **monomer** is one of the repeating units that make up a polymer. Many biological molecules, such as silk, are natural polymers that are built inside living organisms. In the last couple of centuries, humans began manufacturing synthetic polymers for a wide range of applications, including textile fibres, rubber, and plastics. The polymer industry is now critically important to our economy and standard of living.

Figure 2 illustrates one of the simplest reactions to form a synthetic polymer. In this addition reaction, the double bond in each monomer is converted into a single bond, freeing up two electrons that form carbon-carbon single bonds with other monomers. Polyethene (more commonly known as polyethylene) is an example of a **homopolymer**: a polymer formed by reactions involving a single type of monomer.

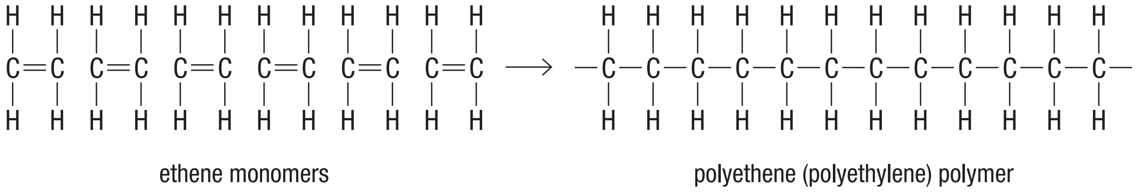
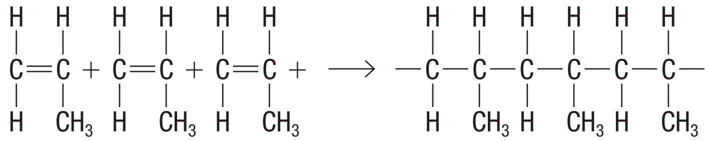
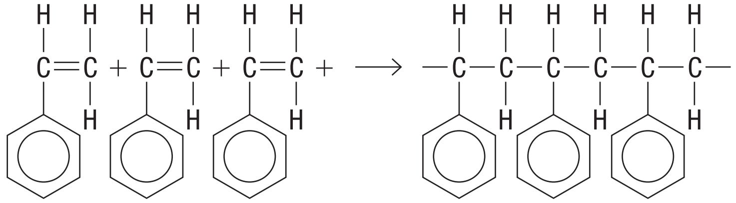


Figure 2 Polymerization of ethene molecules produces polyethene (polyethylene).

Substituents on the chain of carbon atoms give the polymer different properties. Other polymers that form by addition reactions include polypropene (polypropylene) and polystyrene (**Figure 3**).



(a) propene monomers polypropene (polypropylene)



(b) styrene monomers polystyrene

Figure 3 Homopolymers formed by addition reactions: (a) polypropene from propene monomers and (b) polystyrene from styrene monomers

copolymer a polymer made of two or more different types of monomers combined

Other polymers are chains of two or more types of monomers. A **copolymer** has different types of monomers combined to form the polymer chain. They may join in an addition reaction or in a condensation reaction, in which a molecule of water is eliminated as each new bond forms. **Figure 4** shows the chemical equation for the condensation reaction of three different amino acids to form part of a silk polymer. (Amino acids are the monomers in silk.) This reaction happens millions of times in the formation of a strand of silk.

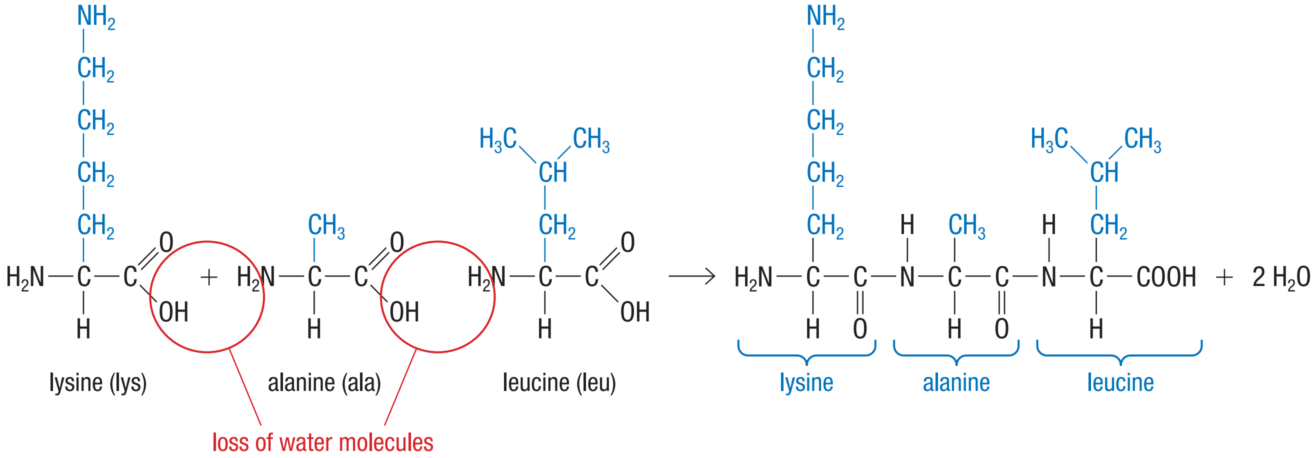


Figure 4 Silk is a protein: a natural polymer. Amino acids are the monomers of proteins. They join into chains in a condensation reaction. A molecule of water is released when two amino acids connect.

Natural and Synthetic Polymers

Natural polymers are made by all living things, from bacteria to mammals. Those manufactured in the cells of plants include starch and cellulose, which are homopolymers of the monomer glucose. Other natural polymers include the molecules RNA and DNA (**Figure 5**) that are produced within cell nuclei. You will learn more about natural polymers in Section 2.6.

Scientists developing new synthetic polymers often look to natural polymers, such as silk, for desirable properties. Synthetic polymers are usually made from monomers sourced from plants or from petrochemicals. Examples of synthetic polymers include polyester and polyamide fabrics, containers made of polyethene or polypropene (Figures 2 and 3), fluoropolymers used as non-stick coatings on cookware, the rubber of automobile tires, and the super-strong Kevlar fibres used in body armour.

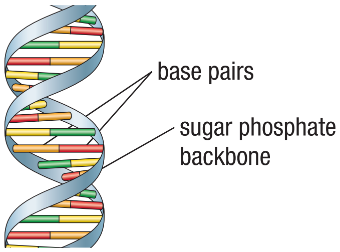


Figure 5 DNA is a polymer. The monomers, called nucleotides, are each made up of a base, phosphate, and a sugar. There are billions of unique strands of DNA.

A Short History of Synthetic Polymers

The first commonly used polymers were naturally occurring materials, such as bitumen, amber, waxes, rubber, and animal horns. These products were moulded or shaped with tools to create objects, or used as coatings. Then, chemists began to modify natural polymers to make products with different properties. WEB LINK

Sometimes polymers with useful properties are created by accident. In 1968, organic chemist Spencer Silver created an adhesive that did not appear to have a useful function because it did not stick very well. In 1974, another scientist, Arthur Fry, suggested using the adhesive to make small, sticky pieces of notepaper that could be easily removed. The adhesive was applied to paper squares and the squares were pressed onto other surfaces. The adhesive was sticky enough that the squares stayed in place, but not so sticky that they could not be easily removed.

1839: Vulcanized rubber was developed by American Charles Goodyear to make natural rubber stronger. Natural rubber is a polymer produced from the liquid sap of rubber trees. Natural rubber tends to be brittle when cold and soft when warm. Heating natural rubber with sulfur—vulcanizing—made the product harder and raised its melting point. Vulcanized rubber was used for battery boxes, pumps, dental plates, fountain pens, and, eventually, automobile tires.

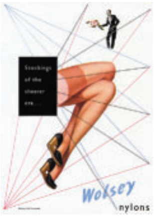
1868: Celluloid was invented to replace ivory in billiard balls. In the form of celluloid film, this polymer played a central role in the development of the movie industry

1909: Bakelite, invented by Leo Hendrik Baekeland, was the first fully synthetic polymer. It was widely used to replace wood, ivory, and ebony (thereby reducing the pressure on some endangered species). A lightweight plastic, it was non-conductive, heat and moisture resistant, chemically unreactive, and could be coloured. It revolutionized the design of consumer and industrial products. Many things made of Bakelite, such as jewellery, dishes, telephones, and toys, are collectables today.

1910: Formica was invented for use as an electrical insulator. The polymer was modified during the 1930s to make it more durable. Formica is widely used as a laminate on household surfaces, such as kitchen or bathroom counters.

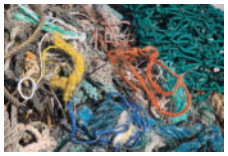
1929: Vinyl (PVC), invented by Waldo Semon, came to be used worldwide in products such as flooring, shower curtains, and plumbing pipes. It was the first durable material that was used to record and play back music.

1933: Saran was invented by Ralph Whiley. It was originally used as a coating: sprayed onto fighter planes to protect the surfaces against corrosion from sea salt. It was eventually approved for use in food packaging.



1935: Nylon, invented by Wallace Carothers to replace silk in parachutes and stockings, became widely used in many consumer goods.

1997/1998: The existence of the Great Pacific Garbage Patch was predicted and confirmed. In an attempt to reduce the quantity of discarded plastics, polymer chemists worked to develop better biodegradable plastics.



As the chemistry of polymerization was better understood, scientists were able to design many more synthetic polymers with specific, desired properties. Some more familiar trade names of some of these polymers are Lycra, Dacron, Styrofoam, and Kevlar. Developments of these and other polymers have had a significant impact on the environment and society. CAREER LINK

The development and use of so many polymer products have brought drawbacks, however. There are concerns regarding the breakdown of some polymers during use, releasing potentially carcinogenic compounds. Some people are particularly worried about this possibility in products used to transport, store, or cook food, such as plastic water bottles and non-stick cookware surfaces. There is also the issue of disposing of the vast volumes of synthetic products at the end of their useful lives. Unlike materials such as wood, paper, cotton, and leather, synthetic compounds do not break down quickly. They can remain unchanged for decades or centuries.

2.1 Review

Summary

- Polymers are very large molecules—natural or synthetic—made up of many monomers linked together.
- Monomers are small molecules with functional groups that allow them to link together to form polymers.
- Homopolymers are polymers made of only a single type of monomer. Copolymers are polymers made of two or more types of monomers.
- Polymers may form in addition reactions or condensation reactions.
- Synthetic polymers bring both benefits and drawbacks.

Questions

1. Classify each of the following substances as a natural or a synthetic polymer. Explain. K/U
   - (a) DNA
   - (b) polyethene
   - (c) celluloid
   - (d) cellulose
   - (e) protein
   - (f) rubber
   - (g) Kevlar
   - (h) bitumen
2. Explain the difference between the terms in each pair. K/U
   - (a) monomers and polymers
   - (b) homopolymers and copolymers
3. What do the three different monomers shown in Figures 2, 3, and 4 have in common? Explain how this feature allows them to form polymers. K/U T/I
4. **Figure 6** shows the structure of a polymer called cellulose. Draw a diagram of the monomer that makes up this polymer. K/U C

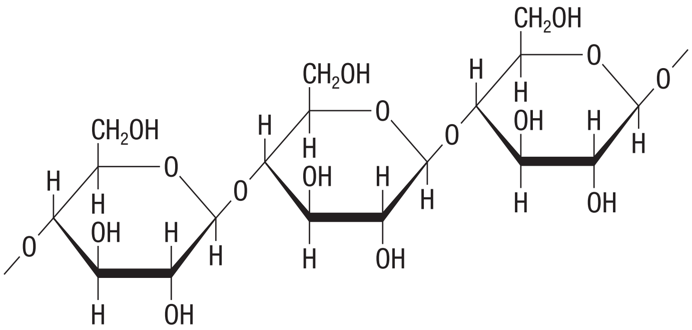


Figure 6 Cellulose

5. Use a graphic organizer to describe the similarities and the differences between natural and synthetic polymers. Include an example of each. K/U C
6. Suggest properties that might make polymers useful additions to paint, auto, or wood finishes. A
7. The rubber tree produces a resin, called latex, that is the raw material for making natural rubber. Research the developments that led to the process of making synthetic rubber and the social and environmental circumstances that occurred around the time this process was invented. Communicate your findings in a format of your choice. 🌐 T/I C A
8. Research the Great Pacific Garbage Patch. What is it? Why is it so hard to track and map? What impact does it have on the marine ecosystem? What is being done to clean it up? Present your findings in an illustrated report for inclusion in an environmental magazine or on a web page. 🌐 T/I C A
9. The monomer 2,2-bis(4-hydroxyphenol)propane, better known as BPA, is used in the production of hard plastics. In recent years there has been some concern that it could leach out of plastics and have negative health effects. According to Health Canada, “the current dietary exposure to BPA through food packaging uses is not expected to pose a health risk to the general population, including newborns and infants.” Research the pros and cons of BPA, summarizing your research in a table or similar graphic organizer. 🌐 T/I C A
10. Research two types of plastic, other than those illustrated in the timeline, and prepare a short illustrated history for each one. 🌐 T/I C A

🌐 WEB LINK

2.2 Synthetic Addition Polymers

addition polymer a very long organic molecule formed as the result of addition reactions between monomers with unsaturated carbon–carbon bonds

If you have ever stuffed used sports clothing in a plastic bag, or cooked eggs in a non-stick pan, you have handled an addition polymer. An **addition polymer** is the result of the reaction between monomers with unsaturated carbon–carbon bonds, similar to the addition reactions previously discussed for alkenes. Many plastic bags are made of polyethene, a very common addition polymer. (See Section 2.1, Figure 2.) Similarly, when tetrafluoroethene is the monomer, the resulting polymer is polytetrafluoroethene, PTFE (**Figure 1**). The brand name of this compound is Teflon: the slippery surface that prevents eggs from sticking to the pan.

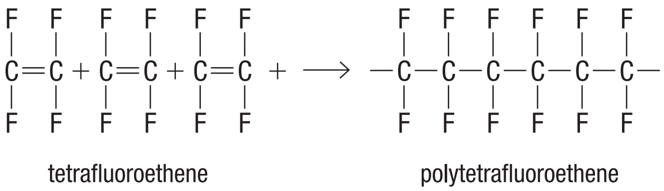


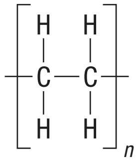
Figure 1 The formation of polytetrafluoroethene (PTFE)

The discovery of Teflon illustrates the role of chance in chemical research. In 1938, DuPont chemist Roy Plunkett was studying the chemistry of gaseous tetrafluoroethene. He synthesized about 50 kg of the chemical and stored it in steel cylinders. When the valve on one of the cylinders was opened to release some of the gas for testing, nothing happened. Rather than assuming that the cylinder was empty and discarding it, Plunkett decided to cut the cylinder open. Inside, he found a white powder: a polymer of tetrafluoroethene. This substance was eventually developed into Teflon. Why is Teflon such an inert, tough, non-flammable material? These properties are the result of the strong C–F bonds of the polymer molecule. These bonds are very resistant to chemical change. Because of its lack of chemical reactivity, Teflon is widely used for electrical insulation, non-stick coatings on cooking utensils, and low-friction surface coatings. CAREER LINK

LEARNING **TIP**

Shorthand for Polymers

Polymers might be thousands of carbon atoms long. So far, we have represented polymer molecules as long chains of repeating units that end in a line at each end. This implies that the molecule continues indefinitely in each direction. We can show the structure of a polymer in a condensed form by writing the repeating monomer in parentheses with an "*n*" subscript to indicate the number of repeating units.



Other addition polymers can be made from monomers containing chloro–, methyl–, cyano–, and phenyl– substituents (**Table 1**). In each case, the carbon–carbon double bond in the substituted ethene monomer becomes a single bond in the polymer. The variety of substituent groups leads to a wide range of properties.

The reaction to form polypropene is very similar to the reaction that forms polyethene. You could think of propene molecules as ethene molecules with a methyl group as a substituent. The polymer formed from propene looks just like that of polyethene, except that it contains methyl groups on every other carbon atom in the long chain: one per monomer (**Figure 2**). These methyl groups give the polymer added strength.

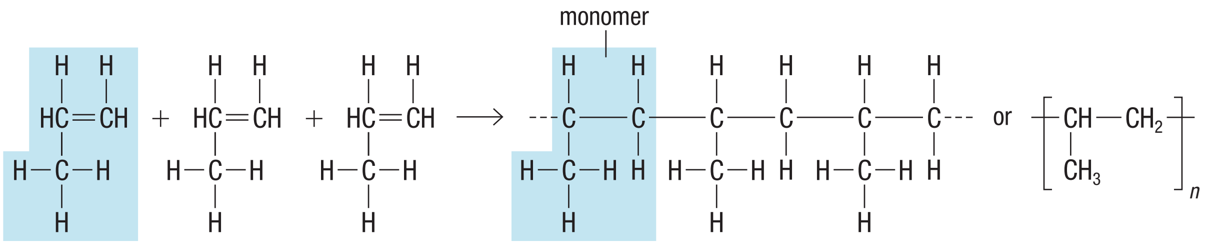
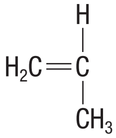
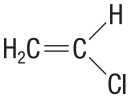
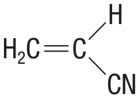
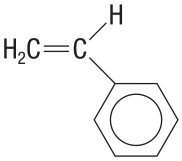
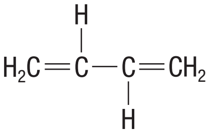
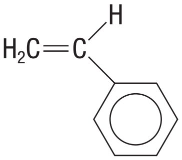
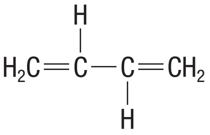


Figure 2 The polymerization of propene produces polypropene. Note how the structures of the reactant molecules are drawn so that their carbon–carbon double bonds are all aligned but the single bonds are above and below.

Table 1 Familiar Addition Polymers

Monomer		**Polymer**	
Name	**Formula**	**Name**	**Uses**
ethene	$H_2C{=}CH_2$	polyethene (polyethylene)	plastic bottles and pipes, insulation on electric wires, toys
propene	 $\mathrm{H_2C{=}\overset{\overset{H}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}}$	polypropene (polypropylene)	rope, packaging film, carpet fibres, toys 
chloroethene (vinyl chloride)		polyvinyl chloride (PVC)	pipes, construction materials, floor tile, clothing, reusable bags 
cyanoethene (acrylonitrile)		polyacrylonitrile (PAN)	carpet fibres, synthetic fabrics
tetrafluoroethene	$F_2C{=}CF_2$	polytetrafluoroethene (Teflon)	non-stick cookware, electrical insulation, ball bearings
vinylbenzene (styrene)		polystyrene	food and beverage containers, insulation, toys 
butane-1,3-diene (butadiene)	 $\mathrm{H_2C{=}\overset{\overset{H}{\vert}}{C}{-}\underset{\underset{H}{\vert}}{C}{=}CH_2}$	polybutadiene	tires, industrial coatings
vinylbenzene (styrene) and butane-1,3-diene (butadiene)	  $\mathrm{H_2C{=}\overset{\overset{H}{\vert}}{C}{-}\underset{\underset{H}{\vert}}{C}{=}CH_2}$	styrene–butadiene rubber (a copolymer)	synthetic rubber

Just as propene is similar to ethene with a methyl substituent group, other monomers are also similar to ethene with other substituents. These substituents could be chlorine, an alkyl group, or a benzene ring. These compounds also can undergo addition polymerization to produce a range of polymers, as Table 1 shows.

For example, polyvinyl chloride (PVC) is a polymer of the chloroethene monomer (also called vinyl chloride) (**Figure 3**).

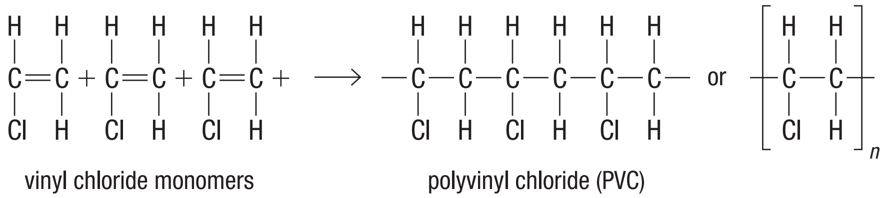


Figure 3 The formation of polyvinyl chloride (PVC)

If the substituent in ethene is a benzene ring, the compound is ethylbenzene (also known as styrene). The addition reaction of ethylbenzene molecules produces the polymer polystyrene (**Figure 4**). Polystyrene is used to make heat-resistant disposable drinking cups and it is used in many plastic toys.

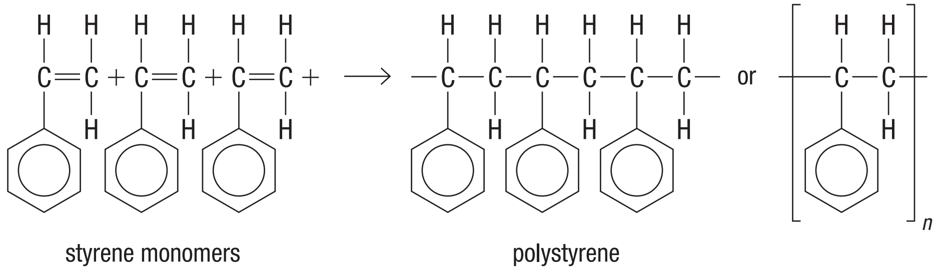


Figure 4 Styrene monomers react to produce polystyrene, which is the polymer in familiar Styrofoam products.

Tutorial 1 Drawing Addition Polymers and Their Monomers

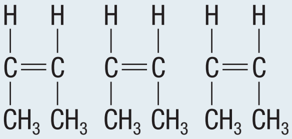
In this tutorial you will learn how to draw an addition polymer given the name of its monomer, and how to draw the monomer given the structure of the polymer.

Sample Problem 1: Drawing a Polymer

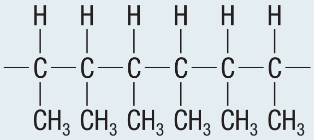
Draw a structural diagram showing three repeating units of the addition polymer formed from cis-but-2-ene.

Solution

First, draw three structural diagrams of cis-but-2-ene, $CH_3CH{=}CHCH_3$. Show each molecule with the double-bonded carbon atoms all in a line, and place other atoms below or above that line.

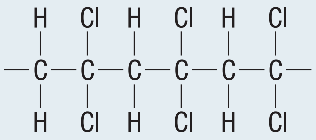


Next, connect the monomers with single bonds to form a chain. Remove the double bonds within the monomer, replacing them with single bonds so that each carbon atom has exactly four bonds. Add lines at each end to indicate that this is just one segment of the longer polymer molecule.



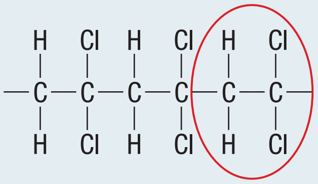
Sample Problem 2: Drawing a Monomer from a Polymer Structure

Draw a structural diagram of the monomer used to make Saran, shown below. Name the monomer.

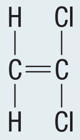


Solution

First, identify the repeating unit. In this case, the repeating unit in the polymer is CH_2–CCl_2, circled below. (Note that it would also be correct to identify the repeating unit as CCl_2–CH_2.)



Next, draw the monomer, replacing the single bond between the 2 carbon atoms with a double bond. (Remember that, during an addition reaction, double bonds between carbon atoms in a monomer become single bonds between carbon atoms in the polymer.)

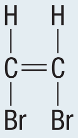


The name of this compound is 1,1-dichloroethene.

Practice

1. Draw and name the polymers that would be produced from each of the following monomers. Circle the repeating unit. K/U C

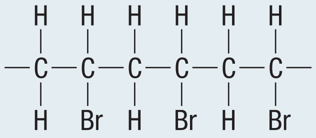
(a)



(b) $CH_3—CH_2—CH═CH—CH_2—CH_3$

(c) $CHCl═CH—CH_3$

2. Draw a section of the addition polymer polyacrylonitrile, showing 3 monomers. (See Table 1). K/U C
3. Draw and name the monomer used to produce the following polymer: K/U C



Plastics

plastic a synthetic substance that can be moulded (often under heat and pressure) and that then retains its given shape

A **plastic** is a synthetic polymer that can be moulded into shape (often under heat and pressure) and will then retain its shape when cooled. There are many kinds of plastics, including polymers of substituted ethene monomers: polystyrene, polyvinyl chloride, nylon, polyesters, rubber, polyethene, and polypropene. We see products made from plastics all around us: tires, DVDs, automobile trim, packaging materials, and eyeglass lenses. Plastics are usually manufactured from petrochemicals. Not all polymers are plastic, but all plastics are polymers.

Research This

Paying with Plastic

Skills: Researching, Analyzing, Evaluating, Communicating SKILLS HANDBOOK A5.1

In 2011, Canada joined the small number of countries that manufacture banknotes from synthetic polymers (**Figure 5**). The polymer is a biaxially oriented polypropene (BOPP) and is replacing the traditional cotton fibre. BOPP is made by stretching polypropene uniformly in two directions. The resulting synthetic polymer makes the bills more durable, more resistant to dirt and water, and more difficult to counterfeit. The new $100 bill feels smoother than the traditional paper bill, but the size remains unchanged. The Bank of Canada plans to replace all bills with polymer bills.

Used with the permission of the Bank of Canada.

Figure 5 The new $100 bill has two see-through sections and a smooth surface.

1. Research anti-counterfeit technology that is incorporated into Canadian polymer bills. Choose one type and explore how successful this technology is at preventing counterfeiting.
2. Research to find out what properties of BOPP influenced the Bank of Canada to choose it as a material for making notes.
3. Research the advantages and disadvantages of using polymer-based bills compared to traditional cotton-paper bills.

A. List the advantages and disadvantages of using polymer-based bills and cotton-paper bills. T/I

B. How are the polymer bills designed to foil counterfeiters? T/I A

C. How successful are anti-counterfeiting technologies? Do you think this technology could be applied to coins? T/I A

WEB LINK

Properties of Plastics

Most plastics are chemically unreactive. This can be explained by their structure: they are held together by stable single bonds. Because these single carbon–carbon bonds are very strong and less reactive than double bonds, the resulting polymer molecules tend to be very stable chemically. The fact that plastics resist breakage makes them a good replacement for glass in containers for food, water-based liquids, some solvents, and many other chemicals. Some plastics, however, are weakened or even dissolved by non-polar organic solvents. Not all plastics are suitable for all uses.

Plastics are moulded to give them the required shape. Many plastics, such as those used in plastic bags and upholstery foam, are flexible and can be bent and folded. Others, such as those used in car fenders and plastic water bottles, retain their shapes during normal use. What holds the polymer chains together so effectively? Polymer molecules, like all molecules, are attracted to one another by van der Waals forces. Although these intermolecular forces are generally weak on an individual basis, polymer chains are often thousands of carbon atoms long and the attractive forces are additive. Certain substituent groups may also cause electrostatic attractions between molecules.

Most plastics become softer and more flexible when they are heated because heat increases molecular motion. This motion disrupts the intermolecular forces briefly. The polymer chains slide past each other and the plastic becomes stretchy and flexible (**Figure 6**). This allows heated plastics to be shaped.

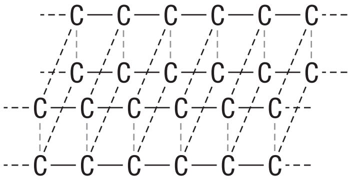


Figure 6 Weak forces between carbon atoms allow the plastic to flex and stretch.

UNIT TASK BOOKMARK

In the Unit Task, described on page 116, you will consider how solvents interact with other materials.

Polyethene plastics are classified according to their density. The most common forms are low-density polyethene (LDPE) and high-density polyethene (HDPE). LDPE is made by adding a small amount of compounds, such as butadiene, that have two or more double bonds. The butadiene results in branches in the polymer chains. These branches prevent the molecules from packing as tightly as those in HDPE, which consist of mostly straight-chain molecules. The branched polymer therefore has a lower density.

LDPE is mostly used for packaging materials (**Figure 7(a)**). The major use of HDPE is for blow-moulded products. These are products in which a bubble of molten HDPE is blown into a mould of the desired shape. Examples of blow-moulded products are milk jugs and bottles for consumer products (**Figure 7(b)**).

Because polypropene has more carbon atoms per monomer than polyethene, it tends to be harder and less flexible. Much of the polypropene that is produced is used for moulded parts, such as bottle caps, parts for appliances and electronics, and plastic toys. The strength of polypropene fibres also makes them useful for manufacturing rope, twine, and carpeting.

Polystyrene flows easily when it is hot, but becomes hard when it cools. Pure polystyrene is hard and colourless, so it is used to make disposable cutlery, DVD cases, and plastic models. When air or nitrogen is injected into the molten polystyrene, it expands into a light, foamy plastic. Expanded polystyrene is used to make cups for hot drinks and building insulation.

Polyvinyl chloride (PVC) also becomes hard when it is cooled. Because it is strong and relatively inexpensive, PVC is widely used in building construction. Door and window frames, water and sewage pipes, and siding are examples of products formed from PVC. Additives make PVC softer and more flexible, so that it can be used as insulation for electrical wires, a waterproof coating for shoes and clothes, and even imitation leather upholstery. PVC is a somewhat controversial material. During its

(a)

(b)

Figure 7 (a) Plastic bags are generally made from LDPE. (b) Plastic bottles with the recycling code “2” are made from HDPE.

use, and especially during incineration after the useful life of an object is over, PVC may release persistent toxic compounds into the environment. These compounds may be harmful to humans and other organisms.

Since having a high molecular mass is associated with a very strong, durable plastic, one might think that polymer chemists' goal would be to produce polymers with chains that are as long as possible. However, this is not necessarily the case. Polymers become much more difficult to process as the molecular mass increases. Molten polymer must be able to flow through pipes as it is processed. As the chain lengths increase, viscosity also increases. The flow requirements of the manufacturing process usually set the upper limit of molecular weight.

Plasticizers

In addition to the polymer itself, many plastic products include plasticizers. Plasticizers are substances added to increase flexibility, making the plastics easier to produce and shape into useful objects. Plasticizer molecules are inserted between polymer chains, keeping the chains spaced apart. This slightly weakens the forces that hold the molecules rigidly in place. However, some plasticizers, such as phthalates, have been linked to negative health effects. You will learn more about phthalates in Section 2.3.

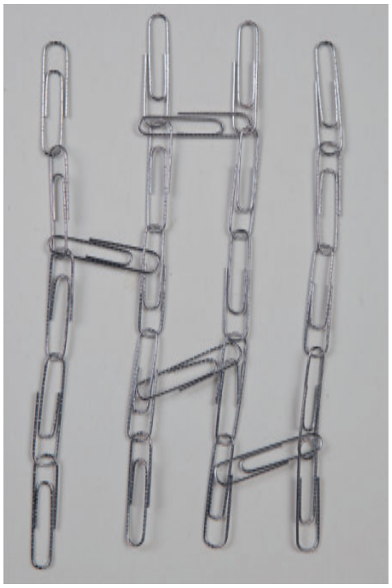


Figure 8 The more paper clips running between the vertical rows, the stronger the structure will be. These are just like cross-links in a polymer.

Polymer Cross-Linking

All of the polymers illustrated above form long chains by joining monomers. Depending on other functional groups attached to the monomers, individual chains of some polymers can link together. Chemical bonds can form between separate polymer strands in a process called cross-linking. Cross-linking binds multiple polymer chains together to form networks (**Figure 8**). These networks may be two-dimensional or three-dimensional structures.

The properties of a polymer depend on a number of factors including the functional groups present, the number of monomers in the polymer molecule, and the degree of cross-linking that occurs. In general, the more cross-links there are, the more tightly the chains are held together and the more rigid and inflexible the polymer (**Figure 9**).

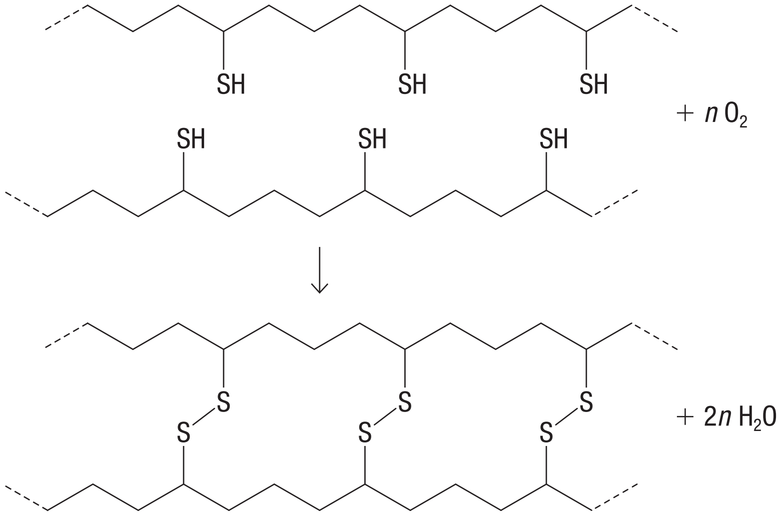


Figure 9 Two polymers with —SH groups can form sulfur–sulfur cross-links.

Dienes are alkenes with two carbon–carbon double bonds. Incorporated into polymer molecules, dienes form strong cross-links from one chain to another. The more dienes that are added to a polymer chain, the more cross-linking will occur. The number of diene monomers added controls the rigidity of the polymer. As cross-links are added, the density of the polymer increases as well. Plastics can be made soft or hard depending on the degree of cross-linking. A hard, dense, inflexible garbage bag would not be that useful nor would a soft, flexible fencepost.

A diene used for cross-linking polymers is 1,4-diethenylbenzene, also called divinylbenzene or DVB. Incorporated into polystyrene, 1,4-diethenylbenzene makes the resulting plastic stronger (**Figure 10**).

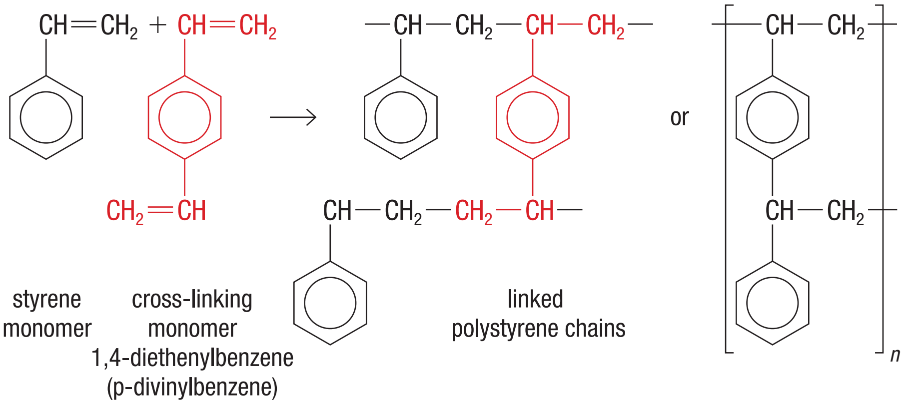


Figure 10 The addition of 1,4-diethylbenzene to polystyrene allows cross-links to form between adjacent polymer chains.

Some cross-linking agents are inorganic. As Figure 9 shows, sulfur is able to form two covalent bonds to connect two different polymer chains. Natural latex from rubber trees is very soft and gooey. The diene monomer in latex, 2-methylbutadiene, forms partially unsaturated polymer chains. This polymerization results in a soft, reactive rubber (**Figure 11(a)**). When sulfur is added to latex and the mixture is heated, the sulfur forms cross-links that make the polymer much tougher and stiffer (**Figure 11(b)**). This process was named “vulcanization” for Vulcan, the Roman god of fire. The cross-links bring the polymer chains back to their original position after the rubber is stretched. The elasticity of rubber makes it suitable for tires, providing a comfortable, bump-less car ride.

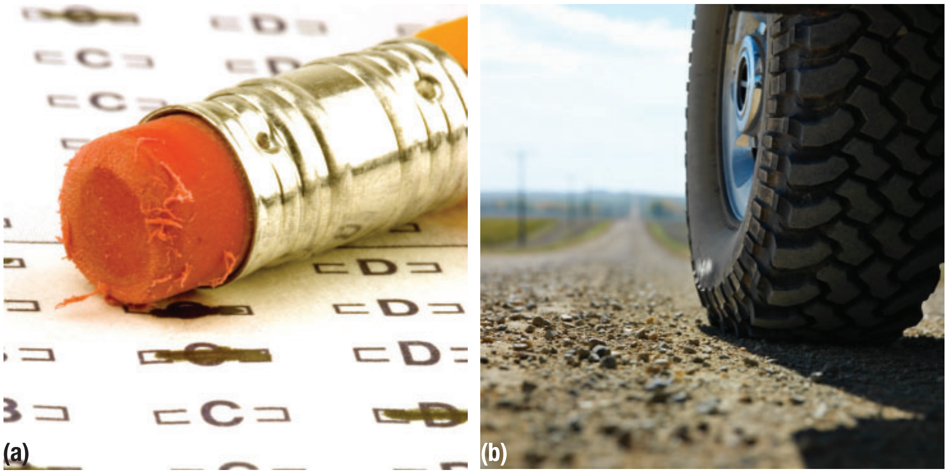


Figure 11 (a) Rubber monomers undergo addition reactions to form a soft rubber polymer. (b) Vulcanization adds sulfur cross-links to the rubber polymer.

Some plastics can withstand more heat than others. This heat tolerance determines how products made from the plastics can be manufactured and used. Some plastics will melt or soften when heated and hold their shape when cooled. These plastics are called thermoplastics and they can be moulded. Thermoplastic polymers do not contain many cross-links. Highly cross-linked plastics will not soften at high temperatures because the cross-links, which are strong covalent bonds, are not overcome by heating. These plastics are called thermoset polymers.

Elastomers are as they sound—elastic. They are polymers with a limited amount of cross-linking, which allows them to stretch and then snap back to their original shape. The polymer chains in an elastomer at rest are condensed and tightly wound up but, when stretched, the chains straighten out. Most elastomers are carbon-based, such as neoprene and rubber. Silly Putty is a type of silicone-based elastomer. It is bouncy and stretchy, and it floats.

Mini **Investigation**

Guar Gum Slime

Skills: Performing, Observing, Analyzing

SKILLS HANDBOOK A1

Guar gum is a natural substance produced by the guar plant. When guar gum is heated in water, it forms polymers that cause the solution to become more solid. Many processed foods include guar gum as a thickener, much like soluble cornstarch that thickens gravy. Oil drillers also mix guar gum into the slurry that they pump into oil wells.

Sodium borate (borax) is a cleaning agent often used for laundry. It is a hydrated ionic compound made up of sodium and polyatomic borate ions: $Na_2B_4O_7 \cdot 10\ H_2O(s)$. In solution the borate ions react with certain organic compounds to form cross-linked polymers. In this investigation, the borate ions link with –OH groups in the guar gum molecules to form a cross-linked substance with interesting physical properties.

Equipment and Materials: lab apron; chemical safety goggles; 250 mL beaker; wooden stir stick; 100 mL measuring cylinder; electronic balance; 100 mL beaker; aluminum pie plate; 110 mL warm distilled water; food colouring (optional); 1.0 g guar gum powder; 0.4 g sodium borate, $Na_2B_4O_7(s)$

Sodium borate is an irritant. Avoid skin and eye contact. If the solution splashes onto your skin or into your eyes, wash the affected area for 15 min with plenty of cool water and inform your teacher. Wash your hands at the end of the investigation.

Do not consume anything in the laboratory or remove anything from the laboratory to consume later.

1. Put on your lab apron and chemical safety goggles.
2. Add 100 mL of warm water to the 250 mL beaker. Add food colouring (optional). Slowly add the guar gum powder, stirring constantly with the stir stick to dissolve the powder.
3. Add 10 mL of warm water to the 100 mL beaker. Add the sodium borate crystals to the water.
4. Add the sodium borate solution to the guar gum solution. Immediately begin stirring the mixture with the stir stick. Within a couple of minutes, a slimy substance will form.
5. Lift some of the "slime" out with the stir stick and place it on the aluminum pie plate. The mixture is safe to touch. Use your hands to manipulate the slime. Try stretching, poking, and slapping it. Move it quickly and slowly. Record your observations.

A. What happened when you first started stirring the mixture? K/U T/I

B. What happened after stirring for a few minutes? K/U T/I

C. Describe the appearance and properties of the slime. Are the properties constant, or do they vary? K/U T/I

D. Describe how cross-linking gives this mixture its properties. K/U T/I

E. How might the use of guar gum by the oil-drilling industry affect the price of food? Comment on the implications of this. A

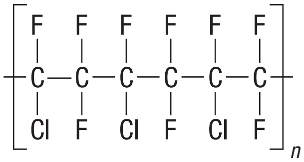
2.2 Review

Summary

- Addition polymers form when monomers link during addition reactions.
- The properties of addition polymers can be varied by selecting monomers with certain substituent atoms or groups, particularly by adding substances that can form cross-links between polymer chains.
- Plastics are synthetic substances that can be moulded, often under heat and pressure. Plastics that can be heated and formed in moulds are called thermoplastics. Those that cannot be heated and formed are called thermoset polymers. Elastomers are flexible polymers that return to their original shape after being stretched.

Questions

1. Kel-F is a polymer with the structure

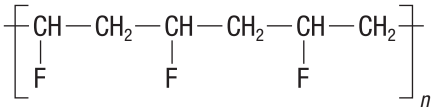


$-[\mathrm{CFCl-CF_2-CFCl-CF_2-CFCl-CF_2}]_n-$

Name and draw the monomer for Kel-F. K/U C

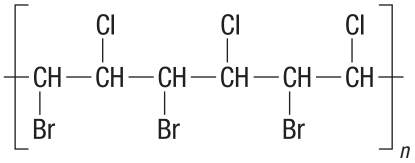
2. Write the name and formula of the monomer that could be used to produce each of the following polymers: K/U C

(a)



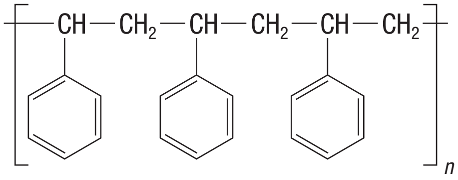
$-[\mathrm{CHF-CH_2-CHF-CH_2-CHF-CH_2}]_n-$

(b)

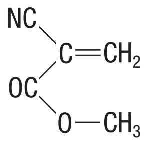


$-[\mathrm{CHBr-CHCl-CHBr-CHCl-CHBr-CHCl}]_n-$

(c)



3. “Super glue” contains methyl cyanoacrylate.



When it is exposed to water or alcohols (for example, on two surfaces to be bonded), ethyl cyanoacrylate quickly polymerizes. Draw the structure of the polymer formed by methyl cyanoacrylate. K/U C

4. Explain how cross-linking occurs and what effects it has on the properties of a polymer. K/U T/I

5. Polystyrene can be made more rigid by copolymerizing styrene with p-divinylbenzene. K/U C
   (a) Draw the structure, and write the IUPAC name, of p-divinylbenzene.
   (b) How does p-divinylbenzene make the copolymer more rigid?

6. Scientists have developed polymers that can “heal” from scratches, much as skin heals. Research how these polymers repair themselves and where they might be used. Prepare an illustrated presentation or blog post to share your information with salespeople in the plastics industry. T/I C A

7. Recycling programs are in place in most parts of Ontario, but not all types of plastic can be recycled. T/I C A
   (a) What are the different classes of plastic? Summarize your findings in a table.
   (b) Find out what types of plastic cannot be recycled in your region, and why.
   (c) How long does it take for plastic garbage bags to decompose in a landfill site?
   (d) What can you do, personally, to reduce the environmental impact of plastics?

8. Polystyrene is a popular packaging material. T/I C A
   (a) What properties of polystyrene make it particularly useful for packaging?
   (b) What biodegradable materials can be used as an alternative packaging material?
   (c) In a graphic organizer, compare polystyrene and the alternative materials.
   (d) Decide which you feel is the better choice. Defend your decision.

WEB LINK

Explore an Issue in Polymer Technology

SKILLS MENU

- Defining the Issue
- Researching
- Identifying Alternatives
- Analyzing
- Defending a Decision
- Communicating
- Evaluating

Figure 1 Look for the PVC symbol on the plastic products that you use every day.

Plasticizers and Human Health

Plasticizers are compounds that increase the flexibility of otherwise brittle synthetic polymers such as PVC (**Figure 1**). Phthalates, which are long esters of polycarboxylic acids, are very effective plasticizers. They are not covalently bonded to the polymers to which they are added.

Accumulated research has connected phthalates to severe negative health effects, including kidney and liver failure. Phthalates may also disrupt the human reproductive system, especially if the exposure occurs during childhood. In 2011, Health Canada placed restrictions on the use of some phthalates in children's products. Industry chemists are now working to develop non-phthalate plasticizers. WEB LINK

The Issue

Phthalate plasticizers are not easily replaced. Other plasticizers do not have the same chemical properties as phthalates and, so far, are not as effective.

ROLE

You are a chemist presenting a paper to a government panel on the use of plasticizers.

AUDIENCE

Your audience includes your Member of Parliament, representatives from the Recycling Council of Ontario and plastics industry associations, and concerned citizens.

Goal

To determine whether phthalates should be replaced by other plasticizers.

Research

SKILLS HANDBOOK A5

Investigate non-phthalate plasticizers. How do these products compare to phthalates in terms of (i) usefulness in the plastics industry and (ii) health and/or environmental concerns? Compare the advantages and disadvantages of each. Consider costs and benefits, including effectiveness, availability, health effects, lifespan, and recyclability.

Possible Solutions

Consider possible actions that could be taken to address this issue. The following suggestions may start your list:

- Ban the use of phthalates in some products or in all products.
- Educate the public about appropriate uses of plastics made with phthalates.
- Fund additional research to replace phthalates. CAREER LINK

Decision

Summarize your findings. Draw a conclusion about the need to replace phthalates with other plasticizers. Justify your conclusion with evidence from your research.

Communicate

Select the most appropriate method to communicate your findings.

Plan for **Action**

Do you currently use plastics containing phthalates? Will you continue to do so? List several criteria to help you decide. Select three or four common products (either commercially available or homemade) that perform the same function as phthalate-containing plastics. Rank the alternatives according to your criteria. Which one is best?

WEB LINK

Synthetic Condensation Polymers

2.4

A firefighter entering a burning building must be protected from intense heat. Imagine a fabric that could withstand the extreme temperatures of an industrial fire. That fabric is likely to be knitted with Nomex fibres. Nomex is a polymer made from amide monomers. It is used to make flame-resistant clothing, electrical insulation, industrial filters, and aircraft parts. Race-car drivers, firefighters, fighter pilots, and astronauts all wear clothing that incorporates this polymer (**Figure 1**). Nomex is a condensation polymer, formed when two monomers bond together with the elimination of a small molecule.

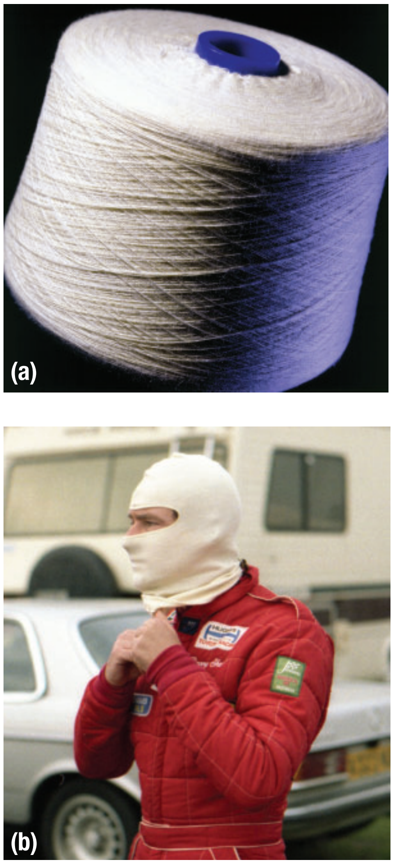
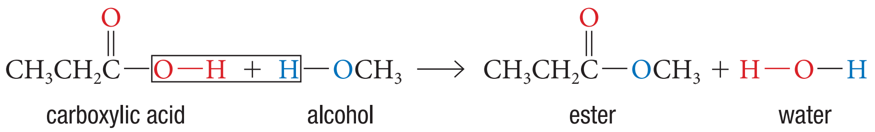


Figure 1 (a) Nomex is a flame-resistant material that can be formed into fine thread. This thread is then woven or knitted into safety clothing. (b) Race-car drivers wear balaclavas made of Nomex.

Producing Condensation Polymers

In Section 2.2, you studied polymers that were made by addition reactions of unsaturated monomers. There are many molecules without carbon–carbon double bonds that can also react to form polymers. What type of reaction can join these monomers together?

Recall what you know about reactions that take place between two organic compounds, resulting in the formation of a larger compound and a small molecule such as water. This type of reaction is called a condensation reaction (Section 1.4). For example, an alcohol reacts in a condensation reaction with a carboxylic acid to form an ester.



$$CH_3CH_2\overset{O}{\overset{\|}{C}}-\boxed{O-H + H}-OCH_3 \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}-OCH_3 + H-O-H$$

Condensation reactions can also be used to produce condensation polymers. A **condensation polymer**, like an addition polymer, is composed of repeating groups of monomers. These monomers, unlike those in addition polymers, have two reactive functional groups involved in the polymerization reaction. They do not necessarily have any carbon double bonds.

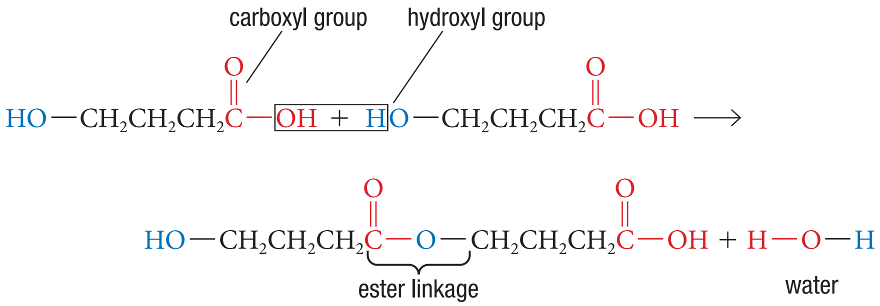
condensation polymer a very long organic molecule formed as a result of condensation reactions between monomers with two functional groups

The two most common types of condensation polymers have either ester linkages or amide linkages. Esters have a carboxyl functional group joining the monomers (R–COOR′); amides have a carbonyl group, –C=O, connected to a nitrogen atom, –N–, joining the monomers (R–CONR′). Let us look at these two types of polymers in more detail.

Polyesters

A **polyester** is a polymer formed by a series of esterification reactions between monomers. Monomers with two functional groups, an –OH (hydroxyl) group and a –COOH (carboxyl) group, form chains by undergoing condensation reactions at both ends. As each monomer molecule is added to the chain, the condensation reaction produces a small by-product molecule, such as water.

polyester a polymer formed by a condensation reaction that results in ester linkages between monomers



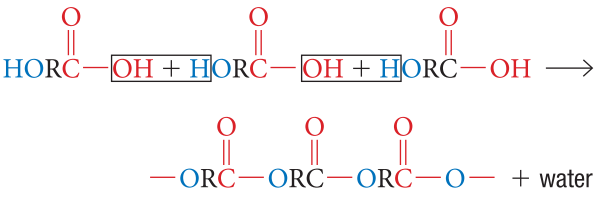
$$HO-CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-\boxed{OH + H}O-CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-OH \longrightarrow$$

$$HO-CH_2CH_2CH_2\underbrace{\overset{O}{\overset{\|}{C}}-O-}_{\text{ester linkage}}CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-OH + H-O-H$$

Figure 2 Clothes that are made of polyester are washable and durable.

To form a polymer chain, a monomer must attach to one end of the chain, either with its carboxyl group reacting with the hydroxyl group on the chain, or with its hydroxyl group reacting with the carboxyl group on the chain. Either way, it forms an ester linkage and eliminates a water molecule. Each end of the growing chain can then react with another monomer, and this process continues until a long polyester polymer is formed. Synthetic condensation polymers are widely used in consumer and industrial textiles (**Figure 2**).

The general reaction equation for the formation of a polyester is



$$HOR\overset{\overset{O}{\|}}{C}-\boxed{OH + H}OR\overset{\overset{O}{\|}}{C}-\boxed{OH + H}OR\overset{\overset{O}{\|}}{C}-OH \longrightarrow$$

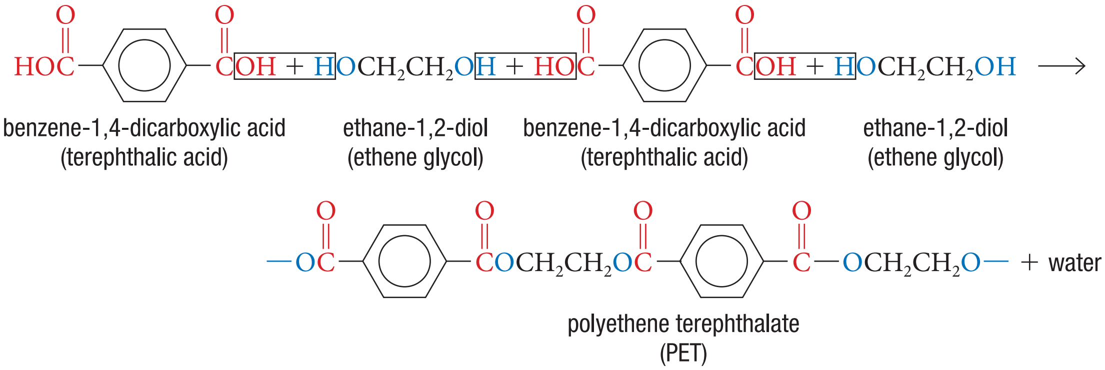
$$-OR\overset{\overset{O}{\|}}{C}-OR\overset{\overset{O}{\|}}{C}-OR\overset{\overset{O}{\|}}{C}-O- \ + \text{water}$$

a polyester

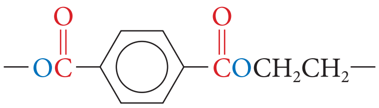
Polyesters can also be formed from two different monomers. One monomer must have two hydroxyl groups (a diol) and the other must have two carboxylic acid groups (a dicarboxylic acid). In this case, the polyester is a copolymer formed with alternating monomers diol and dicarboxylic acid. CAREER LINK

Dacron

Dacron is the brand name for polyethene terephthalate (PET). It is a condensation copolymer formed by the reaction of ethane-1,2-diol (ethene glycol) and benzene-1,4-dicarboxylic acid (terephthalic acid). Ester linkages join the monomers together.



The repeating unit of Dacron is



Polyamides

Recall from Section 1.7 that, in the formation of an amide, a carboxylic acid reacts with ammonia or with a primary or secondary amine. The resulting functional group is an amide group consisting of a carbonyl group, –C–O, in which the carbon atom is bonded to a nitrogen atom.

polyamide a polymer formed by condensation reactions resulting in amide linkages between monomers

A **polyamide** is a polymer formed by a condensation reaction resulting in amide linkages between monomers. Amide linkages are formed by a condensation reaction between an amine and a carboxylic acid (just as ester linkages are formed by a condensation reaction between an alcohol and a carboxylic acid). The second product of the amide reaction is usually water. (In some polyamide reactions a dicarbonyl chloride is used in place of a dicarboxylic acid. In this case, a molecule of hydrogen chloride is eliminated.)

The carboxyl groups allow many hydrogen bonds to form between polymer chains. Together, these hydrogen bonds make polyamides exceptionally strong. Polyamides are also resistant to damage from insects and heat. Kevlar is a polyamide used in body armour (**Figure 3**). Nomex, described above, is valued for its heat resistance.

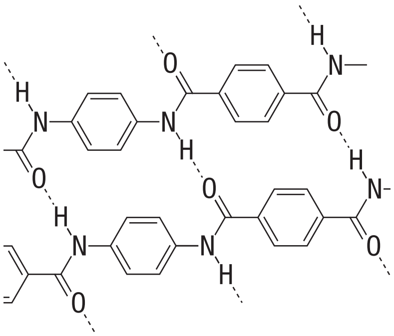
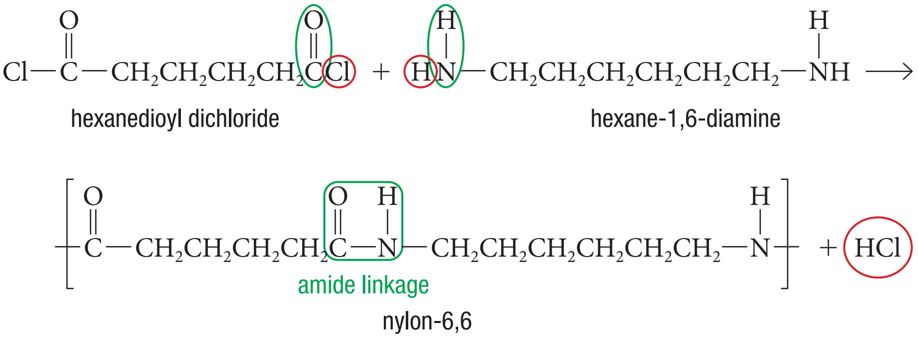


Figure 3 Hydrogen bonds between polymer chains give Kevlar its amazing strength.

Nylon 6,6

Perhaps the most familiar condensation polymer is nylon. Nylon is a copolymer, with two different types of monomers. One common form of nylon is produced when hexane-1,6-diamine (hexamethylenediamine) and hexanedioyl dichloride (adipoyl chloride) react, resulting in the formation of a C–N bond and a hydrogen chloride molecule:



$$\text{Cl}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Cl} + \text{H}\overset{\overset{\text{H}}{|}}{\text{N}}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\overset{\text{H}}{|}}{\text{N}}\text{H} \longrightarrow$$

$$\left[\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\underbrace{\overset{\overset{\text{O}}{\|}}{\text{C}}-\overset{\overset{\text{H}}{|}}{\text{N}}}_{\text{amide linkage}}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\overset{\text{H}}{|}}{\text{N}}\right] + \text{HCl}$$

As the polymer grows, both ends are free to react with another monomer. Repetition of this process leads to a long chain of the units shown in square brackets.

There are several types of nylon, depending on the particular diamine and dicarboxylic acid or dicarbonyl chloride used. The reaction to form nylon occurs quite readily under laboratory conditions (**Figure 4**).

Figure 4 The reaction to form nylon occurs at the interface of two liquid layers in a beaker. The bottom layer is hexanedioyl dichloride dissolved in carbon tetrachloride, CCl_4. The top layer is hexane-1,6-diamine dissolved in water. A molecule of hydrogen chloride is produced as each C–N bond forms.

Tutorial 1 Drawing Condensation Polymers

In this tutorial, you will learn how to draw condensation polymers given the names of the monomers, and how to draw and classify monomers given the structure of the polymer.

Sample Problem 1: Drawing Polymers from Monomers

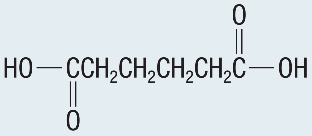
Draw a condensed structural diagram of the polymer made from repeating units of a 4-carbon diamine and a 6-carbon dicarboxylic acid.

Solution

The first monomer is butane-1,4-diamine. The second monomer is hexane-1,6-dicarboxylic acid. These monomers are typical of nylon.

Draw the structure of each monomer.

$NH_2-CH_2CH_2CH_2CH_2-NH_2$



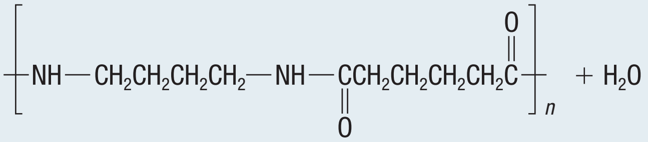
$$\text{HO}-\underset{\underset{\text{O}}{\|}}{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OH}$$

Combine the structures so that an amide linkage is formed between the two molecules. A molecule of water will be produced during the reaction.

LEARNING **TIP**

Stereochemical Formulas
To represent three-dimensional shapes on paper, we need to be able to show which bonds, and hence atoms, are closer to us and which are farther away. Diagrams called stereochemical formulas were developed to do this. They use the following conventions: a solid line — is a bond in the plane of the page, and a wedged line ◀ is a bond to an atom in front of the plane of the page (toward the viewer).

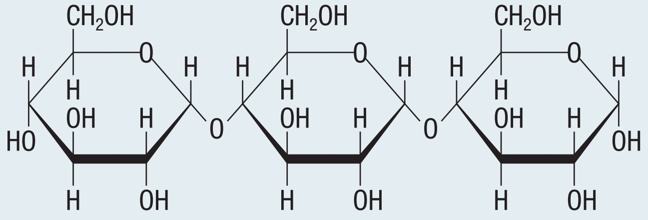
Show that the polymer is continuous by adding bond lines at each end, drawing square brackets around the structure, and writing the subscript *n* to indicate many repeats.



$$\left[-\mathrm{NH}-\mathrm{CH_2CH_2CH_2CH_2}-\mathrm{NH}-\underset{\underset{\textstyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H_2CH_2CH_2CH_2}\overset{\overset{\textstyle \mathrm{O}}{\|}}{\mathrm{C}}-\right]_n + \mathrm{H_2O}$$

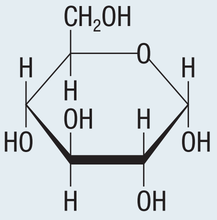
Sample Problem 2: Drawing and Classifying Monomers from a Polymer

Starch is a polymer formed in a condensation reaction in which molecules of water are eliminated from the new bonds. Draw the monomer that makes up starch.



Solution

There is only one repeating unit, so starch is a homopolymer. The repeating units are based on ring structures. Adding the components of a water molecule to either end of each monomer gives the following structure:



Practice

1. Draw a structural diagram of the polymer formed by the reaction of
   (a) propane-1,3-diol and pentanedioic acid
   (b) butanedioic acid and a 5-carbon diamine
   (c) hexanedioic acid and a 3-carbon diamine K/U C

Investigation **2.4.1**

Preparation of a Polyester (page 106)
You have learned about properties of polyesters, polyamides, and condensation reactions. In this observational study, you will perform a condensation reaction and explore the characteristics of the resulting polymer.

Unwanted Plastic

As the quantity of plastics and other polymers used by people around the world grows, disposal of unwanted materials has become a major problem. Polymers in landfills do not degrade and are expected to remain unchanged for centuries—and perhaps even longer. Polyethene and polystyrene packaging materials are particularly long-lived and widely used. In one vast region of the Pacific Ocean, the water near the surface is clogged with floating or partially submerged plastic garbage. This waste is hazardous to marine organisms. Because each addition polymer is essentially a massive alkane molecule, the plastic garbage is very stable chemically: it does not degrade.

Condensation polymers, unlike addition polymers, can be made biodegradable. Certain bacteria can hydrolyze the amide or ester linkages between monomers, chopping up the polymer chain into smaller pieces. Micro-organisms can then consume and digest many of the resulting fragments. Although biodegradable polymers are preferable to plastics that do not break down, they are not a perfect solution to the garbage problem. The most effective solution is to reduce the production of plastics in the first place. We can do this by reducing, reusing, recycling, and using alternative materials.

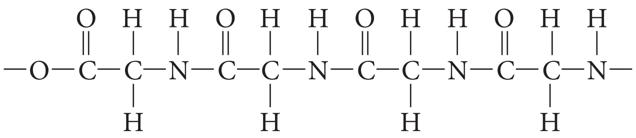
2.4 Review

Summary

- Condensation polymers are polymers formed when monomers join during condensation reactions. A small molecule, such as water or hydrogen chloride, is also produced during the reaction.
- Polyesters are formed by condensation reactions between carboxylic acids and alcohols that result in ester linkages. Polyamides are formed by condensation reactions between carboxylic acids and amines that result in amide linkages.
- Plastic garbage is a serious environmental problem. The most effective solution is to reduce the quantity of waste produced.

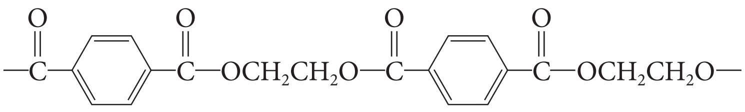
Questions

1. Draw the structure of the monomer that forms this homopolymer by condensation: K/U C

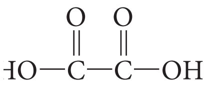


$$-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{N}-$$

2. Draw the structures of the monomers that react to form this polyester copolymer: K/U C

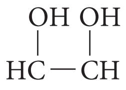


3. A condensation polymer can be formed between propane-1,3-diol and 1,4-diaminobutane. K/U C
   (a) Draw the structures of both reactants, circling the functional groups that are involved with the polymerization.
   (b) Draw the structure of the polymer that is produced.
4. Describe the similarities and differences between polyesters and polyamides. Provide examples. K/U
5. Ethanedioic (oxalic) acid is found in certain vegetables, such as spinach. Ethane-1,2-diol is a toxic synthetic compound better known as ethylene glycol.



$$HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

ethanedioic acid

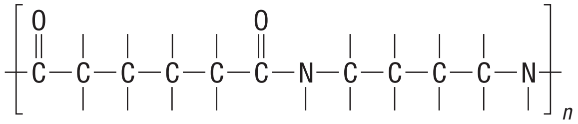


$$\overset{OH}{HC}-\overset{OH}{CH}$$

ethane-1,2-diol

Draw three units of the polymer made from ethanedioic acid and ethane-1,2-diol. K/U C

6. Write the names and draw the structural formulas for the reactants that form this polyamide: T/I C



$$\left[\overset{O}{\overset{\|}{C}}-C-C-C-C-\overset{O}{\overset{\|}{C}}-N-C-C-C-C-N\right]_n$$

7. Sodium polymethacrylate can absorb many times its own mass in water. This property makes the polymer ideal for use in hygiene products and baby diapers. What else do you think this polymer would be suitable for? T/I A
8. Many monomers can form long polymer chains, but some can also form bonds with neighbouring polymer chains, resulting in cross-linking. K/U T/I C
   (a) What properties or structure would such a monomer need?
   (b) Draw an example of a monomer that may be able to form cross-links. Circle any functional groups.
   (c) Draw the resulting polymer before cross-linking has taken place. Circle any functional groups that could be involved in cross-linking.
   (d) Draw the resulting polymer after cross-linking has taken place.
9. You have invented two polymers for use as potting-soil supplement material for plants. T/I C A
   (a) What properties would the polymers need to have?
   (b) Plan an investigation to compare two polymers for the characteristics you listed in (a). Briefly describe the materials, equipment, and procedure, as well as how you could interpret the data.

2.5 Chemistry JOURNAL

The Invention of Nylon

SKILLS HANDBOOK A4

ABSTRACT
Wallace H. Carothers was a brilliant American scientist known for developing nylon and neoprene. His colleagues respected and valued his contributions as one of the pioneers of polymer chemistry.

The Early Years

Wallace H. Carothers was born in 1896 in Burlington, Iowa. As a child, he was fascinated by tools and mechanical devices.

After graduating from Tarkio College in Missouri with a degree in Chemistry, Carothers completed his doctorate at the University of Illinois. His first job was teaching at Harvard University, but after only two years he signed on with DuPont to head the organic chemistry division where Carothers laid the foundations of polymer chemistry. He was the first industrial chemist elected to the prestigious National Academy of Sciences.

The Discovery of "Macromolecules"

Carothers's work on polymers built on that of Hermann Staudinger, a German chemist who first proposed the idea of polymers in the 1920s. At the time, all chemical compounds were thought to have relatively low molecular mass. Any evidence of substances having higher molecular mass was attributed to aggregation (sticking together). Staudinger published papers presenting evidence of compounds with high molecular mass that formed when many smaller molecules linked together. Polymers were, Staudinger said, "macromolecules." Most chemists did not agree with Staudinger's theory at the time but, as new analytical techniques were developed, Staudinger built a good case for the existence of polymers.

Carothers's work at DuPont added more evidence that such compounds existed. He learned that small organic molecules with reactive functional groups at both ends could form longer chains. In one of his earliest projects, Carothers developed neoprene, the first synthetic rubber.

The Impetus for Innovation

In 1931, international relations between the United States and Japan deteriorated. Since Japan was the main source of silk for the United States, silk became scarce. DuPont saw an opportunity to create a synthetic fibre that could replace silk. Carothers switched his focus to polyamides. He reviewed 81 polyamides, but focused on one that he called "the 6,6 polymer" because its monomers were hexane-1,6-diamine (hexamethylene diamine) and hexanedioic acid (adipic acid). Each molecule contributed 6 carbons to the polymer chain.

In 1938, the U.S. government granted a patent for "nylon-6,6" to DuPont. One of the earliest uses for nylon was as a replacement for silk in women's stockings. During World War II, the use of synthetic polymers, including nylon and neoprene, increased rapidly. Because imports had slowed to a trickle due to the war, the U.S.A. needed these materials as replacements for scarce natural materials. Nylon fabric became widely used for parachutes and clothing. Carothers's groundbreaking work on neoprene, polyester, and nylon led to the "synthetic polymer" era.

Further Readings

Adams, R. (1939). Biographical memoir of Wallace Hume Carothers. *The National Academy of Sciences Biographical Memoirs*, 20(12), 293–309.

Hermes, M.E. (1996). *Enough for one lifetime: Wallace Carothers, inventor of nylon.* Philadelphia: Chemical Heritage Foundation.

WEB LINK

2.5 Questions

1. What factors contributed to the early success of nylon and neoprene? K/U A
2. Polymer research is expensive and often does not result in a successful product. What is the benefit to companies (like DuPont) doing this research? What are the risks? T/I A
3. How did Staudinger's work affect Carothers? K/U
4. Nylon is a synthetic polymer, but the chemical bond between the monomer units is the same type of bond that links the monomer units in silk, hair, and wool. These natural polymers are proteins made by joining amino acid monomers together. In amino acids, both the acid and amino groups are on the same molecule. How might having the two reacting groups on completely different molecules avoid complications for a synthetic chemist? T/I
5. Polymers are often made from compounds extracted from petrochemicals. What are the environmental impacts of using these compounds? T/I A

Natural Polymers

2.6

Cellulose is a natural polymer that provides structure to plant tissues. Wood is primarily cellulose. Although humans cannot digest cellulose, it does provide dietary fibre. Some animals, such as cattle, can digest it, so the cellulose parts of plants grown to produce human food are frequently used as animal food. Even so, growing plants for human consumption produces a lot of waste cellulose. Some companies are using this waste to produce biofuels such as cellulosic ethanol (**Figure 1**). Biofuels provide a source of renewable energy and may reduce our dependence on non-renewable petroleum.

Figure 1 Biomass pellets are primarily cellulose and are made from municipal or agricultural waste. The pellets can be burned directly for fuel or further processed into cellulosic ethanol.

Polysaccharides

Although humans cannot digest cellulose, other natural polymers are important components of our food. Carbohydrates, for example, serve as a food source for most organisms and as a structural material for plants. A **carbohydrate**, such as starch or cellulose, is a polymer of monosaccharides, or simple sugars. A **monosaccharide** is a ketone or aldehyde with many additional hydroxyl substituents. For example, glucose has a hexagonal structure with five hydroxyl groups (**Figure 2**). Monosaccharides are often drawn as a ring with multiple hydroxyl groups rather than a straight-chain structure. Either form is correct because both molecular shapes exist.

carbohydrate a polymer food source and structural material for plants with the empirical formula $C_x(H_2O)_y$

monosaccharide an aldehyde or ketone with 5 or 6 carbon atoms and many hydroxyl groups; a simple sugar that is the monomer of a carbohydrate

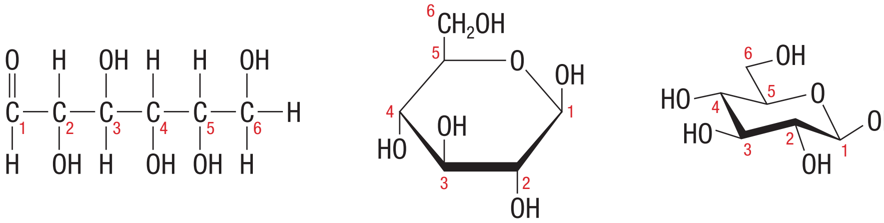
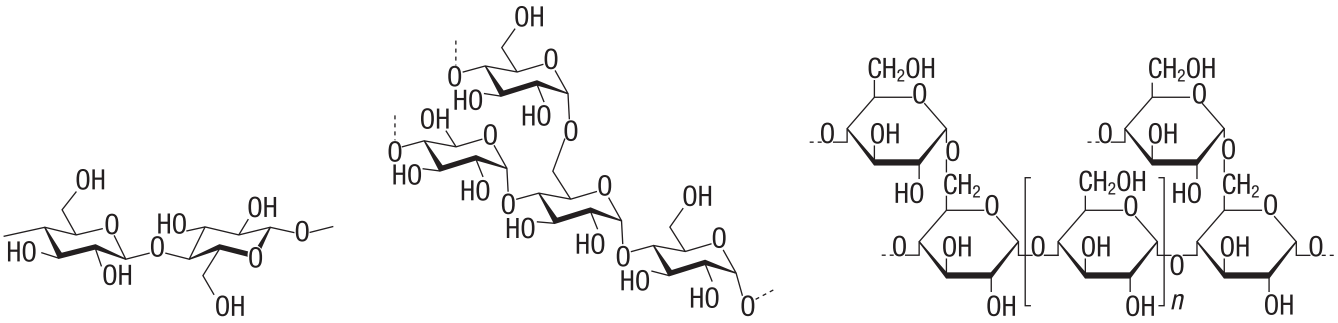


Figure 2 Three ways to draw the structure of glucose

If you are a runner, or participate in other endurance sports, you might know the feeling of "hitting the wall." You run out of energy to keep moving. The energy source that you have depleted is your body's supply of glycogen. Glycogen, like cellulose, is a polysaccharide. When monosaccharide rings join together, they form large polymers consisting of many monosaccharide units. Such a polymer is called a **polysaccharide**. The third important polysaccharide, along with cellulose and glycogen, is starch (**Figure 3**).

polysaccharide a large polymer consisting of many monosaccharides; can form when each ring forms two glycosidic bonds



cellulose starch glycogen

Figure 3 Three polymers of glucose

All the compounds in Figure 3 are polymers of glucose, differing from each other in the type of bond, the degree of branching, and molecular mass. Cellulose is a linear polymer. It is the most common organic compound on Earth and it is found in the cell walls of plants. Glycogen is a branched polymer that stores energy in animal cells. Starch, produced by plants, is usually a mixture of linear and branched forms.

Peptides and Proteins

Figure 4 Tortoiseshell contains a natural polymer. The shell of the hawksbill turtle was once in high demand.

amino acid a compound with a carboxyl group and an amino group attached to the same carbon atom; the building blocks of all protein

During the eighteenth and nineteenth centuries, the shell of the hawksbill turtle was highly prized (**Figure 4**). "Tortoiseshell" was used to make decorative items such as tea caddies, hair combs, and jewellery. Tortoiseshell contains proteins, a class of molecules that are natural polymers. The popularity of tortoiseshell drove the hawksbill turtle almost to extinction. As their shells became more rare and expensive, scientists worked to develop synthetic polymers to replace them. Bakelite was one of the early synthetic polymers. Today, the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) makes it illegal to capture hawksbill turtles or to sell products made from their shell. Unfortunately, tortoiseshell products remain so popular that illegal hunting continues.

All proteins are made of amino acids. An **amino acid** is an organic molecule that contains a carboxyl group ($-COOH$), an amino group ($-NH_2$), and a hydrogen atom all attached to the same carbon atom (**Figure 5**). The fourth bond on that carbon atom links to an additional group or chain of atoms, generically designated as R. The nature of this group gives each amino acid its distinct properties. The 20 amino acids most commonly found in proteins are shown in **Figure 6**.

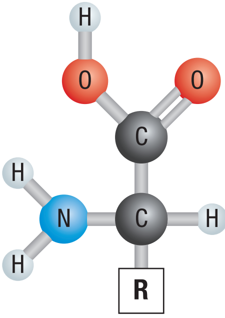


Figure 5 Amino acids all have the same amino group (on the left) and carboxyl group (at the top), but they all have different R groups.

peptide two or more amino acids linked together

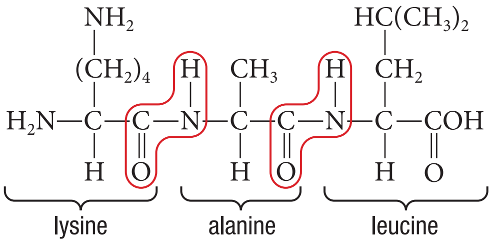
The amino acids are grouped into polar and non-polar classes depending on their side chains. Non-polar side chains contain mostly carbon and hydrogen atoms, whereas polar side chains also contain nitrogen, sulfur, or oxygen atoms. Polar side chains are hydrophilic (water-loving), but non-polar side chains are hydrophobic (water-fearing). Interactions between side chains of the protein molecule determine the three-dimensional structure of the protein.

A protein polymer is built by condensation reactions between amino acids. A **peptide** is two or more amino acids linked together through a condensation reaction between the amine and acid groups. Biochemists call the resulting linkage a peptide bond, but it is identical to an amide linkage. Additional condensation reactions lengthen the chain to produce a polypeptide, eventually yielding a protein.

The 20 amino acids can be assembled in any order, so there is essentially an infinite number of possible protein structures. This flexibility allows an organism to tailor proteins for the many types of functions that must be carried out. CAREER LINK

Protein Structure

The sequence of amino acids in the protein chain is called the primary structure. Biochemists use the convention that the terminal carboxyl group is on the right and the terminal amino group is on the left. For example, one possible sequence for a tripeptide (a chain of three amino acids joined by peptide bonds) containing lysine, alanine, and leucine is



$$\underbrace{\mathrm{H_2N{-}\underset{H}{\overset{NH_2(CH_2)_4}{C}}{-}\underset{O}{\overset{}{C}}}}_{\text{lysine}}\underbrace{\mathrm{{-}\overset{H}{N}{-}\underset{H}{\overset{CH_3}{C}}{-}\underset{O}{C}}}_{\text{alanine}}\underbrace{\mathrm{{-}\overset{H}{N}{-}\underset{H}{\overset{HC(CH_3)_2CH_2}{C}}{-}\underset{O}{C}OH}}_{\text{leucine}}$$

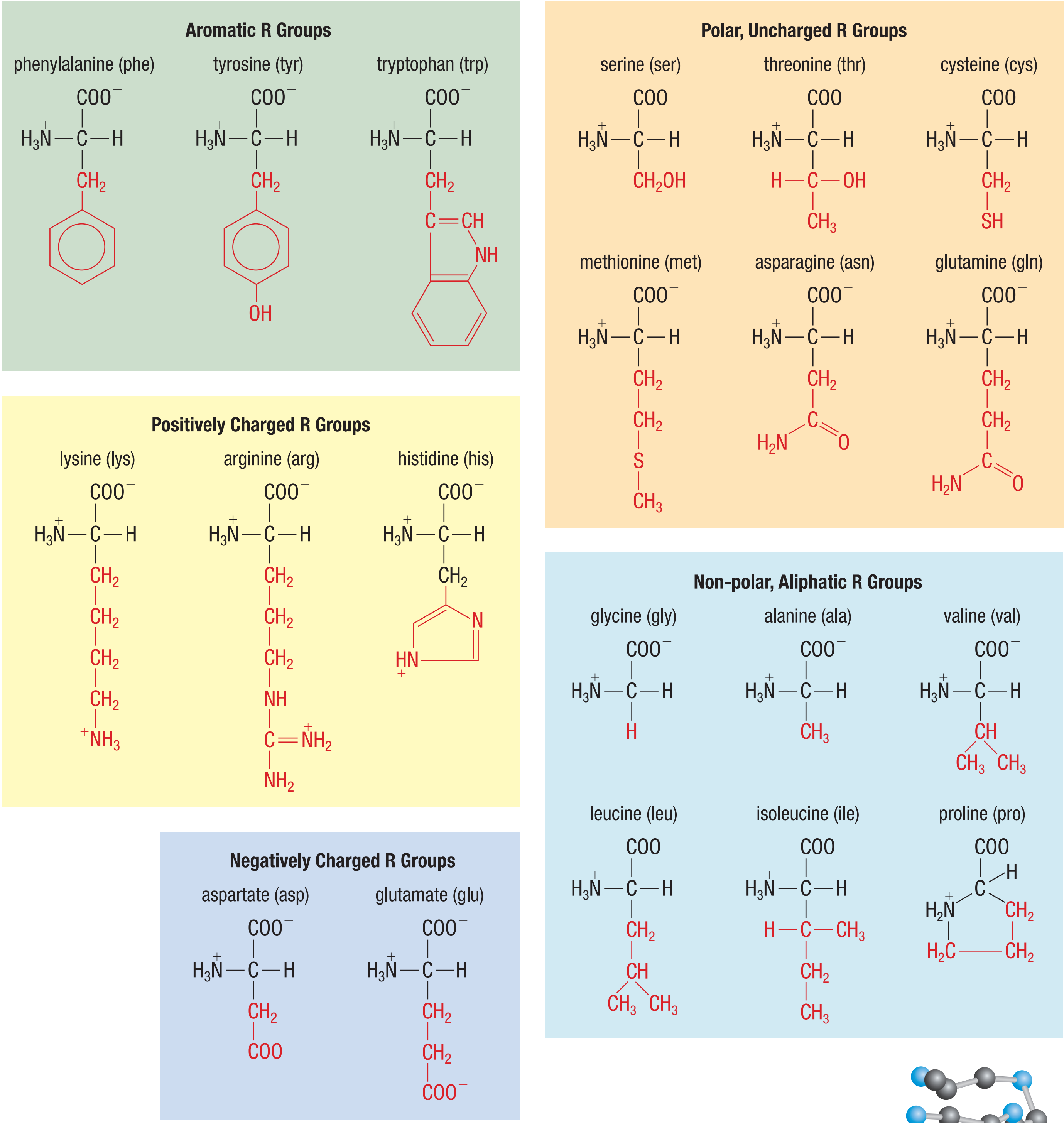


Figure 6 The 20 amino acids all have different side chains (R groups), shown here in red.

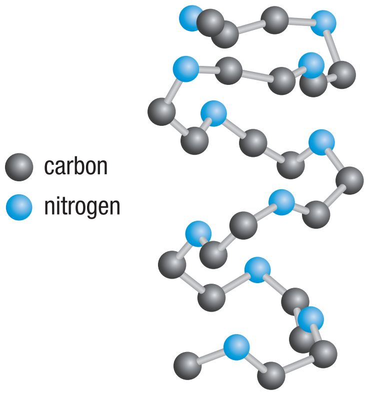


Figure 7 Hydrogen bonding within a protein chain can cause it to form a stable helical structure.

Thousands of amino acids may join together to form very long polypeptide chains that twist and fold into very complicated structures. The secondary structure of a polypeptide chain is determined to a large extent by hydrogen bonding between an oxygen atom in the carbonyl group of an amino acid and a hydrogen atom attached to a nitrogen atom of another amino acid (**Figure 7**).

The overall shape of a protein molecule can be long and narrow, sheet-like, or globular. The three-dimensional shape is important to how the protein functions. This shape is maintained by several different types of interactions: hydrogen bonding, van der Waals forces, ionic bonds, and covalent bonds.

Nucleic Acids

Life is possible only because each and every cell, when it divides, is able to transmit vital information about how it works to the next generation. Scientists have known since the early twentieth century that this process involves chromosomes in the cell nucleus. Only since 1953, however, have scientists understood the molecular basis of this intriguing cellular "talent."

DNA deoxyribonucleic acid; a polymer in the cell nucleus that stores and transmits genetic information

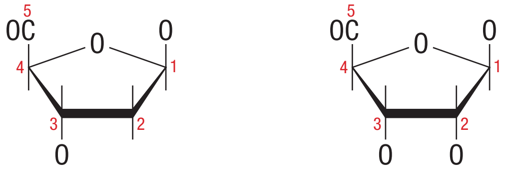
RNA ribonucleic acid; a polymer in the cell cytoplasm that stores and transmits genetic information

nucleic acid the polymer molecules that make up DNA and RNA

The substance that stores and transmits the genetic information is a polymer called deoxyribonucleic acid (**DNA**): a huge molecule with a molecular mass as high as several billion grams per mole. Together with other similar nucleic acids called the ribonucleic acids (**RNA**), DNA is responsible for the synthesis of the various proteins needed to carry out all cell functions. RNA molecules, which are found in the cytoplasm outside the nucleus, are much smaller than DNA polymers, with molecular masses of only 20 000 to 40 000 g/mol. **Nucleic acids** are the polymer molecules that make up DNA and RNA.

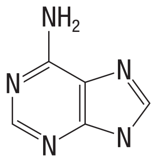
The monomers of the nucleic acids, called nucleotides, are composed of three distinct parts:

1. a 5-carbon sugar: deoxyribose in DNA and ribose in RNA (**Figure 8**)
2. a nitrogen-containing organic base (**Figure 9**)
3. a phosphoric acid molecule, H_3PO_4

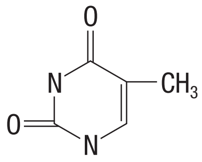


(a) **(b)**

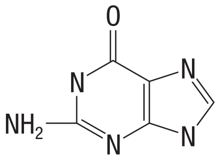
Figure 8 The 5-carbon sugars that make up (a) deoxyribose (b) ribose



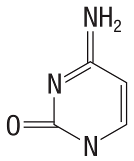
adenine (A)



thymine (T)



guanine (G)



cytosine (C)

Figure 9 The bases that form DNA

nucleotide an ester created when the DNA or RNA base combines with phosphoric acid

The base and the sugar combine to form a unit that in turn reacts with phosphoric acid to create the **nucleotide**, which is an ester. The nucleotides link together through condensation reactions that eliminate water to give a polymer. Such a polymer can contain a billion nucleotides.

The key to DNA's functioning is its double-helical structure with complementary bases on the two strands. The bases form hydrogen bonds with each other. The structures of cytosine and guanine make them perfect partners for hydrogen bonding, and they are always found opposite each other on the two strands of DNA. Thymine and adenine form similar hydrogen-bonding pairs.

Evidence suggests that the two strands of DNA unwind during cell division and that new complementary strands are constructed on the unravelled strands. Because the bases on the strands always pair in the same way—cytosine with guanine and thymine with adenine—each unravelled strand serves as a template for attaching the complementary bases (along with the rest of the nucleotide). This process results in two double-helix DNA structures that are identical to the original one. Each new double strand contains one strand from the original DNA double helix and one newly synthesized strand. This replication of DNA allows for the transmission of genetic information as the cells divide.

A major function of DNA is protein synthesis. A given segment of the DNA, called a gene, contains the code for a specific protein. These codes transmit the primary structure of the protein (the sequence of amino acids) to the construction "machinery" of the cell. There is a specific code for each amino acid in the protein, which ensures that the correct amino acid will be inserted as the protein chain grows. CAREER LINK

2.6 Review

Summary

- Carbohydrate polymers, which serve as a food source and structural material for plants, have the empirical formula $C_x(H_2O)_y$.
- A monosaccharide is one monomer of a carbohydrate polymer.
- Polysaccharides are large condensation polymers consisting of many monosaccharides.
- Starch, cellulose, and glycogen are polymers of glucose.
- Proteins and nucleic acids are condensation polymers.
- The primary structure of proteins results from the sequence of amino acids in the polymer chain. The shape of a protein molecule depends on intermolecular and intramolecular forces.
- DNA stores information for amino acid sequences, enabling the cell to assemble proteins.

Questions

1. Outline the similarities and differences between starch and cellulose. Support your answer with a diagram. K/U C
2. Draw the ring structure of glucose. Use this structure to explain why glucose can form a straight-chain polymer like cellulose and branched-chain polymers such as glycogen and starch. K/U T/I C
3. In plants, glucose molecules are joined together to form the polymer cellulose. K/U C
   (a) Draw a structural diagram illustrating this reaction.
   (b) What type of polymerization reaction is occurring? Explain how you can tell.
4. When a plain, unseasoned, carbohydrate-rich food (such as rice or crackers) is chewed and begins to dissolve in the mouth, it tastes bland at first and then starts to taste sweet. Propose a reason for this change in taste. T/I A
5. A biochemist forms a tripeptide compound using glycine (gly), serine (ser), and phenylalanine (phe). K/U T/I C
   (a) How many unique tripeptides could be made from these three amino acids? Use the three-letter codes to list them all.
   (b) Draw the structural formula of one possible tripeptide that could be produced.
   (c) Explain why so many possible proteins can be made from only 20 amino acids.
6. Examine the structures of the following amino acids in Figure 6. Predict whether each one is hydrophilic or hydrophobic. T/I
   (a) phenylalanine
   (b) serine
   (c) leucine
   (d) arginine
7. DNA and RNA each contain a sugar. K/U C
   (a) Draw the structural diagram of each sugar.
   (b) Discuss the similarities and differences of the sugars.
8. Consumers have many natural and synthetic materials to choose from these days: paper or reusable plastic shopping bags, wood or plastic chairs, cotton or polyester clothes. Choose one such consumer product, identify the natural and synthetic materials from which it could be made, and research the advantages and disadvantages of the two alternatives. Create a graphic organizer or use some other format to communicate your findings. 🌐 T/I C A
9. If you have ever had your hair permed, you have experienced disulfide bonds. Hair is made mostly of protein. When sulfur atoms on one polymer chain bond to sulfur atoms on another polymer chain, the resulting cross-links are called disulfide bonds. Research the chemistry behind perms, including any health or environmental concerns, and present your findings in a brochure or blog that could be read by people thinking of getting a perm. 🌐 T/I C A
10. DNA is one of the largest known natural polymers. DNA molecules can be artificially modified to change the order of amino acids. Use Internet resources to research the uses of recombinant DNA technology. Create an informational web page or poster describing two of these applications. Include information on the benefits and drawbacks of each application. 🌐 T/I C A
11. Research three proteins to determine their functions and the number of amino acids in each. Present your findings in a table or graphic organizer. 🌐 T/I C

🌐 WEB LINK

Investigation 2.4.1 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Preparation of a Polyester

Condensation polymerization reactions produce small molecules, such as water, as the monomers react. When an organic acid containing two or more carboxyl groups reacts with an alcohol with two or more hydroxyl groups, the resulting polymer is a polyester (**Figure 1**).

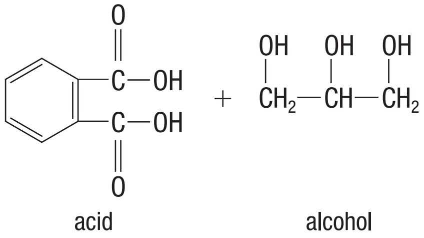


Figure 1 Benzene-1,2-dicarboxylic acid (phthalic acid) and propane-1,2,3-triol (glycerol) can undergo a condensation reaction to form a polyester polymer.

Many paints and enamels are based on alkyd resins, which are polyester polymers modified with other ingredients. (**Figure 2**).

Figure 2 Alkyd paints have a non-polar organic solvent in which the other components are dissolved.

In a condensation polymerization, the reaction proceeds faster if the reaction mixture is heated. Heating tends to drive the reaction by causing water molecules to evaporate as they are produced. In some reactions, an alternative monomer can be used to decrease the amount of water produced. For example, 2-benzofuran-1,3-dione (phthalic anhydride), shown in **Figure 3**, produces half as much water as benzene-1,2-dicarboxylic acid when it reacts with alcohols. Since less energy is required to evaporate off the water, this reactant is often used in place of benzene-1,2-dicarboxylic acid in polymerization reactions.

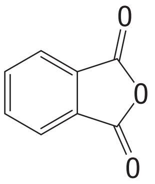


Figure 3 2-benzofuran-1,3-dione (phthalic anhydride)

Purpose

- To synthesize the alkyd resin, glyptal, from 2-benzofuran-1,3-dione and propane-1,2,3-triol
- To investigate some of the properties of glyptal

Equipment and Materials

- chemical safety goggles
- laboratory apron
- protective gloves
- two 100 mL beakers
- glass stirring rod
- hot plate
- utility stand with ring clamp
- watch glass to fit beakers
- beaker tongs
- shallow metal container
- paper towel
- small covered beakers containing
  - 3 g 2-benzofuran-1,3-dione (phthalic anhydride powder)
  - 2 g propane-1,2,3-triol (glycerol)
  - 5 mL paint thinner or nail polish remover

Use caution around the hot plate. Avoid touching the heating surface with your hands. To unplug the hot plate, pull on the plug itself rather than the cord.

Phthalic anhydride is toxic, a skin irritant, and can cause blindness. Handle with care, and wear gloves, eye protection, and a lab apron. Avoid skin contact and wash your hands before leaving the laboratory.

Paint thinner and nail polish remover are flammable. They should be used only in a well-ventilated area. There should be no open flames or other sources of ignition in the laboratory.

Procedure

SKILLS HANDBOOK A1, A2.3

1. Put on your safety goggles, lab apron, and protective gloves.
2. Place the phthalic anhydride powder and glycerol in a 100 mL beaker and mix with the stirring rod.
3. Secure the beaker on the hot plate using a ring holder attached to a utility stand. Heat the mixture and stir gently to dissolve the solid.
4. Cover the beaker with the watch glass and continue heating until the mixture comes to a boil. Boil for 5 min.
5. Carefully pour the hot mixture into a metal container. Let it cool completely at room temperature.
6. Observe the plastic formed and record its properties.
7. Break off a piece of the plastic and place it in the second beaker. Add about 5 mL of water to the beaker and try to dissolve the plastic in the water. Record your observations.
8. Retrieve the piece of plastic and pour the water down the sink. Dry the beaker with the paper towel.
9. Break off another piece of plastic and place it in the dry beaker. Add 5 mL of paint thinner or nail polish remover to the beaker and try to dissolve the plastic in the solvent. Record your observations.
10. Place the beaker containing the solvent in the fume hood. Allow the solvent to evaporate. Observe the remaining residue.
11. Dispose of the materials as instructed by your teacher.

Analyze and Evaluate

(a) Organize your observations into a table. C

(b) Describe the product and its observed properties. T/I

(c) Evaluate the procedure. Do you feel that each step was necessary? For example, was it necessary to heat the mixture? Was it appropriate to put the hot mixture into a metal container? Explain. T/I

(d) Evaluate this polymer as an ingredient to use in paint. T/I

Apply and Extend

(e) Use the structural formulas in Figures 1 and 3, and your knowledge of intermolecular forces to explain the observed properties of the polymer. Include diagrams in your explanation. T/I C A

(f) Suppose you repeated this investigation using 1,2-ethanediol instead of glycerol. Predict the reaction that would occur. Illustrate your answer using structural formulas or line diagrams. Predict the properties of the resulting polymer. T/I C

UNIT TASK **BOOKMARK**

Your observations regarding the solubility of polymers in polar and non-polar solvents may be relevant as you work on the Unit Task described on page 116.

CHAPTER 2 SUMMARY

Summary Questions

1. Create a study guide for this chapter based on the Key Concepts on page 78. For each point, create three or four sub-points that provide further information, relevant examples, explanatory diagrams, or general equations.
2. Look back at the Starting Points questions on page 78. Answer these questions using what you have learned in this chapter. Compare your latest answers with those that you wrote at the beginning of the chapter. Note how your answers have changed.
3. Create a concept map to summarize what you have learned in this chapter. Starting with the term "polymer," add branches to include various kinds of polymers, how they are formed, their properties, and examples.
4. Create a quiz based on the summary at the end of each section. Your quiz could be online or on index cards. Write a question for each summary point, and then devise a way to present the correct answer.

Vocabulary

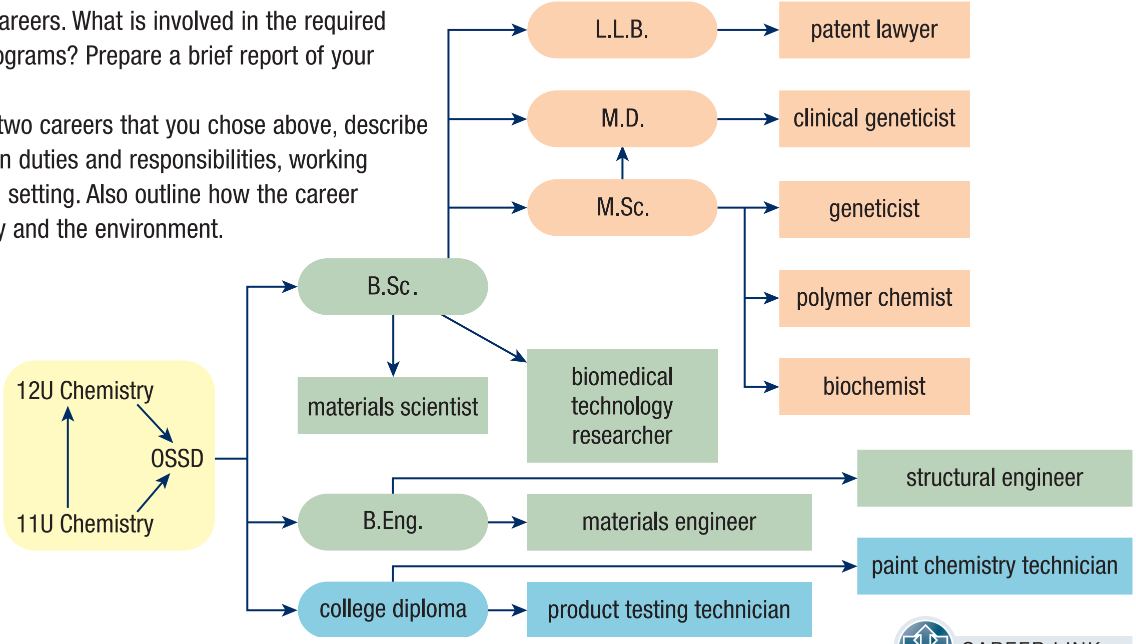
polymer (p. 80)
monomer (p. 80)
homopolymer (p. 80)
copolymer (p. 81)
addition polymer (p. 84)
plastic (p. 88)
condensation polymer (p. 95)
polyester (p. 95)
polyamide (p. 96)
carbohydrate (p. 101)
monosaccharide (p. 101)
polysaccharide (p. 101)
amino acid (p. 102)
peptide (p. 102)
DNA (p. 104)
RNA (p. 104)
nucleic acid (p. 104)
nucleotide (p. 104)

CAREER **PATHWAYS**

SKILLS HANDBOOK **A7**

Grade 12 Chemistry can lead to a wide range of careers. Some require a college diploma or a B.Sc. degree. Others require specialized or postgraduate degrees. This graphic organizer shows a few pathways to careers mentioned in this chapter.

1. Select two careers related to Polymers that you find interesting. Research the educational pathways that you would need to follow to pursue these careers. What is involved in the required educational programs? Prepare a brief report of your findings.
2. For one of the two careers that you chose above, describe the career, main duties and responsibilities, working conditions, and setting. Also outline how the career benefits society and the environment.



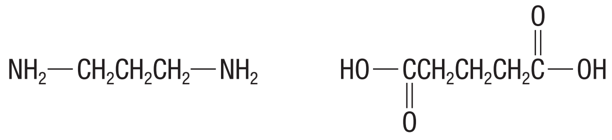
CAREER LINK

CHAPTER 2 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. The individual units that make up all polymers are called
   (a) monomers
   (b) alkanes
   (c) plastics
   (d) esters (2.1) K/U
2. Polymers that are made from many identical units are called
   (a) bipolymers
   (b) copolymers
   (c) homopolymers
   (d) elastomers (2.1) K/U
3. Bonds can form between polymer chains, creating sheets of polymers. One of these bonds is called a(n)
   (a) atomic link
   (b) cross-link
   (c) molecular link
   (d) peptide link (2.1, 2.2) K/U
4. What kind of carbon–carbon bonds are involved in the formation of addition polymers? (2.2) K/U
   (a) hydrogenated
   (b) cross-linked
   (c) saturated
   (d) double
5. Vulcanization of rubber involves heating a mixture of natural latex and
   (a) carbon
   (b) hydrogen
   (c) oxygen
   (d) sulfur (2.2) K/U
6. Phthalate is commonly added as a plasticizer in the manufacture of many polymers. However, phthalates are easily released into the environment because
   (a) they are gaseous
   (b) they are held within the polymer chains
   (c) they are not covalently bonded to the polymers to which they are added
   (d) they are immiscible with the polymerized monomers (2.3) K/U
7. What kind of polymer is formed when water is one of the products during the polymerization reaction? (2.4) K/U
   (a) an addition polymer
   (b) a condensation polymer
   (c) a hydropolymer
   (d) a copolymer
8. What functional groups must the monomers have, to form a polyester? (2.4) K/U
   (a) two carboxyl (—COOH) groups
   (b) a hydroxyl (—OH) group and a carbonyl (—C=O) group
   (c) a hydroxyl group and a carboxyl group
   (d) a carboxyl group and a carbonyl group
9. What type of polymer is produced by the reaction of the two compounds in **Figure 1**? (2.4) K/U



$NH_2—CH_2CH_2CH_2—NH_2$

$HO—\underset{\displaystyle O}{\underset{\|}{C}}CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}—OH$

Figure 1

   (a) a monopolymer
   (b) an addition polymer
   (c) a polyester
   (d) a polyamide
10. The polyamide linkages in nylon also occur in
   (a) amino acids
   (b) plasticizers
   (c) polyethene
   (d) proteins (2.4) K/U

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

11. Polymers tend to be very strong because they are held together by ionic bonds. (2.1) K/U
12. The two polyethene polymers, LDPE and HDPE, have different properties because they have different degrees of branching within their chains. (2.2) K/U
13. All plastics are polymers, but not all polymers are plastics. (2.2) K/U
14. Plasticizers are chemicals added to a polymer to decrease its flexibility. (2.3) K/U
15. The two most common types of bonds between monomers in condensation polymers are hydrogen bonds and disulfide bonds. (2.4) K/U
16. Wallace H. Carothers's work on nylon inspired Hermann Staudinger's research. (2.5) K/U
17. Glucose, a product of photosynthesis, has a pentagonal structure with 5 hydroxyl groups. (2.6) K/U
18. Proteins are polymers made up of many amino acid monomers. (2.6) K/U

Go to Nelson Science for an online self-quiz.

WEB LINK

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. What do all polymers have in common? (2.1) K/U
   (a) They contain double bonds.
   (b) They contain cross-links.
   (c) They contain long chains of repeating units.
   (d) All of the above

2. Which of the following substances is a natural polymer? (2.1) K/U
   (a) polyester
   (b) silk
   (c) Kevlar
   (d) polypropene

3. Which of the following is a property of Teflon? (2.2) K/U
   (a) a good conductor of electricity
   (b) flammable
   (c) inert
   (d) sticky

4. No atoms are lost from starting material in making which kind of polymer? (2.2) K/U
   (a) addition polymer
   (b) branched polymer
   (c) condensation polymer
   (d) polyester polymer

5. Which of the following terms describes materials that recover their shape after being deformed? (2.2) K/U
   (a) elastomers
   (b) inhibitors
   (c) plasticizers
   (d) thermoplastic polymers

6. What gives polyethene polymers their strength and toughness? (2.2) K/U
   (a) the presence of oxygen atoms in the polymer chains
   (b) disulfide bonds that form cross-links between chains
   (c) the large numbers of London dispersion forces between long chains
   (d) many short chains stabilized by strong hydrogen bonding

7. Which of the following statements is true about plastics? (2.2) K/U
   (a) All plastics are polymers.
   (b) Plastics are generally made from materials derived from petrochemicals.
   (c) Plastics are synthetic, not natural, materials.
   (d) All of the above

8. Which of the following conditions can cause a plasticizer to be released from a plastic? (2.3) K/U
   (a) exposure to visible light
   (b) scratching the surface
   (c) heating at high temperatures
   (d) exposure to arid conditions

9. When an alcohol reacts with a carboxylic acid, what type of bond is formed? K/U
   (a) peptide bond
   (b) amide linkage
   (c) carboxyl bond
   (d) ester linkage

10. The carboxyl groups on a polyamide allow many hydrogen bonds to form between polymer chains. Together, these hydrogen bonds make polyamides
    (a) form loops
    (b) form sheets
    (c) soluble in water
    (d) exceptionally strong (2.4) K/U

11. Which of the following polymers is not based on a substituted ethene monomer? (2.2, 2.4, 2.5) K/U
    (a) nylon
    (b) polypropene (polypropylene)
    (c) polystyrene
    (d) polyvinyl chloride

12. What type of reaction results in the formation of nylon? (2.4, 2.5) K/U
    (a) the addition polymerization reaction of unsaturated hydrocarbons
    (b) the addition polymerization reaction of a styrene with a carboxylic acid
    (c) the condensation polymerization reaction of a dicarboxylic acid with a diol (di-alcohol)
    (d) the condensation polymerization reaction of a dicarboxylic acid with a diamine

13. Nylon is an example of a
    (a) copolymer
    (b) monomer
    (c) homopolymer
    (d) monopolymer (2.4) K/U T/I

14. What natural polymer was difficult for the United States to obtain from Japan in the early 1930s, motivating research to find a synthetic replacement? (2.5) K/U
    (a) silk
    (b) wool
    (c) cellulose
    (d) cotton

15. Which of the following compounds is not a polymer of glucose? (2.6) K/U
    (a) cellulose
    (b) glycogen
    (c) an amino acid
    (d) a polysaccharide
16. What are the building blocks of proteins? (2.6) K/U
    (a) amino acids
    (b) esters
    (c) lipids
    (d) nucleotides
17. What type of bond is responsible for DNA's double-helix structure? (2.6) K/U
    (a) hydrogen bonds
    (b) amide linkages
    (c) London dispersion forces
    (d) disulfide bonds

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

18. Polymers are large, chain-like molecules built from small molecules called homomers. (2.1) K/U
19. A copolymer is produced from the reaction between two or more different types of monomers. (2.1) K/U
20. Addition polymers are produced from the reaction of unsaturated hydrocarbons. (2.2) K/U
21. Most plastics are chemically reactive and virtually indestructible. (2.2) K/U
22. A plasticizer is a chemical added to any substance to improve its flexibility. (2.3) K/U
23. Condensation polymers are composed of repeating groups of monomers containing two different reactive functional groups. (2.4) K/U
24. Polyamides are polymers formed by condensation reactions resulting in ester linkages between monomers. (2.4) K/U
25. Examples of synthetic polymers are carbohydrates, silk, and DNA. (2.6) K/U

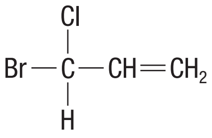
Match each term on the left with the most appropriate description on the right.

26. (a) amino acid
    (b) amide
    (c) starch
    (d) PVC
    (e) silk
    (f) ethene
    (g) addition
    (h) condensation
    (i) nylon
    (j) vulcanization
    (k) substituent

    (i) natural protein polymer
    (ii) type of reaction between unsaturated monomers
    (iii) monomer of proteins
    (iv) component of monomers that can affect the properties of their polymers
    (v) polymer designed to replace silk
    (vi) type of linkage within proteins
    (vii) addition polymer containing chlorine
    (viii) process that makes rubber more heat resistant
    (ix) typical monomer of synthetic polymers
    (x) type of reaction releasing a small molecule as a by-product
    (xi) polymer produced by plants
    (2.1, 2.2, 2.4, 2.5, 2.6) K/U

Write a short answer to each question.

27. Define the term "polymer." (2.1) K/U
28. Differentiate between the terms "copolymer" and "homopolymer." (2.1) K/U
29. (a) Name the compound shown in **Figure 1**.



$$\mathrm{Br{-}\underset{\displaystyle H}{\overset{\displaystyle Cl}{C}}{-}CH{=}CH_2}$$

Figure 1

    (b) Draw the polymer that could be formed from this monomer. (2.2) T/I C
30. The properties of polymers are affected by the monomers that compose them. Which feature increases the rigidity of a polymer? (2.2) K/U
31. List at least four synthetic polymers and an example of an application of each one. (2.2) K/U
32. Teflon is a synthetic polymer of the monomer tetrafluoroethene. (2.2) K/U C A
    (a) Draw the structure of the monomer.
    (b) Explain how Teflon's structure allows it to perform its functions.

33. Health Canada has restricted the use of phthalates in certain products made from polymers.
    (a) Why are phthalates mixed with some polymers?
    (b) From what products has Health Canada banned the use of phthalates? (2.3) K/U

34. Nylon is a copolymer. (2.1, 2.4, 2.5) K/U C
    (a) What is a copolymer?
    (b) What type of polymerization reaction occurs to produce nylon?
    (c) Draw diagrams to show the polymerization reaction that produces nylon-6,6.
    (d) What types of bonds form between the monomers during the reaction?

35. Many workers in hazardous environments—including race-car drivers—wear protective clothing made from a polymer called Nomex. Nomex is synthesized using the two monomers shown in **Figure 2**. (2.4) T/I C

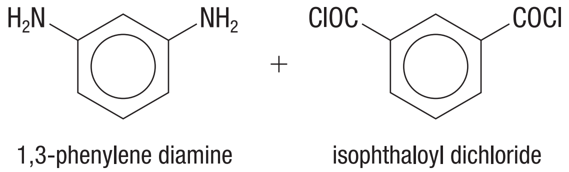


Figure 2

    (a) What type of polymerization reaction must occur to form Nomex?
    (b) Will there be a by-product of the polymerization reaction? If so, what is the by-product?
    (c) Draw a structural diagram showing a portion of the polymer product.

36. Why is Dacron classified as a polyester? (2.4) K/U

37. What by-product is commonly released during condensation polymerization? (2.4) K/U

38. To form amide linkages in a polyamide, which two types of organic molecules must react? (2.4) K/U

39. Oxirane (ethylene oxide) is an important industrial chemical. It is a cyclic ether (**Figure 3**). Although most ethers are unreactive, oxirane is quite reactive. It can undergo addition polymerization reactions at one of the C–O bonds. Draw the structure of this polymer. (2.4) T/I C

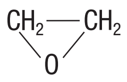


Figure 3 Oxirane (ethylene oxide)

40. Wallace H. Carothers developed several synthetic polymers in the 1930s. Name one, and the natural product it was designed to replace. (2.5) K/U

41. Define the following terms: (2.6) K/U
    (a) monosaccharide
    (b) polysaccharide
    (c) carbohydrate

42. Which natural polymer is produced by
    (a) animals to store energy?
    (b) plants to provide structure?
    (c) many organisms to pass on genetic information? (2.6) K/U

43. Why are the cellulose-rich parts of food plants often used as animal food? (2.6) K/U A

44. Define each of the following terms: (2.6) K/U
    (a) protein
    (b) peptide bond
    (c) DNA

45. (a) List the component parts of nucleotides.
    (b) What class of organic compounds includes nucleotides?
    (c) Cytosine and guanine pair up in DNA. What forces hold these two nucleotides together?
    (d) What functional groups in the nucleotides enable these forces to occur? (2.6) K/U T/I

Understanding

46. Spider silk is a very strong, flexible polymer. Why might an organic chemist want to determine its chemical structure? (2.1) K/U

47. Use a Venn diagram to summarize the differences between synthetic and natural polymers. (2.1) K/U C

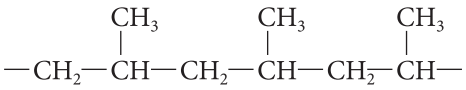
48. In 1868, celluloid was invented to replace ivory in the manufacture of billiard balls. Since then, many synthetic polymers have been developed to replace natural polymers. Why? (2.1) K/U

49. Vulcanization converts natural rubber, which becomes soft and sticky when heated, into a form that maintains its solid form at high temperatures. The process was discovered by Charles Goodyear, who found that heating a mixture of rubber and sulfur improved the rubber's properties. How did the addition of sulfur change rubber's structure to make it more rigid at high temperatures? (2.1, 2.2) T/I A

50. Make a table listing three common addition polymers. For each polymer,
    (a) write its name
    (b) draw a structural formula of the monomer
    (c) draw a structural formula of the polymer
    (d) give an example of a common use (2.2) K/U C A

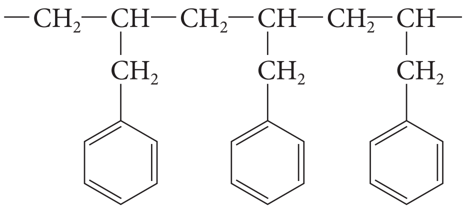
51. For each polymer shown, draw the monomer used in its synthesis. (2.2) T/I C

(a)

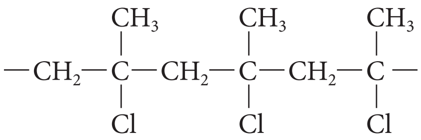


$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-$$

(b)



(c)



$$-CH_2-\overset{CH_3}{\underset{Cl}{C}}-CH_2-\overset{CH_3}{\underset{Cl}{C}}-CH_2-\overset{CH_3}{\underset{Cl}{C}}-$$

52. Why does the addition of divinylbenzene (**Figure 4**) make polystyrene more rigid? (2.2) K/U T/I

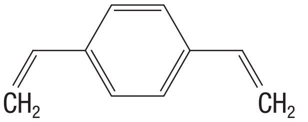


Figure 4 Divinylbenzene is sometimes added to styrene when producing polystyrene.

53. The use of plasticizers has become a concern for the average citizen. (2.3) K/U A
    (a) What are plasticizers and why are they used?
    (b) Why is their use causing concern?

54. A classmate is having problems determining the monomer by looking at a polymer. To help your classmate, explain in point form
    (a) how to tell a polymer produced during an addition reaction from a polymer produced during a condensation reaction
    (b) how to predict the monomer from an addition polymer
    (c) how to predict the monomer from a condensation polymer (2.2, 2.4) K/U T/I C

55. Given the following monomer(s), predict the structure of the polymer produced. Draw the structural formula of each polymer. (2.2, 2.4) K/U T/I C
    (a) pent-2-ene
    (b) 1,5-diaminopentane and propane-1,3-diol
    (c) 1,5-dichlorohex-2-ene

56. Using a graphic organizer, describe the similarities and differences between addition and condensation polymers. (2.2, 2.4) K/U C

57. Molecules of lactic acid can be used as monomers in a condensation polymerization reaction (**Figure 5**). The main product is polylactic acid (PLA), a biodegradable plastic. (2.4) T/I C A

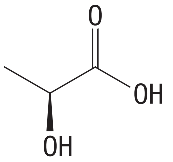


Figure 5 Lactic acid

    (a) Predict the structure of polylactic acid.
    (b) Is any other product formed? If so, what is it?
    (c) Predict any forces or bonds that might occur between PLA chains.
    (d) PLA is used to make packaging for food. What properties must the plastic have for this application?

58. Use a graphic organizer to compare and contrast polyesters and polyamides. (2.4) K/U C

59. (a) Describe the factors that make synthetic polymers so useful in our world.
    (b) Why can these factors also cause problems? (2.1, 2.2, 2.3, 2.4, 2.5) T/I A

60. Simple sugars are aldehydes or ketones with 5 or 6 carbon atoms per molecule. **Figure 6** shows an example of a simple sugar molecule. (2.4, 2.6) T/I C

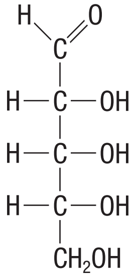


Figure 6 A simple sugar

    (a) Is this sugar an aldehyde or a ketone?
    (b) This sugar can form a ring structure. Look at the functional groups and predict what type of reaction occurs when it rearranges to form a ring structure.
    (c) Draw the ring structure produced.

61. Monosaccharides can be classified by the number of carbon atoms in each molecule. (2.6) K/U
    (a) How many carbon atoms would a molecule of hexose contain?
    (b) What would a monosaccharide with 5 carbon atoms be called?

Analysis and Application

62. Plastics can be used in a variety of materials, from plastic wrap used for covering foods to support structures on the International Space Station. (2.1, 2.2) T/I A
    (a) Describe the desirable qualities of a plastic used to wrap food.
    (b) Describe the desirable qualities of a plastic used to build the International Space Station.
    (c) Why can there be so many different types of plastics with so many different properties?
63. Summarize the differences between thermoplastics and thermoset polymers. Based on these differences, which would be easier to recycle? Explain. (2.2) T/I A
64. (a) For each copolymer shown in **Figure 7**, draw the monomers used in its synthesis.
    (b) Predict which of these two copolymers would have more hydrogen bonding between its chains. How would this affect its heat stability? Explain your prediction. (2.4) T/I C

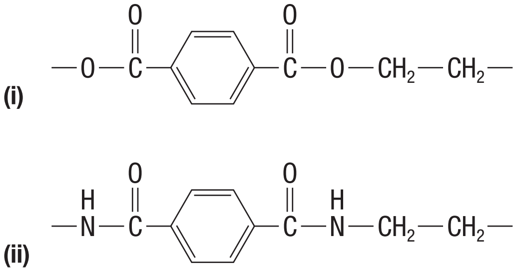


Figure 7 Two copolymers

65. (a) Suggest how condensation polymers might be made biodegradable.
    (b) What problems might still occur even though these plastics can be made biodegradable? (2.4) T/I A
66. Hair is mostly protein. The protein polymer chains are held together by cross-links involving sulfur. Use what you know about chemical bonds to explain how hair perms (permanent wave treatments) can change the texture of hair from straight to curly. (2.2, 2.6) T/I A
67. **Figure 8** shows the hydrogen bonds that form between adenine and thymine (A–T) and between guanine and cytosine (G–C) in DNA. When DNA is heated, the hydrogen bonds holding together the two strands break, resulting in two single strands. Would you expect to have to use more heat to separate a strand composed mostly of G–C pairs or a strand composed mostly of A–T pairs? Explain. (2.6) T/I A

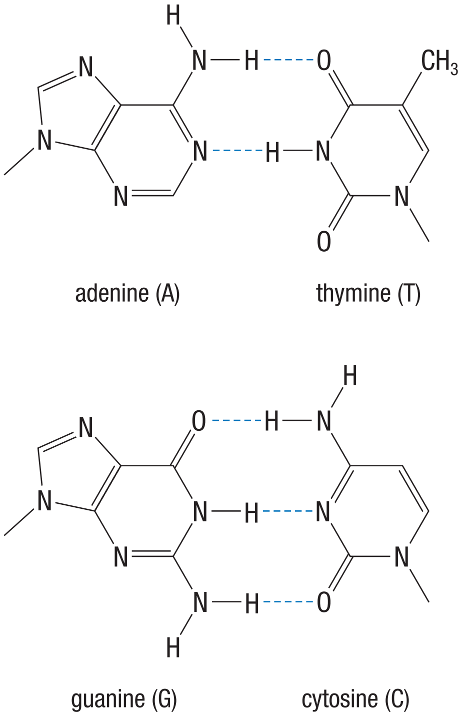


Figure 8

68. When you eat food containing starch, your mouth produces saliva. An enzyme in the saliva immediately starts to break down the starch into its monomer molecules. (2.6) T/I C A
    (a) Draw a structural diagram representing starch.
    (b) Draw a structural diagram representing the monomer of starch. Name this monomer.
    (c) How could you test the hypothesis that starch is broken down to form this monomer? (*Hint*: Your test could involve eating plain, unsalted crackers.) Predict the evidence that would support the hypothesis.

Evaluation

69. (a) For each polymer shown in **Figure 9**, draw the monomer used in its synthesis.
    (b) Which of these two polymers would be more rigid? Would either of them be appropriate for manufacturing structural building components? Explain. (2.4) T/I C

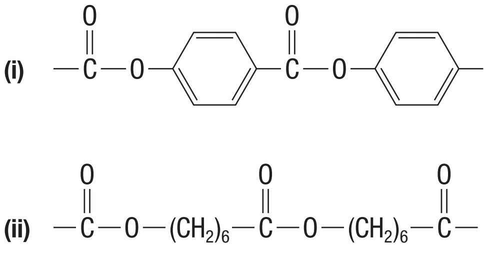


Figure 9 Two homopolymers

70. In your opinion, is it more important that plastics be durable and long-lasting, or that they be biodegradable? Defend your position. (2.4) A

71. A chemistry class is studying condensation polymerization reactions. They learn that benzene-1,2-dicarboxylic acid (phthalic acid) and propane-1,2,3-triol (glycerol) react to produce a polyester polymer. When they prepare to carry out the reaction in the lab, they are given phthalic acid but there is no glycerol in stock. Two possible substitutes are available: butan-1,4-diol and propan-1-ol. Which of these compounds should they use in their polymerization reaction? Support your answer with equations. (2.4) K/U T/I

72. When the research department of a petrochemical company is developing a new polymer, there are many factors to consider. (2.1, 2.2, 2.3, 2.4, 2.5) T/I A
    - (a) Suggest at least six factors that the company might consider, regarding the new polymer.
    - (b) How might the company rank the importance of these factors?
    - (c) How would you rank the importance of these factors?
    - (d) Comment on any differences in your two rankings.

Reflect on Your Learning

73. Before you began studying polymers, were you aware of the existence of both synthetic and natural polymers? Did you know that the characteristics of each polymer depend on its chemical structure? Write a paragraph explaining how your understanding of the polymers you use every day has changed or been confirmed as a result of your studies. K/U A

74. How has your thinking about the recycling of plastics changed as a result of your studying this chapter? Do you think more research should be done to develop plastics that can be easily broken down into their monomers for later re-use? Why or why not? Write a paragraph explaining your thoughts. T/I A

Research

🌐 WEB LINK

75. Research the methods being used to recycle carpeting. Are these processes in place in your region? Prepare a poster that can be displayed in a public place such as a library or shopping mall, or a web page, to inform the general public about these methods. Include information about why recycling is important as well as information about how it is carried out. 🌐 T/I C A

76. Look for news articles or press releases describing at least four new polymers being developed for different purposes. Record notes on each polymer and then use your notes to create a fictional scenario set 50 years in the future when these polymers are used in everyday life. Your fictional scenario may be constructed as a visual art piece with labels describing each polymer and its function, or it may be constructed as a short story that incorporates the polymers into the story. 🌐 C A

77. Find information about new biodegradable polymers being developed for medical purposes. Prepare a news report suitable for your local newspaper or online news site that explains the concept to readers and provides a few examples. Be sure to include information that readers would want to know about the effectiveness and safety of these devices. 🌐 C A

78. The fashion industry is always searching for new fabrics with special properties or unique sources. One such fabric is made from milk protein. Research the starting materials, manufacturing process, cost, and environmental impact of this fabric. From the information you collect, decide whether you would choose to wear a garment made from milk. Explain your reasons in a poster, blog, or cartoon. 🌐 T/I C A

79. Spider silk is extraordinarily strong. A Dutch team has used this property to grow a remarkable substance that incorporates human skin cells. The resulting material is strong enough to stop a bullet. Research bulletproof skin. Do you think this is a useful avenue of scientific discovery? Present your point of view using a medium of your choice. 🌐 T/I C A

80. Vitamin A is a group of organic compounds, one of which is an alcohol called retinol. Health workers in some developing countries administer doses of vitamin A to children who may be suffering from malnutrition. There is hope that this treatment might limit blindness caused by vitamin A deficiency. Conduct research to learn whether vitamin A can help with vision. Summarize your findings in a blog post or web page that could be linked to the website of an international aid organization. 🌐 T/I C A

Using Safer Solvents

Volatile organic compounds (VOCs) are chemical compounds that evaporate into the air, generally from liquid solvents. Since the middle of the nineteenth century, solvents derived from petroleum have been a part of many everyday products that people use in homes and businesses. For example, from the 1800s until fairly recently, most commercially available paints were based on oil. Paintbrushes had to be cleaned using organic solvents such as mineral spirits (distilled from petroleum) or turpentine (distilled from pine resin).

Many other products that you use regularly contain organic solvents. These include cleaning supplies, glues, cosmetics, aerosol sprays, and even air fresheners (**Figure 1**). Some of the VOCs in these products are, like mineral spirits, derived from petroleum. Others, such as methanol and propan-2-one (acetone), are manufactured in chemical plants. Volatile organic compounds are often used in products from which they are expected to evaporate, such as paint, floor wax, or adhesives. Even the highlighting pen you use when you take notes needs some sort of solvent for its ink.

Figure 1 Droplets of aerosol spray evaporate, filling the air with volatile organic compounds.

Unfortunately, many VOCs are extremely toxic and easily absorbed into the human body through the skin or lungs. When people use the products, particularly indoors, they expose themselves to the vapours of the organic compound as it evaporates. Regulatory agencies have identified indoor air pollution as a major health hazard. Exposure to VOCs can cause irritation to the eyes, nose, and throat, as well as headaches and nausea. Severe symptoms from frequent exposure or exposure to high concentrations of VOCs can even cause damage to the kidneys, liver, and central nervous system. In addition to health concerns, VOCs can cause environmental damage, polluting air and water resources.

For several decades, as the hazards of VOCs have become better understood, government and industry researchers have worked to develop alternatives to using VOCs in home and office products. Because they are so widely used indoors, paints were one of the first products to be addressed (**Figure 2**). Paint forms a polymer coating on a wall that is embedded with inorganic particles and dyes. By switching to compounds that are soluble in water, manufacturers have designed paint products that do not release organic vapours as they dry. Almost all indoor paints and most outdoor paints for home use are now water-based solutions of latex or alkyd resins. As the paint dries, only harmless water vapour evaporates.

Figure 2 Low-VOC paints are available in every colour that you can imagine. These paints do not use organic solvents, so they release only water vapour into the room.

For some household applications, the VOC has a different purpose. Many cleaning products, particularly those designed for removing grease and oil, are organic compounds. Switching to a low-VOC cleaner will reduce your exposure to volatile toxins. Many "green" products substitute non-volatile natural oils or their derivatives for more volatile ingredients. Less volatile compounds evaporate less readily, so are less likely to be inhaled.

One challenge in creating low-VOC products is that the replacement must meet the same performance requirements as existing products. For example, customers expect a water-based paint to be as durable as an oil-based paint.

In this task, you will act as a delegate to an International Conference on Green Alternatives. You will work in a group to explore a household product that emits VOCs. Possibilities include household cleaners, cosmetics, room deodorizers, printer inks, and adhesives. Each group will research their household product and investigate alternatives that reduce VOC emissions. The group will present their findings and include scientific, economic, social, and environmental advantages and disadvantages for the selected alternative compared with a more traditional product.

The Issue

SKILLS HANDBOOK A5

You will investigate a household product that can be identified as a source of VOCs and try to recommend the best low-VOC alternative.

Role

Your group will inform the attendees of the International Conference on Green Alternatives about an alternative (if you can find one) that could replace a familiar product that contains VOCs. Your task is to advise the attendees about your "green alternative" and its benefits.

Audience

Your audience will include the attendees of the International Conference on Green Alternatives (represented by your peers at school).

Goal

Your goal is to research and suggest alternatives to products used in everyday applications that emit VOCs into the indoor environment. Some additional benefits could include the reduction of waste, lower costs, and decreased risk of pollution during disposal of unused products.

Research and Identify Solutions

Conduct research to find alternatives to fossil fuel–based products. Use resources at your library, on the Internet, or at retail stores to identify more environmentally friendly products that could be substituted for high-VOC products. WEB LINK

Make a Decision

Apply what you have learned about VOCs in household products, their alternatives, and their relative impacts on the indoor environment in order to establish criteria by which to evaluate the "green" products. Using these criteria, which of the alternatives appears to be the best replacement for the conventional product? Identify the ways your alternative could be used and develop a preliminary implementation strategy.

Communicate

Present your findings to the attendees of the International Conference on Green Alternatives. You may use any combination of tools to present your findings, such as a photo slideshow, multimedia presentation, poster board, audio clip, video recording, or handouts. Engaging your audience is an important presentation skill and your presentation could include audience participation.

WEB LINK

ASSESSMENT **CHECKLIST**

Your completed Unit Task will be assessed according to the following criteria:

Knowledge/Understanding

- ✓ Identify a commonly used household product and its intended uses.
- ✓ Describe ways that the use of the product exposes consumers to volatile organic compounds (VOCs).

Thinking/Investigation

- ✓ Investigate the advantages and disadvantages of low-VOC household products.
- ✓ Research alternatives to VOCs in household products, and their benefits and drawbacks.
- ✓ Establish criteria for evaluating comparable low-VOC products.
- ✓ Compare the properties of low-VOC products to those of a traditional high-VOC product.

Communication

- ✓ Present findings and comparisons in a visual or audiovisual format.
- ✓ Defend the feasibility of replacing oil-based products with low-VOC products.

Application

- ✓ Propose a course of action for replacing a specific high-VOC household product.

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. What is the main product of the halogenation of an alkane? (1.1) K/U
   (a) an alkene
   (b) an alkyne
   (c) an alkyl halide
   (d) a halogen
2. Which of the following is a structural isomer of C_7H_{16}? (1.1) K/U
   (a) 3,3-dimethylpentane
   (b) 3-methylhexane
   (c) heptane
   (d) all of the above
3. How many carbon atoms does the formula for 3-ethylhexane contain? (1.1) K/U
   (a) 4
   (b) 6
   (c) 8
   (d) 12
4. What is the name of the compound with the condensed formula $CH_3CH_2CH_2CH_2CH_3$? (1.1) K/U
   (a) hydropentane
   (b) pentane
   (c) hexane
   (d) methylbutane
5. Which of the following compounds is a saturated hydrocarbon? (1.1, 1.2) K/U
   (a) ethene
   (b) benzene
   (c) 2,2-dimethylhexane
   (d) butane-1,4-diene
6. Stereoisomers have
   (a) the same number of atoms
   (b) the same types of atoms
   (c) the same molecular formula
   (d) all of the above (1.2) K/U
7. Which of the following is a property of aromatic hydrocarbons? (1.3) K/U
   (a) They are solids at room temperature.
   (b) They are insoluble in water.
   (c) They have a sweet odour.
   (d) none of the above
8. What is the product of the hydration of a hydrocarbon? (1.2, 1.4) K/U
   (a) an alkyl halide
   (b) a cyclic alkene
   (c) an alcohol
   (d) benzene
9. Which of the following elements is present in all alcohols? (1.4) K/U
   (a) chlorine
   (b) sulfur
   (c) oxygen
   (d) nitrogen
10. What functional group is present in a propan-2-one (acetone) molecule? (1.5) K/U
    (a) hydroxyl
    (b) carboxyl
    (c) carbonyl
    (d) none of the above
11. What is the IUPAC name of formaldehyde? (1.5) K/U
    (a) methanol
    (b) methanal
    (c) formic acid
    (d) methanoic acid
12. The boiling points of aldehydes and ketones
    (a) are the same as alcohols of similar mass
    (b) are higher than alcohols of similar mass
    (c) are lower than alkanes of similar mass
    (d) are higher than alkanes of similar mass (1.5) K/U
13. What is the product of the oxidation of an aldehyde? (1.5) K/U
    (a) a ketone
    (b) an organic (carboxylic) acid
    (c) a primary alcohol
    (d) a secondary alcohol
14. What are the reactants in an esterification reaction? (1.6) K/U
    (a) alcohol and water
    (b) an ester and a carboxylic acid
    (c) an alcohol and a carboxylic acid
    (d) an ester and water
15. Lipids are esters of
    (a) glycerol and fatty acids
    (b) an alcohol and a phosphate group
    (c) a salt and a carboxylic acid
    (d) glycerol and a base (1.6) K/U

16. Which type of compound contains a carbonyl group? (1.7) K/U
    (a) amine
    (b) ether
    (c) alcohol
    (d) amide
17. Which of the following compounds is a natural polymer? (2.1) K/U
    (a) cellulose
    (b) glucose
    (c) polyethene
    (d) all of the above
18. What are copolymers? (2.1) K/U
    (a) compounds that contain two functional groups
    (b) compounds made up of two or more different monomers
    (c) two identical monomers bonded together
    (d) compounds with the same molecular formulas but different structural formulas
19. An addition polymerization reaction always involves
    (a) at least two different compounds
    (b) a water molecule
    (c) a multiple bond
    (d) cross-linking (2.2) K/U
20. Which of the following compounds is not a polymer of glucose? (2.6) K/U
    (a) glycogen
    (b) cellulose
    (c) starch
    (d) DNA
21. What are the monomers of proteins? (2.6) K/U
    (a) lipids
    (b) amino acids
    (c) simple sugars
    (d) nucleic acids
22. DNA and RNA are
    (a) made up of amino acids
    (b) polymers that store and transmit genetic information
    (c) catalysts for biochemical reactions
    (d) monomers that make up proteins (2.6) K/U

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

23. Ethane is the simplest alkane. (1.1) K/U
24. Carbon dioxide gas is produced when carbon-based fuels are burned. (1.1) K/U
25. Cycloalkanes are named by adding *cyclo-* as a prefix to the name of the alkane. (1.1) K/U
26. The general chemical formula for an alkene is C_nH_{2n+2}. (1.2) K/U
27. A *cis* isomer has both groups of interest located on the same side of the double bond. (1.2) K/U
28. The formula of benzene is C_6H_{12}. (1.3) K/U
29. The structure of aromatic hydrocarbons is based on a 6-carbon ring with six identical carbon-carbon bonds. (1.3) K/U
30. A secondary alcohol is an alcohol in which the hydroxyl group is bonded to a carbon with three alkyl groups bonded to it. (1.4) K/U
31. The compound 2-butanone is an alcohol. (1.4, 1.5) K/U
32. A ketone contains an oxygen atom between two alkane groups. (1.4, 1.5) K/U
33. Aldehydes and ketones are non-polar. (1.5) K/U
34. Aldehydes have lower boiling points than alcohols of similar mass. (1.5) K/U
35. Carboxylic acids contain at least one carboxyl group. (1.6) K/U
36. A fatty acid is a long-chain carboxylic acid. (1.6) K/U
37. Oils have a higher melting point than fats. (1.6)
38. Soap is the sodium salt of an ester. (1.6) K/U
39. Diethylamine is a primary amine. (1.7) K/U
40. Polymers are large molecules that are built from smaller units called alkanes. (2.1) K/U
41. Addition polymers are the only product formed when smaller molecules are linked during addition reactions. (2.2) K/U
42. Addition polymers are made from unsaturated organic compounds. (2.2) K/U
43. Nylon is formed in an addition polymerization reaction. (2.4) K/U
44. Nylon was invented to replace natural rubber. (2.5) K/U
45. The structure of a protein depends on its amino acid sequence. (2.6) K/U
46. Nucleic acids are the molecules that make up DNA and RNA. (2.6) K/U

UNIT 1 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

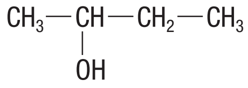
Knowledge

For each question, select the best answer from the four alternatives.

1. Which of the following compounds is an alkane? (1.1) K/U
   (a) methyl butanoate
   (b) ethene
   (c) ethylbenzene
   (d) ethane
2. How many isomers have the formula C_6H_{14}? (1.1) K/U
   (a) 2 (c) 5
   (b) 3 (d) 6
3. Which of the following compounds is unsaturated? (1.2) K/U
   (a) methylchloride
   (b) 2-chloroprop-1-ene
   (c) 1,1-dimethylcyclopropane
   (d) heptane
4. Which of the following compounds is an alkene with the molecular formula C_4H_8? (1.2) K/U
   (a) methylpropene
   (b) but-2-ene
   (c) but-1-ene
   (d) all of the above
5. Which of the following compounds can exhibit *cis–trans* isomerism? (1.2) K/U
   (a) 2-methylhex-2-ene
   (b) 2-methylbut-1-ene
   (c) 5-methylhex-2-ene
   (d) methylpropene
6. Which of the following compounds could be a product of the dehydration of 4-methylhexan-2-ol? (1.4) K/U
   (a) 3-methylhexane
   (b) 4-methylhex-2-ene
   (c) 4-methylhex-2-yne
   (d) hex-2-ene
7. How are alcohols classified? (1.4) K/U
   (a) by the number of carbon substituents bonded to the hydroxyl-bearing carbon
   (b) by the number of alkyl groups attached to the hydroxyl group
   (c) by the number of hydroxyl groups attached to the longest continuous chain of carbon atoms
   (d) by the number of organic groups bonded to the nitrogen atom
8. A carboxylic acid contains
   (a) a carbonyl group and a hydroxyl group bonded to the same carbon atom
   (b) a hydroxyl group bonded to an alkyl group
   (c) an oxygen atom bonded to two alkyl groups
   (d) a carbonyl group at the end of a carbon chain (1.6) K/U
9. Which of the following compounds is a carboxylic acid? (1.6) K/U
   (a) acetone (c) phosphoric acid
   (b) ethanoic acid (d) propanal
10. Which of the following compounds is an ester? (1.6) K/U
    (a) ethanamide
    (b) propan-2-one
    (c) ethanoic acid
    (d) methyl ethanoate
11. Which of the following is a property of all amines? (1.7) K/U
    (a) They have distinctive odours.
    (b) They are insoluble in water.
    (c) They have higher boiling points than alcohols.
    (d) They have extremely low melting points.
12. Which of the following is a synthetic polymer? (2.1) K/U
    (a) DNA (c) polyester
    (b) silk (d) cellulose
13. What is the process that results in bonds between polymer chains? (2.2) K/U
    (a) condensation
    (b) addition
    (c) cross-linking
    (d) dehydration
14. Which of the following phrases is always true of the formation of a condensation polymer? (2.4) K/U
    (a) Each monomer molecule has two different functional groups.
    (b) Water is a by-product.
    (c) The functional group on one monomer reacts with the functional group on another monomer.
    (d) One of the reactants is a carboxylic acid.
15. Which of the following is a component of DNA? (2.6) K/U
    (a) pentose sugar
    (b) phosphate group
    (c) nitrogen-containing base
    (d) all of the above

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

16. Hydrocarbons contain only carbon and hydrogen. (1.1) K/U
17. Alkanes are unsaturated hydrocarbons. (1.1) K/U
18. In methane, each carbon atom is connected to 3 hydrogen atoms. (1.1) K/U
19. Butane molecules contain 2 carbon atoms. (1.1) K/U
20. Alkanes can be solids, liquids, or gases depending on the number of carbon atoms. (1.1) K/U
21. Alkyl groups are named by replacing the *-ane* ending of the parent alkane with *-ol*. (1.1) K/U
22. In the *trans* isomer, the two matching alkyl groups are on the same side of the double bond. (1.2) K/U
23. Alkenes have at least one triple bond between adjacent carbon atoms. (1.2) K/U
24. The compound illustrated in **Figure 1** is a tertiary alcohol. (1.4) K/U



$$\mathrm{CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2-CH_3}$$

Figure 1

25. Ethers are formed by the condensation reaction of two alcohols. (1.4) K/U
26. Aldehydes and ketones are polar due to the presence of the carbonyl group. (1.5) K/U
27. A carbonyl group consists of a carbon atom double-bonded to an oxygen atom and single-bonded to a hydroxyl group. (1.6) K/U
28. Most carboxylic acids are strong acids. (1.6) K/U
29. Cellulose is a polymer made up of glucose. (2.1) K/U
30. Addition polymers are the result of the reaction between monomers with unsaturated carbon–carbon bonds. (2.2) K/U
31. Thermoplastics are plastics that can be heated and formed in moulds. (2.2) K/U
32. Bonds form between monomers by either addition reactions or condensation reactions. (2.2, 2.4) K/U
33. To undergo condensation polymerization, a compound must have at least one functional group. (2.4) K/U
34. Monosaccharides may be aldehydes or ketones and may have chain or ring structures. (2.6) K/U
35. Proteins are polymers built from amino acids. (2.6) K/U
36. The repeating units in nucleic acids are called monosaccharides. (2.6) K/U

Match each term on the left with the most appropriate description on the right.

37. (a) saturated hydrocarbon
    (b) unsaturated hydrocarbon
    (c) alcohol
    (d) ether
    (e) aldehyde
    (f) carboxylic acid
    (g) amine
    (h) addition polymer
    (i) polyester
    (j) polyamide
    (k) polysaccharide

    (i) a synthetic compound incorporating many $-N-C=O$ groups
    (ii) formed by breaking $C=C$ bonds
    (iii) named by adding *-al* to the root of the alkane name
    (iv) a compound containing only carbon atoms and the maximum possible number of hydrogen atoms
    (v) a compound that can be produced by combining two alcohols
    (vi) made up of many simple sugar molecules
    (vii) a compound containing double or triple carbon–carbon bonds
    (viii) a natural compound that includes nitrogen
    (ix) produced by the condensation reaction of a diol and a dicarboxylic acid
    (x) named by adding *-ol* to the root of the alkane name
    (xi) an organic compound that releases hydrogen ions when mixed with water (1.1, 1.2, 1.4, 1.5, 1.6, 1.7, 2.2, 2.4, 2.6) K/U

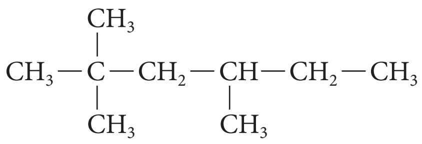
38. (a) addition reaction
    (b) hydrogenation reaction
    (c) condensation reaction
    (d) hydration reaction

    (i) the reaction of water with an unsaturated hydrocarbon to produce an alcohol
    (ii) the combination of two reactants to form one new product with no extra atoms
    (iii) the combination of two reactants to form a large molecule and a smaller molecule
    (iv) a reaction that results in a more saturated hydrocarbon (1.2, 1.4, 1.6, 2.4) K/U

Write a short answer to each question.

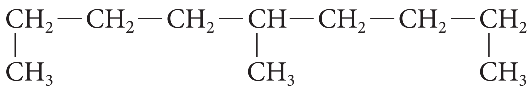
39. Name each of the following compounds: (1.1) K/U

(a)



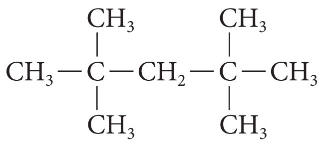
$$\begin{array}{ccccccccccc} & & CH_3 & & & & & & & & \\ & & | & & & & & & & & \\ CH_3 & - & C & - & CH_2 & - & CH & - & CH_2 & - & CH_3 \\ & & | & & & & | & & & & \\ & & CH_3 & & & & CH_3 & & & & \end{array}$$

(b)



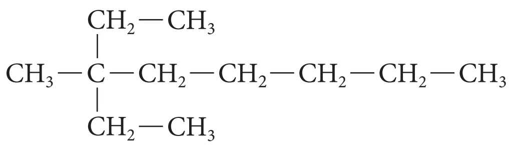
$$\begin{array}{ccccccccccccc} CH_2 & - & CH_2 & - & CH_2 & - & CH & - & CH_2 & - & CH_2 & - & CH_2 \\ | & & & & & & | & & & & & & | \\ CH_3 & & & & & & CH_3 & & & & & & CH_3 \end{array}$$

(c)



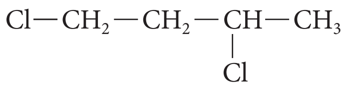
$$\begin{array}{ccccccccc} & & CH_3 & & & & CH_3 & & \\ & & | & & & & | & & \\ CH_3 & - & C & - & CH_2 & - & C & - & CH_3 \\ & & | & & & & | & & \\ & & CH_3 & & & & CH_3 & & \end{array}$$

(d)



$$\begin{array}{ccccccccccccc} & & CH_2-CH_3 & & & & & & & & & & \\ & & | & & & & & & & & & & \\ CH_3 & - & C & - & CH_2 & - & CH_2 & - & CH_2 & - & CH_2 & - & CH_3 \\ & & | & & & & & & & & & & \\ & & CH_2-CH_3 & & & & & & & & & & \end{array}$$

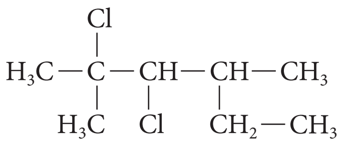
(e)



$$\begin{array}{ccccccccc} Cl & - & CH_2 & - & CH_2 & - & CH & - & CH_3 \\ & & & & & & | & & \\ & & & & & & Cl & & \end{array}$$

(f) $CH_3CH_2CH_2CCl_3$

(g)



$$\begin{array}{ccccccccc} & & Cl & & & & & & \\ & & | & & & & & & \\ H_3C & - & C & - & CH & - & CH & - & CH_3 \\ & & | & & | & & | & & \\ & H_3C & & & Cl & & CH_2-CH_3 & & \end{array}$$

(h) CH_2FCH_2F

40. Draw a structural formula for each of the following compounds: (1.1) K/U C
    (a) 2-methylbutane
    (b) methylcyclopropane
    (c) 1-chloro-3-methylhexane
    (d) 1,3-difluorocyclopentane
    (e) 4-ethyl-2,3-dimethylheptane
    (f) 1-bromo-4-ethylcyclohexane

41. Write the names and molecular formulas of the four possible products of the reaction of methane with chlorine, Cl_2. (1.1) K/U C

42. What is the name of the straight-chain alkane with the molecular formula $C_{10}H_{22}$? (1.1) K/U

43. Draw and name the 5 structural isomers of hexane. (1.1) T/I C

44. What is the relationship between the boiling point of an alkane and the length of its carbon chain? (1.1) K/U

45. (a) What is an alkyl group?
    (b) Give an example of two compounds that contain alkyl groups. (1.1) K/U

46. How many hydrogen atoms does a molecule of each of the following compounds contain? (1.1) K/U
    (a) butane
    (b) the straight-chain alkane with 6 carbon atoms
    (c) 2-chloropentane

47. Write the general chemical formula for each of the following types of compounds: (1.1) K/U
    (a) a straight-chain alkane (b) a cyclic alkane

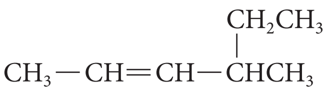
48. How many carbon atoms are in a molecule of each of the following compounds? (1.1, 1.2) K/U
    (a) cyclopentane (b) but-1-yne

49. What are the differences between a saturated hydrocarbon and an unsaturated hydrocarbon? (1.1, 1.2) K/U

50. Name each of the following alkenes: (1.2) K/U

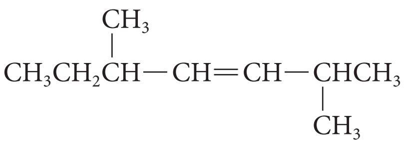
(a) $CH_2{=}CH-CH_2-CH_3$

(b)



$$\begin{array}{ccccccc} & & & & & & CH_2CH_3 \\ & & & & & & | \\ CH_3 & - & CH & = & CH & - & CHCH_3 \end{array}$$

(c)



$$\begin{array}{ccccccc} CH_3 & & & & & & \\ | & & & & & & \\ CH_3CH_2CH & - & CH & = & CH & - & CHCH_3 \\ & & & & & & | \\ & & & & & & CH_3 \end{array}$$

51. Draw a structural formula for each of the following unsaturated hydrocarbons: (1.2) K/U C
    (a) non-2-ene
    (b) 1-chloro-2-fluorohex-3-yne
    (c) *cis*-2,3-dichloropent-2-ene
    (d) butane-1,3-diene

52. Compare substitution reactions and addition reactions in alkenes. (1.2) K/U

53. What rule is used to determine the results of the addition of a hydrogen halide to an alkene? (1.2) K/U

54. The names of the following compounds are incorrect. Write the correct name for each compound. (1.2) K/U
    (a) 2-methylhex-4-ene
    (b) 2,5-hexadiene
    (c) 1,2-dimethylcyclohex-3-ene

55. Briefly explain the difference between a *cis* isomer and a *trans* isomer. Include diagrams. (1.2) K/U C

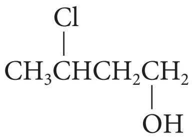
56. Why are alkenes, alkynes, and aromatic compounds classified as unsaturated compounds? (1.2, 1.3) K/U

57. Describe the structure of benzene. (1.3) K/U

58. For each of the following alcohols, give the systematic IUPAC name and specify whether the alcohol is primary, secondary, or tertiary. (1.4) K/U

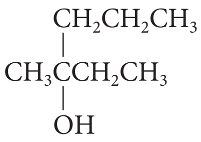
(a) $CH_3CH_2CH_2CH_2CH_2OH$

(b)



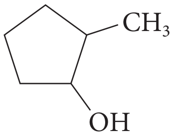
$$CH_3\overset{\begin{array}{c}Cl\\|\end{array}}{C}HCH_2\underset{\begin{array}{c}|\\OH\end{array}}{C}H_2$$

(c)



$$CH_3\overset{\begin{array}{c}CH_2CH_2CH_3\\|\end{array}}{\underset{\begin{array}{c}|\\OH\end{array}}{C}}CH_2CH_3$$

(d)



59. Draw a structural diagram to show each of the following alcohols: (1.4) K/U C

(a) pentan-2-ol

(b) 1-chlorohexan-3-ol

(c) 2,6-dimethylheptan-1-ol

(d) 2,4-dibromobutane-1,3-diol

(e) 3-methylphenol

60. Why are alcohols polar compounds? (1.4) K/U

61. What is the product of the oxidation of a secondary alcohol? (1.4) K/U

62. Name the four isomers of butanol. Determine whether each isomer is a primary, secondary, or tertiary alcohol. (1.4) K/U C

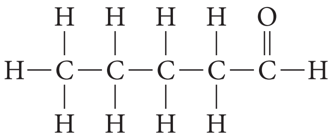
63. What is the product of each of the following reactions? (1.4, 1.5) K/U

(a) oxidation of a secondary alcohol

(b) hydrogenation of an aldehyde

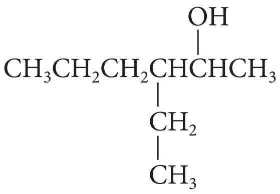
64. Name the following compounds: (1.4, 1.5) K/U

(a)



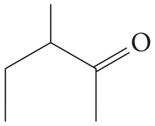
$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & O & & \\ & & | & & | & & | & & | & & \| & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & & & \\ & & H & & H & & H & & H & & & & \end{array}$$

(b)

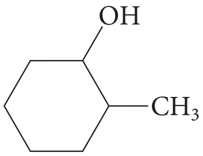


$$CH_3CH_2CH_2\underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{C}H\overset{\begin{array}{c}OH\\|\end{array}}{C}HCH_3$$

(c)



(d)



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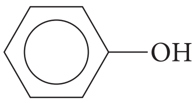


65. (a) Predict the product of the oxidation of cyclohexanol.

(b) Write the chemical equation for this reaction, showing the structural formulas. (1.5) K/U

66. Classify each of the following compounds as an aldehyde or ketone, then name each one: (1.5) K/U

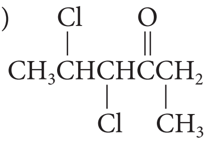
(a)

$$CH_3\overset{\begin{array}{c}O\\\|\end{array}}{C}CH_2CH_2CH_3$$

(b)

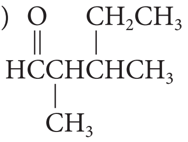
$$H\overset{\begin{array}{c}O\\\|\end{array}}{C}CH_2CH_2CH_3$$

(c)



$$CH_3\overset{\begin{array}{c}Cl\\|\end{array}}{C}H\underset{\begin{array}{c}|\\Cl\end{array}}{C}H\overset{\begin{array}{c}O\\\|\end{array}}{C}\underset{\begin{array}{c}|\\CH_3\end{array}}{C}H_2$$

(d)



$$H\overset{\begin{array}{c}O\\\|\end{array}}{C}\underset{\begin{array}{c}|\\CH_3\end{array}}{C}H\overset{\begin{array}{c}CH_2CH_3\\|\end{array}}{C}HCH_3$$

67. Compare and contrast aldehydes and ketones. (1.5) K/U

68. Draw a structural formula to represent each of the following compounds, and classify each one as an aldehyde or a ketone: (1.5) K/U C

(a) octan-3-one

(b) 2-methylpropanal

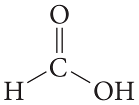
(c) 2-chloro-3-methylpentanal

(d) 1,2-dichlorohexan-3-one

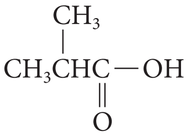
69. What is wrong with the name hexan-1-one? (1.5) K/U

70. Name the following compounds: (1.6) K/U

(a)

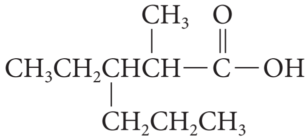


(b)



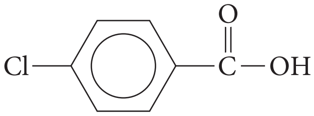
$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{O}{\|}}{C}-OH}$$

(c)



$$\mathrm{CH_3CH_2\underset{\underset{CH_2CH_2CH_3}{|}}{C}H\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{O}{\|}}{C}-OH}$$

(d)



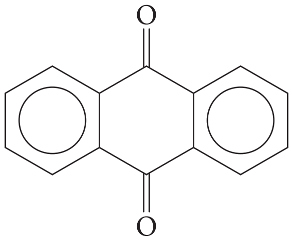
71. Using appropriate reactants, some alcohols can be oxidized into aldehydes or ketones. (1.4, 1.5, 1.6) K/U C
    - (a) Draw the structure of the product(s) resulting from the oxidation of each of the following alcohols:
        - (i) 3-methylbutan-1-ol
        - (ii) 3-methylbutan-2-ol
        - (iii) 2-methylbutan-2-ol
    - (b) Which of the products that you listed in (a) could undergo further controlled oxidation? What would be the product in each case?

72. What two compounds react to produce ethyl butanoate? (1.6) K/U

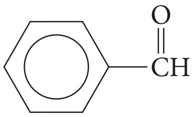
73. What category of organic compounds includes triglycerides? (1.6) K/U

74. What compounds are produced by the hydrolysis of ethyl benzoate? (1.6) K/U

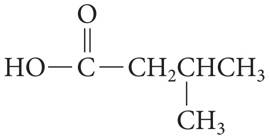
75. Classify each of the following compounds as a carboxylic acid, an ester, a ketone, an aldehyde, or an amine: (1.5, 1.6, 1.7) K/U
    - (a) $\mathrm{CH_3CH_2CHO}$
    - (b) $\mathrm{CH_3COCH_3}$
    - (c) $\mathrm{CH_3CH_2CH_2NH_2}$
    - (d) $\mathrm{CH_3CH_2CH_2COOH}$
    - (e)



(f)

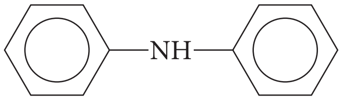


(g)



$$\mathrm{HO-\overset{\overset{O}{\|}}{C}-CH_2\underset{\underset{CH_3}{|}}{C}HCH_3}$$

(h)



76. Describe or draw the structure of an amine. Name its functional group(s). (1.7) K/U C

77. What is the difference between natural and synthetic polymers? Give at least two examples of each. (2.1) K/U

78. (a) What is the difference between a homopolymer and a copolymer?
    - (b) Can you tell from looking at the structure of a polymer whether it is a homopolymer or a copolymer? Explain. (2.1) K/U T/I

79. (a) Describe the necessary features of a compound that can undergo addition polymerization reactions.
    - (b) Briefly describe the process of addition polymerization. (2.2) K/U

80. Draw structural diagrams of the monomer of each of the following addition polymers: (2.2) K/U C
    - (a) polypropene
    - (b) polyethene

81. Draw three repeating units of the polymer formed from each of the following monomers: (2.2) K/U C
    - (a) but-2-ene
    - (b) methylpropene

82. Distinguish between the terms in the following pairs. Include examples with your answer. (2.2) K/U
    - (a) plastic and polymer
    - (b) thermoset and thermoplastic
    - (c) plasticizer and elastomer

83. Many polymers have bonds holding the polymer chains together. (2.2) K/U T/I
    - (a) What are these bonds called?
    - (b) How are they able to form? Include an example.
    - (c) How do they affect a polymer's properties?

84. Why has Health Canada placed restrictions on the use of some phthalates in children's products? (2.3) K/U A

85. Can a condensation polymer be made from just one type of monomer? Explain your answer. (2.4) K/U

86. Explain why water is often a by-product of a condensation polymerization reaction. (2.4) K/U

87. **Figure 2** shows a section of an addition polymer. Draw and name the monomer that reacts to form this polymer. (2.4) K/U C

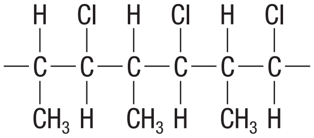
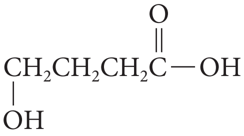


Figure 2

88. Draw the polymer that can be formed from each of the following monomers or pairs of monomers, and classify each polymer as either a polyester or a polyamide: (2.4) K/U C

(a)

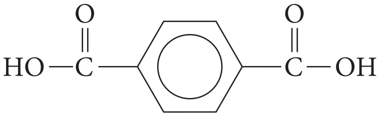


$$\underset{\mathrm{OH}}{\underset{|}{\mathrm{CH_2}}}\mathrm{CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}$$

(b)

$$\mathrm{H_2N-CH_2CH_2CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}$$

(c)



and

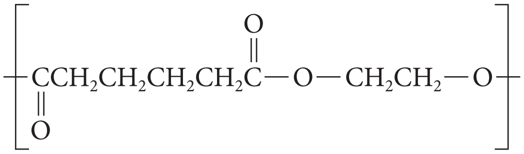
$HO—CH_2CH_2—OH$

(d) $H_2N—CH_2CH_2CH_2CH_2CH_2—NH_2$ and

$$\mathrm{HO-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}$$

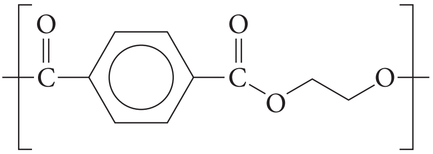
89. Copy the following structural formulas into your notebook. Classify each polymer as a polyester or a polyamide, circle the linkages, and identify the types of monomers involved. (2.4) K/U

(a)

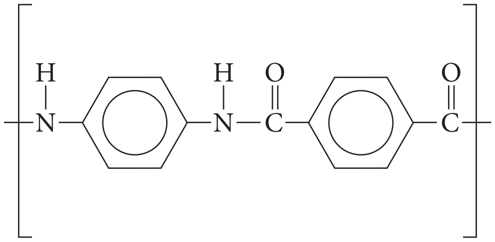


$$\left[-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{CH_2CH_2CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\mathrm{CH_2CH_2}-\mathrm{O}-\right]$$

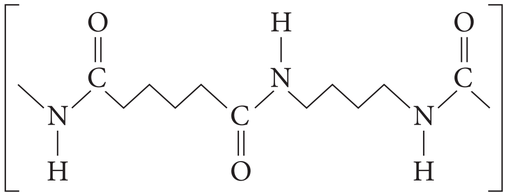
(b)



(c)



(d)



90. What chemical properties of plastics result in disposal problems? (2.4) K/U A

91. Wallace Carothers developed some of the first synthetic polymers. (2.5) K/U A
    (a) What natural polymer was neoprene designed to replace?
    (b) Carothers developed a polymer to replace silk. What was this synthetic polymer called and what type of polymer was it?
    (c) What two types of organic compounds were combined to make the silk substitute?

92. List at least three polymers of monosaccharides. For each polymer, state its function, and whether it is produced by plants or animals. (2.6) K/U

93. Amino acids all have at least two functional groups on each molecule. The functional groups enable the molecules to form polymers. (2.6) K/U
    (a) What two functional groups are common to all amino acids?
    (b) What are the main product and by-product of the polymerization of amino acids?
    (c) What type of synthetic polymer is formed from a similar reaction?

94. A peptide bond is a particular kind of amide linkage. When is it appropriate to use the term "peptide bond"? (2.6) K/U

Understanding

95. Is ethane soluble in water? Explain. (1.1) K/U

96. Why are alkanes relatively stable, compared to alkenes and alkynes? (1.1, 1.2) K/U

97. What enables *cis–trans* isomerism to occur in alkenes? (1.2) T/I

98. What are functional groups, and how are they used to classify organic molecules? (1.2) T/I

99. A classmate mentions a compound called methene. Is this an appropriate name? Explain. (1.2) T/I

100. Use a Venn diagram to compare and contrast benzene and cyclohexane. (1.1, 1.3) K/U C

101. Two conventions are used when naming compounds containing an aromatic group. Outline when each of these conventions is used, giving an example of each. (1.3) K/U T/I

102. Predict which has a higher boiling point: ethanol or chloroethane. Justify your prediction. (1.4) T/I

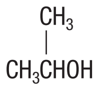
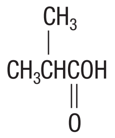
103. Why are the boiling points of aldehydes and ketones lower than those of similar alcohols? (1.5) K/U

104. Name and draw the condensed structural formula for the product of the oxidation of butanal. (1.5, 1.6) K/U

105. Explain why the boiling points of carboxylic acids are higher than the boiling points of alkanes of similar size. (1.6) K/U

106. Copy and complete **Table 1** in your notebook. (1.1, 1.2, 1.4, 1.5, 1.6, 1.7) K/U C

Table 1

Name	Type of compound	Condensed structural formula
methylpropane		
		$CH_3CH_2CHCH_2$
chloroethyne		
		 $CH_3\overset{\overset{CH_3}{\vert}}{C}HOH$
1-chlorobutan-2-ol		
		CH_3CH_2CHO
2-methylbutanal		
2-chloropentan-3-one		
		 $CH_3\overset{\overset{CH_3}{\vert}}{C}H\underset{\underset{O}{\Vert}}{C}OH$
methyl butanoate		
		$CH_3OCH_2CH_3$
		$CH_3NHCH_2CH_3$

107. Draw a structural formula equation for each of the following reactions: (1.2, 1.4, 1.5, 1.6) T/I C
   (a) methanol + propan-1-ol
   (b) propene + chlorine
   (c) 2-methylbutan-1-ol + (O)
   (d) butanoic acid + propan-1-ol
   (e) hex-3-yne + excess hydrogen
   (f) pentanal + (O)

108. Arrange the following compounds in order of increasing boiling point: propanamine, propane, and propan-1-ol. Briefly explain your reasoning. (1.1, 1.4, 1.7) T/I

109. Create a table to organize the following information regarding hydrogen bonding: (1.4, 1.6, 1.7) K/U T/I C
   (a) List at least three types of organic compounds that can form hydrogen bonds.
   (b) Draw the functional group that makes hydrogen bonding possible in each case.
   (c) Predict the solubility of these compounds in water and in a non-polar solvent.
   (d) Predict how the boiling point of a compound of this type compares to the boiling point of an alkane of similar size.

110. Using a graphic organizer, compare and contrast addition polymers and condensation polymers. (2.2, 2.4) K/U

111. Explain the role of hydrogen bonding in the structure of DNA. (2.6) T/I A

112. Create a graphic organizer to compare the polymerization of amino acids and the polymerization of monosaccharides. (2.6) K/U C

113. Create a table summarizing at least 10 different types of organic compounds. Use the following column headings: Type of compound; Functional group; Sample structure; Sample name. (1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 2.2, 2.4, 2.6) K/U T/I C

Analysis and Application

114. List and discuss at least four properties of organic compounds that can cause health or environmental problems. (1.1) T/I A

115. For an investigation, you are expected to design a procedure to determine the identity of two unlabelled samples. You know that one is cyclohexene and the other is 2-methylpropan-2-ol. (1.2, 1.4) T/I
   (a) Using a flow chart, summarize the steps you would carry out to identify each sample.
   (b) List any necessary materials or chemicals.
   (c) Describe your expected results.
   (d) List any necessary safety precautions.

116. Many industrial solvents are non-polar compounds with low molecular masses. (1.3, 1.4, 1.5) K/U T/I A
   (a) List at least three organic compounds that are (or used to be) widely used as industrial solvents.
   (b) What types of compounds will dissolve in these solvents?
   (c) What potential health hazards do they pose?
   (d) How might industrial solvents damage the environment?

117. A mixture of organic compounds is known to contain pentane, pentan-1-ol, and pentanoic acid. (1.1, 1.4, 1.6) T/I
   (a) Describe a procedure that could be used to separate these compounds.
   (b) Outline any safety concerns and describe how to reduce the hazards.

118. Create a table listing the following compounds, the WHMIS symbols that should be displayed on their containers, and the safety precautions you should take when handling them: (1.1, 1.4, 1.5, 1.6) K/U C A
   (a) propan-2-ol
   (b) propane
   (c) concentrated ethanoic acid
   (d) methanal (formaldehyde)

119. (a) Explain how the structure of lipid molecules affects the physical properties of the fat or oil.
  (b) How do margarine manufacturers manipulate the lipid molecules to obtain a more desirable product?
  (c) Unsaturated fats tend to break down very quickly and become rancid. In order to delay rancidity, food manufacturers add more hydrogen to unsaturated fats in a process called hydrogenation. How does hydrogenation change the structure of unsaturated fats? (1.6) T/I A

120. When ethanol reacts with benzoic acid, a cherry-scented ester is produced. (1.6) T/I C
  (a) Draw structural formulas to illustrate the reactants and product(s) of this reaction. Name the product(s).
  (b) When performing this reaction in the lab, a student added hot water to rinse the benzoic acid crystals into the reaction vessel. What effect will this have on the reaction? Explain your reasoning.

121. Fish odour is caused by amines. Explain why lemon juice can be used to remove fish odour from a person's hands. (1.7) T/I A

122. (a) List at least three drawbacks to using plastics.
  (b) Suggest how you, personally, could reduce the effects of these problems. (1.1, 2.2, 2.3, 2.4) A

123. Modern medicine uses polymers in many ways. Heart valve replacements and stints placed in blood vessels are often made of plastic. (2.2, 2.3, 2.4) K/U A
  (a) List the properties of plastic that make it ideal for these uses.
  (b) What dangers might be associated with using plastics in this way?

124. Nylon-5,10 was synthesized by DuPont before nylon-6,6. It is not as widely used, however, because it is more expensive to make. Predict the names and structures of the monomers used to make nylon-5,10. (*Hint:* The "5" refers to a diamine.) (2.4, 2.5) T/I C

Evaluation

125. Write a one-page paper giving your opinion about which functional group is the most biologically important, and which has the least importance in the body. (1.2, 2.6) A C

126. The phenols commonly known as BHT and BHA are antioxidants. They prevent or reduce oxidation reactions from occurring. Why are these compounds used as preservatives in foods that contain unsaturated fats? List the potential positive and negative effects of the use of these preservatives. Do the benefits of their use outweigh the negative aspects? (1.3, 2.6) A

127. Since fossil fuels are a non-renewable resource, many industries are searching for alternative sources of chemical energy. One possibility is the manufacture of ethanol from the sugars in corn. Is this a good idea? Give reasons for your answer. (1.4, 2.6) T/I A

128. Many synthetic organic compounds have been developed as an alternative to natural compounds. Citing at least two examples, argue whether it is more environmentally responsible to use synthetic or natural polymers. (2.1, 2.2, 2.6) A C

Reflect on Your Learning

129. Construct a concept map using organic compounds as the central concept and including all of the key terms from this unit. K/U T/I C

130. Consider the concepts you learned in this unit. Which do you think are most relevant and important to your future education and career goals? Why? A

131. What concepts in this unit do you think are most confusing? Why? How could you help another student understand them? K/U A

Research

WEB LINK

132. What is gasohol and what is it used for? Research the compounds that go into this mixture, and their sources. Research the drawbacks and benefits (including the environmental impact) of gasohol. Do you think gasohol should be more or less commonly used? Summarize your conclusions as a letter to the editor of a daily newspaper or as a comment posted to an online news source. T/I C A

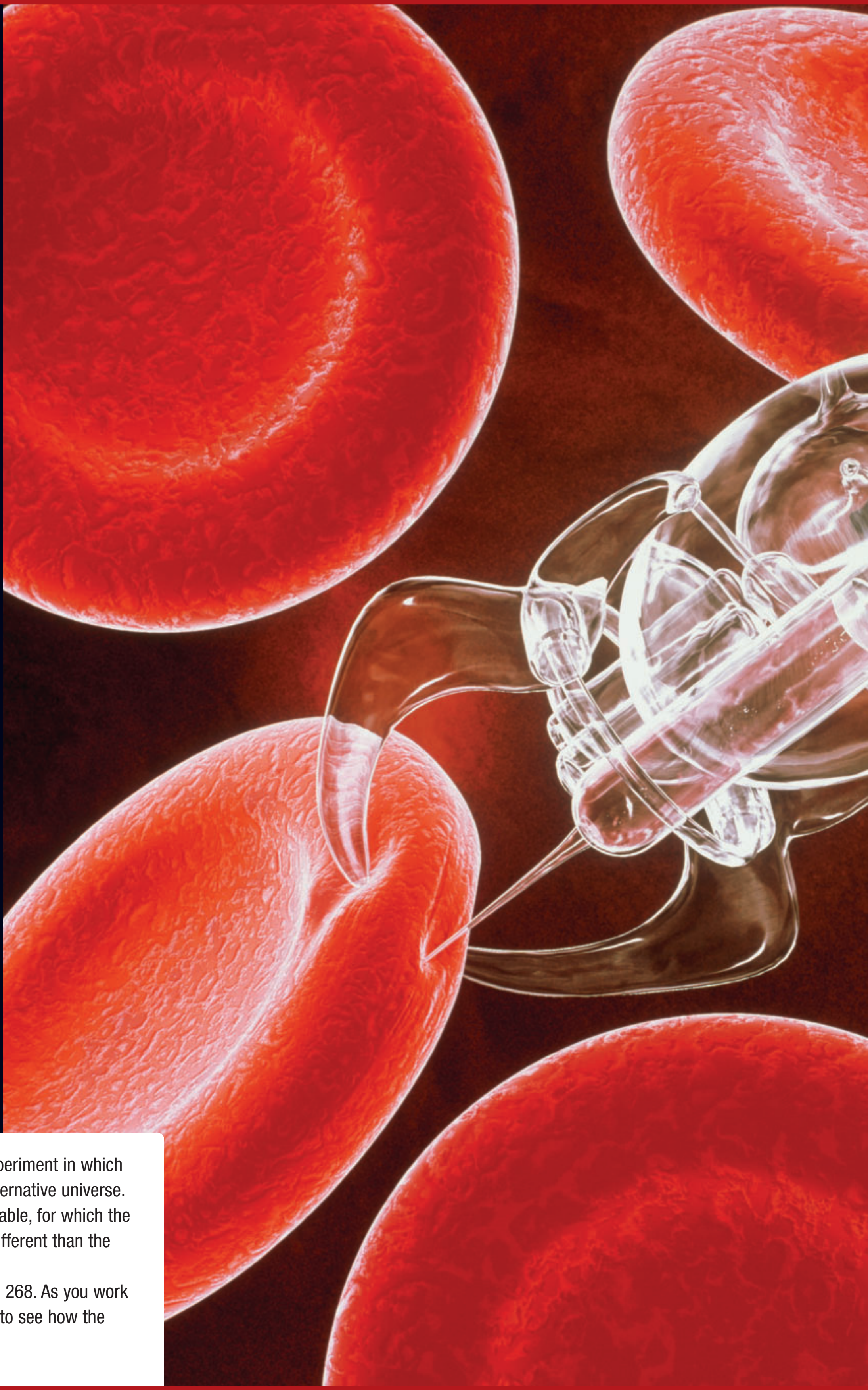
133. Morphine, codeine, and heroin are closely related compounds. Research these three drugs. Write a brief illustrated report that includes their historical uses, their structures and properties, and the benefits and drawbacks of their medical uses. T/I C A

134. Car manufacturers are using plastics to make more and more of their vehicles' components. List at least five car parts that are made of plastic. Research the properties of the plastic that make it appropriate for each specific use, and the benefits and drawbacks of using plastics rather than the more traditional materials. Summarize your findings as a table or graphic organizer. T/I C A

135. There are many applications of organic chemical reactions in the world in which we live. Research how organic reactions affect living organisms and the environment. Focus on four specific examples. Summarize your findings in a format of your choice, including complete chemical equations for all reactions. Describe the implications or applications of each reaction. T/I C A

UNIT 2

Structure and Properties of Matter



OVERALL EXPECTATIONS

- assess the benefits to society and evaluate the environmental impact of products and technologies that apply principles related to the structure and properties of matter
- investigate the molecular shapes and physical properties of various types of matter
- demonstrate an understanding of atomic structure and chemical bonding, and how they relate to the physical properties of ionic, molecular, covalent network, and metallic substances

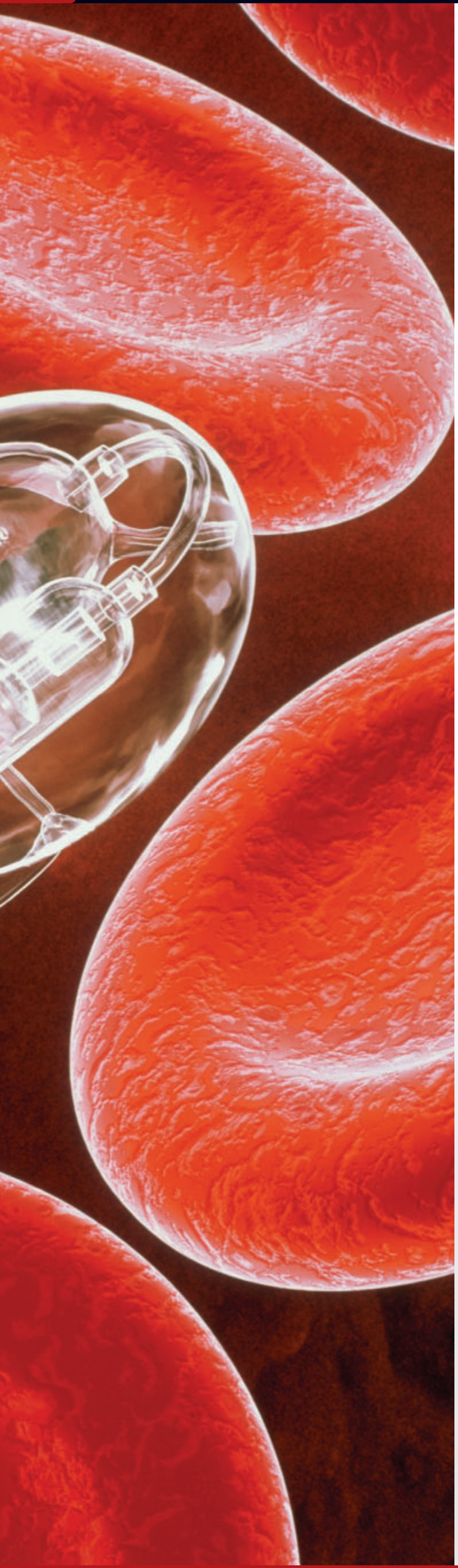
BIG IDEAS

- The nature of the attractive forces that exist between particles in a substance determines the properties of that substance.
- Technological devices that are based on the principles of atomic and molecular structures can have societal benefits and costs.

UNIT TASK **PREVIEW**

In this Unit Task, you will perform a thought experiment in which you will develop a detailed description of an alternative universe. At the heart of this universe will be a periodic table, for which the rules for working with quantum numbers are different than the accepted rules in our universe.

The Unit Task is described in detail on page 268. As you work through the unit, look for Unit Task Bookmarks to see how the section relates to the Unit Task.



NANOTECHNOLOGY: A TINY TECHNOLOGICAL REVOLUTION

Nanotechnology is a branch of technology that involves engineering functional systems at the molecular or atomic scale. A functional system is a series of connected components that work together to carry out a specific function. A nanometre is one billionth of a metre—a human hair is 50 000 to 100 000 as thick. Nanotechnology first emerged in the 1980s and, since then, has been applied widely to many different fields. For example, medical scientists are trying to develop tiny cellular-repair nanobots that can be injected into the human body. Once in the body, these nanobots could repair damaged or sick cells or kill harmful ones, such as cancer cells. Researchers in the pharmaceutical industry are experimenting with nanotechnology to produce microscopic needles that can inject drugs into single cells.

Nanotechnology also plays (or will play) a role in advancing the fields of electronics, materials science, and biomaterials. Nanotechnology may also be used in the toy, food, and beverage industries. Some nanomaterials, such as carbon nanotubes, are extraordinarily strong, despite their small size. This makes them extremely useful in the manufacture of construction materials used in space vehicles, airplanes, and even new types of reinforced concrete. Nanochemicals can be added to fabrics and textiles to resist stains and eliminate unwanted odours. Solar cells, lighting, and chemical imaging all involve the use of nanomaterials and can be less expensive than those made using conventional materials. Nanotechnology has many practical applications. You likely own some devices that were constructed using nanotechnology!

Although there are many exciting potential uses of nanotechnology, this new field is not without risks. Since nanomaterials are not naturally occurring substances, we cannot predict their possible negative consequences. For example, researchers Niraj Kumar and Virginia Walker of Queen's University in Kingston, Ontario, made a discovery regarding the negative effects of nanoparticles on the Arctic ecosystem. They found that silver nanoparticles, which are commonly used as antibacterial agents in fabrics (such as those used in socks), are toxic to nitrogen-fixing bacteria. When the populations of these bacteria are reduced, plants do not grow as quickly or as vigorously. It is amazing and concerning that these silver nanoparticles were found in regions that are largely undisturbed by human activity. This is one example of why, as we move forward in the field of nanotechnology, we need to be cautious to minimize any unforeseen negative consequences.

Questions

1. What is unique about nanotechnology, compared with other branches of science?
2. What are some current applications of nanotechnology?
3. What are some areas of research for future uses of nanotechnology?
4. Are technologies always beneficial to society and the environment? Give an example of another technology that has benefits for and negative impacts on society and/or the environment.

CONCEPTS

- predict the nature of a chemical bond
- outline major historical accomplishments in atomic theory
- describe characteristics of the atom
- describe elements, including isotopes and radioisotopes
- identify periodic trends
- identify properties of ionic and molecular compounds

SKILLS

- draw Bohr–Rutherford diagrams and Lewis structures
- name substances and write chemical formulas
- classify compounds
- understand safety in the laboratory
- use IUPAC rules to name compounds

Concepts Review

1. Predict whether the chemical bonds in the following substances are ionic or covalent: K/U T/I
   (a) KCl
   (b) SF_6
   (c) LiBr
   (d) N_2O_4
   (e) RbS
2. Construct a timeline or a graphic organizer that illustrates the major historical accomplishments in atomic theory by Dalton, Thomson, and Rutherford. K/U C
3. Use the Dalton model of the atom to explain the law of conservation of mass in chemical reactions. K/U
4. What are the major components of the atom? K/U
5. State the number of protons, neutrons, and electrons in each of the following entities: K/U T/I
   (a) a neutral atom with atomic number 5 and mass number 11
   (b) a neutral atom with atomic number 25 and mass number 54
   (c) a neutral atom with atomic number 25 and mass number 55
   (d) an ion with atomic number 17, mass number 35, and a charge of -1
6. Explain the difference between isotopes and radioisotopes of an element. K/U
7. (a) What are periodic trends?
   (b) Name two properties that exhibit periodic behaviour and discuss their trends. K/U
8. Predict whether compounds with the following properties are ionic or molecular, based on the given information: K/U T/I
   (a) insoluble in water
   (b) low melting point
   (c) high boiling point
   (d) solid at SATP
   (e) forms an electrolyte in water
   (f) brittle
9. Describe the structure of a solid ionic compound using the terms “crystalline” and “formula unit.” K/U
10. Ionic and molecular compounds have certain characteristic properties. Summarize these by copying **Table 1** into your notebook and completing it. K/U C

Table 1

Characteristic	Ionic compounds	Molecular compounds
Classes of elements involved?		
Melting point (high/low)?		
State at SATP (solid, liquid, gas)?		
Electrolyte (yes/no)?		

11. Distinguish between the following terms: scientific model, scientific law, and scientific theory. K/U
12. Define the following terms, and state the trends for each on the periodic table: K/U
    (a) atomic radius
    (b) ionization energy
    (c) electron affinity
    (d) electronegativity

13. Copy the periodic table in **Figure 1** into your notebook, and identify the following groups: alkali metals, alkaline earth metals, transition metals, halogens, noble gases, lanthanides, and actinides. K/U C

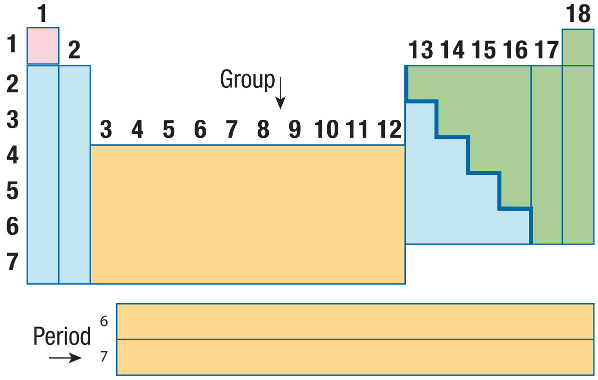


Figure 1

14. What information is included in the WHMIS symbol for a chemical? K/U

15. What does MSDS stand for? What information is included in an MSDS? K/U

16. What is meant by the term "stable octet"? Explain how the octet rule works when drawing Lewis structures. K/U T/I A

17. State the similarities and differences between the Bohr–Rutherford diagrams of the atoms in each pair below. Explain their relative location on the periodic table based on these similarities and differences. K/U C
   - (a) lithium and potassium
   - (b) magnesium and sulfur

18. Copy **Table 2** into your notebook and complete it. K/U C

Table 2

Element name	Symbol	Lewis symbol	Are electrons lost or gained when ion forms?	Lewis symbol of ion formation	Charge on ion
magnesium					
	Br				
sulfur					
	Na				
tin					
	P				

Skills Review

19. Draw a Bohr–Rutherford diagram for each of the following elements: K/U T/I C
   - (a) H
   - (b) C
   - (c) P
   - (d) K
   - (e) Na

20. Draw the structural formula for each of the following molecular compounds: K/U T/I C
   - (a) H_2O
   - (b) CH_4
   - (c) CO_2
   - (d) C_2H_4
   - (e) NH_3

21. Give the IUPAC name for the following compounds: K/U T/I
   - (a) CBr_4
   - (b) ClO_2
   - (c) N_2O
   - (d) SF_6
   - (e) N_2O_4

22. In a graphic organizer, show the steps involved in drawing the Lewis structure of
   - (a) an ionic compound
   - (b) a covalent compound K/U T/I C

23. Draw Lewis structures showing the formation of the following compounds, and state whether each is ionic or covalent. K/U T/I C
   - (a) sodium fluoride
   - (b) hydrogen sulfide
   - (c) aluminum oxide
   - (d) methane

24. Write the IUPAC name for each of the following compounds: K/U T/I
   - (a) $CaCl_2$
   - (b) $Fe(NO_3)_2$
   - (c) CO
   - (d) $CaSO_3$
   - (e) NH_4NO_3
   - (f) $(NH_4)_2S$
   - (g) $Cu(ClO_2)_2$
   - (h) NaClO
   - (i) HgS
   - (j) $Ca(C_2H_3O_2)_2$

25. Design and create a poster that clearly states and illustrates an important safety rule in your chemistry classroom. K/U T/I C

CAREER PATHWAYS **PREVIEW**

Throughout this unit you will see Career Links. Go to the Nelson Science website to find information about careers related to Structure and Properties of Matter. On the Chapter Summary page at the end of each chapter you will find a Career Pathways feature that shows you the educational requirements of the careers. There are also some career-related questions for you to research.

CHAPTER 3

Atoms

KEY CONCEPTS

After completing this chapter you will be able to

- describe atomic structure and theory, including key experiments
- understand the basics of quantum mechanics, the wave model, quantum numbers, and electron configuration
- explain energy levels, subshells, orbitals, and electron spin
- use the aufbau principle, the Pauli exclusion principle, and Hund's rule to write electron configurations for elements
- explain how the arrangement of elements in the periodic table is directly related to their electron configurations
- compare characteristic properties of elements
- apply atomic theories to help explain methods in analytical chemistry and medical diagnosis, and assess the impact of such technologies

What Is the Nature of Atoms and Molecules?

Modern medicine has many different tools to help physicians look for evidence of disease without having to resort to surgery. For example, an MRI (magnetic resonance imaging) machine uses powerful magnets to align hydrogen atoms in the same direction in the body. (Hydrogen atoms usually spin in random patterns.) When a specific radio frequency is applied to the aligned hydrogen atoms, some of them emit energy, which can be used to create detailed images. MRI technology allows medical professionals to scan a living person in a matter of minutes and see images of what is happening inside the tissues. Each of the 3 MRI scans on the facing page shows an adult human brain. The first is a three-dimensional MRI scan, the second is an MRI scan of a brain with a cancerous tumour, and the third is an MRI scan of a healthy brain. Can you identify the tumour by comparing these?

The invention of medical imaging machines such as MRI depended on scientists understanding the nature of atoms and molecules. Before MRI, doctors were limited to X-ray imaging, which provides only limited views of soft tissues (such as muscles inside the body). CAT scans (computerized axial tomography, also sometimes called CT scans), which also use X-rays, were commonly used before MRI became accessible. These technologies are still widely used, but MRI has revolutionized the field of medical treatment by providing a way to diagnose disease and monitor the effects of treatment in a way that is safer, more accurate, and more detailed than ever before.

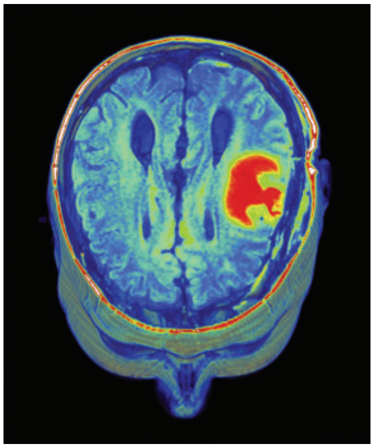
As our knowledge of the nature of atoms and molecules advances, so does the development of useful applications. The new field of nuclear medicine is one example: further non-invasive diagnostic imaging techniques that interact with atoms, such as positron emission tomography (PET), allow physicians even clearer images of living tissues.

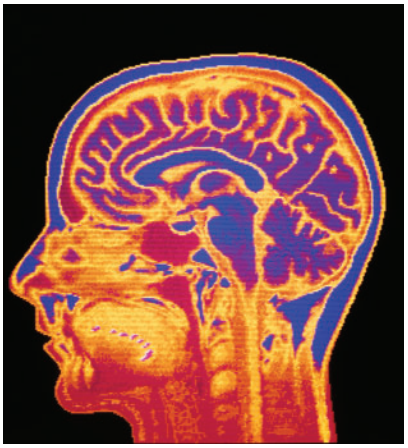
Many of the devices you use every day have been developed thanks to advances in understanding the nature of atoms and molecules. These devices include cellphones, televisions, sensors in automobiles, and computers. As well as making life more interesting and convenient, a greater understanding of atomic structure plays an important economic role.

STARTING **POINTS**

Answer the following questions using your current knowledge. You will have a chance to revisit these questions later, applying concepts and skills from the chapter.

1. (a) If you could see a single carbon atom, what do you think it would look like?
    (b) Based on your answer to (a), what are the strengths and weaknesses of your model of a carbon atom?
2. Describe an electron, where it is found in an atom, and the evidence that supports its existence.
3. Describe a proton, where it is found in an atom, and the evidence that supports its existence.
4. Compare and contrast MRI to X-ray imaging.
    (a) In what situations do you think MRI techniques can be used?
    (b) What are the risks to patients or doctors and technicians using MRI technology?
    (c) In your opinion, do the benefits of MRI technology outweigh the risks?





Mini **Investigation**

Exploring the Black Box

Skills: Planning, Performing, Observing, Analyzing, Evaluating, Communicating

SKILLS HANDBOOK **A2, A2.4**

In this activity, you will work with a sealed box that has a small hole on the side and a raised pattern on the inside bottom surface that forms a maze. You will insert a ball bearing or marble and move it around to infer the pattern of the hidden maze.

Equipment and Materials: rectangular box with an internal raised maze and a small hole in one wall; ball bearing or marble; pencil; paper

1. Work with a partner to determine a strategy to figure out the pattern of the maze hidden inside the box.
2. Place the ball bearing or marble inside the box and carry out your strategy.
3. Describe to your partner what you think the maze looks like. Have your partner draw the maze as you describe it.
4. Switch roles with your partner, and repeat Steps 2 and 3.
5. If time permits, trade boxes with another group and repeat Steps 2–4, but this time allow your partner to describe the maze first.

A. What strategy did you use to solve the maze? T/I

B. What were the challenges of not being able to see inside the black box? T/I

C. What strategies helped you to successfully communicate your findings to your partner? T/I C

D. Were you able to solve the maze using your partner's map and vice versa? Explain any difficulties you encountered. T/I C

E. How do you think this activity compares with trying to determine the structure of an atom? T/I

F. This activity is a simple analogy of how scientists try to determine the structure of the atom. Do you think you should be able to open up your black box and see inside it? Justify your response. T/I

3.1 Early Atomic Theories and the Origins of Quantum Theory

What is matter made of? People have wondered about the answer to this question for thousands of years. Around 460 BCE, the Greek philosopher Democritus speculated that matter is composed of elementary particles called atoms. However, it was not until thousands of years later, after collecting a lot of evidence and developing very complex technology, that scientists were able to state with some certainty that matter is composed of atoms. Recently, something very exciting happened. For the first time, scientists are able to "see" individual atoms through a special microscope, called a scanning tunnelling microscope (STM). The STM passes an extremely fine, electrically charged needle over the surface of an object. Changes in the current through the needle indicate changes in the distance between the surface and the needle. These changes indicate the "bumps" of atoms and the "valleys" between them. An STM image of the surface of graphite shows an orderly arrangement of carbon atoms (**Figure 1**). WEB LINK

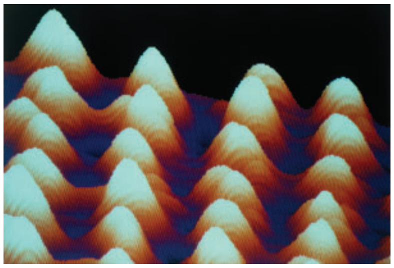


Figure 1 STM image of atoms on the surface of graphite (a form of carbon)

Early Developments in Atomic Structure

To understand chemistry, it helps to be able to visualize matter at the atomic level. Before the invention of the STM, scientists speculated that matter consisted of individual atoms. When Democritus first suggested the existence of atoms, his ideas were based on intuition and reason, not experimentation. For the following 20 centuries, no convincing experimental evidence was available to support the existence of atoms. As new tools to experiment with matter were developed, our understanding of the structure of matter grew. In the late 1700s, French chemist Antoine Lavoisier and others used experimentation to gather the first accurate quantitative measurements of chemical reactions. These measurements were made possible by the invention of instruments that could precisely measure mass and volume. Based on the results of these experiments, John Dalton (1766–1844) proposed the first modern atomic theory: elements consist of atoms, which cannot be created, destroyed, or divided, and atoms of the same element have identical size, mass, and other properties. Dalton's theory, although simple, has stood the test of time extremely well. In the past 200 years, a great deal of experimental evidence has accumulated to support atomic theory.

Figure 2 The English physicist J.J. Thomson (1856–1940) studied electrical discharges in partially evacuated tubes called cathode ray tubes.

electron a negatively charged subatomic particle

Discovering the Electron

The experiments by the English physicist J.J. Thomson (**Figure 2**) were the first to provide evidence for the existence of the **electron**, a negatively charged subatomic particle. In his experiments, Thomson applied high voltage to a partially evacuated tube with a metal electrode at each end. He observed that a ray was produced that started from the negative electrode, or cathode. As a result of these observations, he called his tube a cathode ray tube (**Figure 3(a)**). WEB LINK

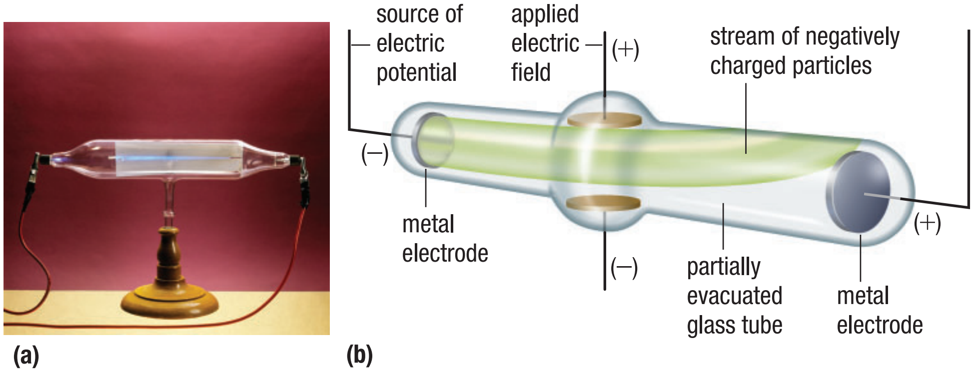


Figure 3 (a) A cathode ray tube under high voltage produces a visible ray. (b) A cathode ray is deflected away from the negative pole in an applied electric field, which is consistent with the ray being composed of a stream of negatively charged particles (electrons).

Thomson also observed that the negative pole of an applied electric field repelled the ray (**Figure 3(b)**). He explained these observations by hypothesizing that the ray was composed of a stream of negatively charged particles, which we now know to be electrons.

By measuring the deflection of the beam of electrons in a magnetic field, Thomson was able to determine the charge-to-mass ratio of an electron, using the formula

$$\frac{e}{m} = -1.76 \times 10^{8}\ \text{C/g}$$

where e represents the charge on the electron in coulombs (C), and m represents the electron mass in grams (g).

One of Thomson's goals in his cathode ray tube experiments was to understand the structure of the atom. He reasoned that since electrons could be produced from electrodes made of various metals, all atoms must contain electrons. Since atoms are electrically neutral, Thomson further reasoned that atoms must also contain a positive charge. Thomson postulated that an atom consists of a diffuse cloud of positive charge with negatively charged electrons embedded randomly in it. This model is sometimes called the "blueberry muffin model"; the electrons are analogous to negatively charged blueberries dispersed in a positively charged muffin (**Figure 4**).

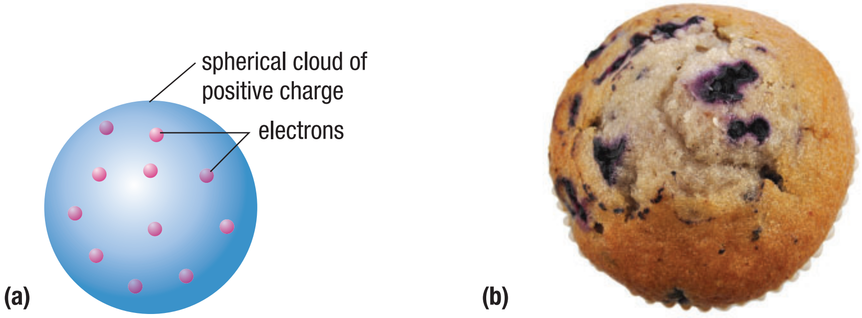


Figure 4 (a) According to Thomson's model, electrons are randomly embedded in a cloud of positive charge. (b) Thomson's model of an atom is sometimes called the "blueberry muffin model." In the model, electrons are represented by the blueberries.

In 1909, scientist Robert Millikan conducted experiments at the University of Chicago in which he used charged oil drops to determine the charge of an electron. Using the apparatus shown in **Figure 5**, Millikan discovered that the fall of charged oil droplets due to gravity could be halted by adjusting the voltage across two charged plates. He was able to calculate the charge on the oil drop from the voltage and the mass of the oil drop. Using this value and the charge-to-mass ratio determined by Thomson, Millikan calculated the mass of an electron to be 9.11×10^{-31} kg.

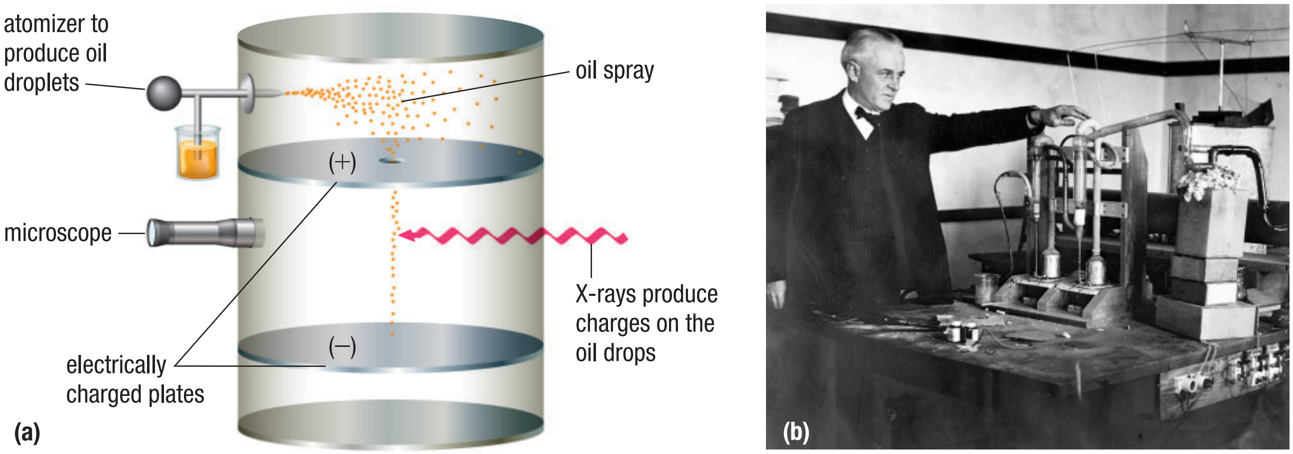


Figure 5 (a) A schematic representation of the apparatus Millikan used to determine the charge of an electron. (b) Robert Millikan using his apparatus

Exploring Radioactivity

In the late nineteenth century, scientists discovered that certain elements emit high levels of energy. In 1896, French scientist Henri Becquerel found that, in the absence of light, a piece of mineral containing uranium produces an image on a photographic plate. He attributed this phenomenon to uranium atoms spontaneously emitting radiation: energy, particles, or waves that travel through space or substances. Elements that emit radiation are said to be radioactive.

radioactivity the spontaneous decay or disintegration of the nucleus of an atom

Today we know that **radioactivity** is the spontaneous decay of the nucleus of an atom. This idea was first proposed by Ernest Rutherford (**Figure 6**). Rutherford showed that radioactivity resulted from the disintegration of atoms. He also discovered the alpha particle and named the beta particle and the gamma ray (**Table 1**).

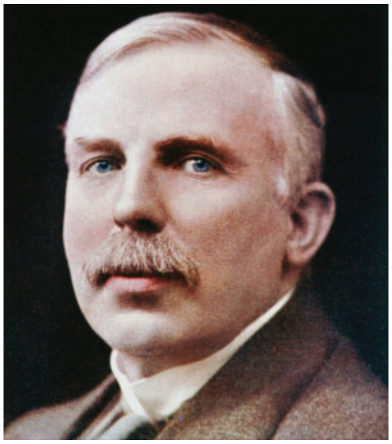


Figure 6 Ernest Rutherford (1871–1937) did much of the early work characterizing radioactivity at McGill University in Montréal, Québec. He received the Nobel Prize in Chemistry in 1908.

Table 1 Characteristics of Three Types of Radioactive Emissions

	Alpha particle	Beta particle	Gamma ray
Symbol	α or ${}^{4}_{2}\alpha$ or ${}^{4}_{2}\mathrm{He}$	β or β^- or e	γ
Atomic mass (u)	4	$\frac{1}{2000}$	0
Charge	+2	−1	0
Speed	slow	fast	very fast (speed of light)
Ionizing ability	high	medium	none
Penetrating power	low	medium	high
Stopped by	paper	aluminum	lead

Rutherford's Model of the Atom

In 1911, Rutherford carried out a series of experiments to look for evidence in support of Thomson's "blueberry muffin model" of the atom. Rutherford devised experiments in which positively charged alpha particles were fired at a thin sheet of gold foil. He hypothesized that if Thomson's model was accurate, the massive alpha particles should break through the thin foil like bullets through paper, with only minor deflections (**Figure 7**).

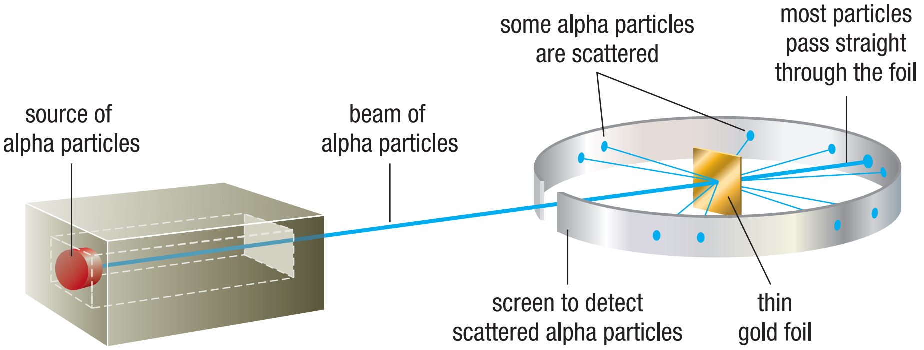


Figure 7 Rutherford's experimental design for the alpha particle bombardment of gold foil

The results of the experiments were very different from what Rutherford had anticipated. Although most of the alpha particles passed straight through the gold foil, some were deflected at various angles while others were reflected back toward the source, never reaching the detector.

Rutherford realized that these experimental results did not support Thomson's model of the atom (**Figure 8(a)**). The only possible explanation was that the observed deflection of alpha particles was caused by a concentrated positive charge at the centre of the atom. Rutherford predicted that the positive charge at the centre of the atom must contain most of the atomic mass, which would account for the deflection of the massive alpha particles. Rutherford also reasoned that since most of the alpha particles passed directly through the foil, the atom must be made up of mostly empty space, and the positive centre must be small in volume relative to the atom (**Figure 8(b)**). The deflected alpha particles must have travelled close to the positively charged centres of the atoms and, since like charges repel, changed paths. The alpha particles that bounced back must have made a direct hit on the much more massive positively charged centres.

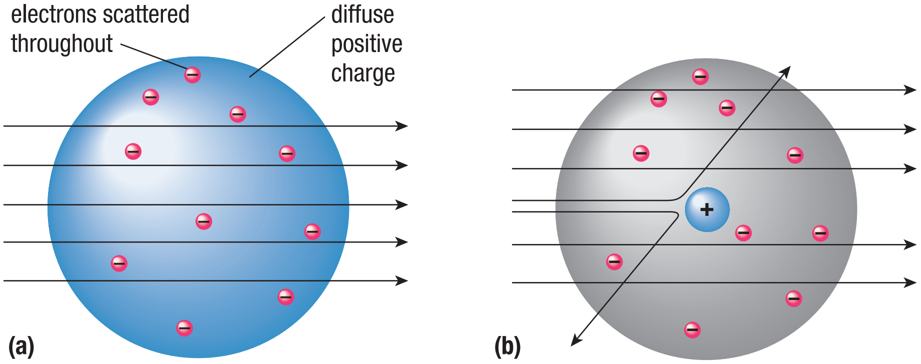


Figure 8 (a) Rutherford predicted that the alpha particles would pass right through the gold foil if Thomson's model was correct. (b) The actual results of Rutherford's experiments revealed that the atom is mostly open space with a small, positively charged centre that contains the bulk of the atomic mass.

Rutherford concluded that these results could be explained only in terms of an atom with a **nucleus**: a dense, positively charged atomic centre. He proposed that electrons move around the nucleus at a relatively far distance, similar to planets orbiting the Sun. Rutherford later named the positive charges in the nucleus **protons**.

Scientist James Chadwick worked with Rutherford to determine the masses of the nuclei of different elements. In these experiments, he found that the observed masses of the nuclei were not the same as the sum of the masses of the protons. Chadwick concluded that a nucleus must contain not only positively charged protons, but also neutral (uncharged) particles called **neutrons**.

nucleus the dense centre of an atom with a positive charge

proton a positively charged subatomic particle

neutron an electrically neutral subatomic particle

Atoms and Isotopes

An atom can be described as consisting of a tiny nucleus with a diameter of about 10^{-15} m and electrons that move around the nucleus at an average distance of about 10^{-10} m. The nucleus is very small compared to the overall size of the atom: if an atom were the size of a sports stadium, the nucleus would be about the size of a ball bearing (**Figure 9**). However, nuclear material is so dense that a ball bearing–sized piece would have a mass of 226 million tonnes!

The nucleus of an atom contains protons, which have a positive charge equal in magnitude to the negative charge of an electron, and neutrons, which have virtually the same mass as a proton but no charge. **Table 2** summarizes the masses and charges of the electron, proton, and neutron.

Figure 9 If the atomic nucleus were the size of this ball bearing, a typical atom would be the size of this stadium.

Table 2 The Mass and Charge of the Electron, Proton, and Neutron

Particle	Mass (kg)	Charge*
electron (e^-)	9.109×10^{-31}	−1
proton (p^+)	1.673×10^{-27}	+1
neutron (n^0)	1.675×10^{-27}	none

*The magnitude of the charge of the electron and the proton is 1.60×10^{-19} C.

If all atoms are composed of these same particles, why do different atoms have different chemical properties? The answer lies in the number of electrons in each atom. An electrically neutral atom has the same number of electrons as protons. Electrons constitute nearly all of the volume of an atom, but an insignificant amount of its mass. Electrons of different atoms interact when atoms combine to form molecules. The number of electrons in an atom and their arrangement determine the chemical behaviour of the atom. Neutral atoms of different elements have unique numbers of protons and electrons and, therefore, different chemical properties.

What makes the atoms of a certain element radioactive? You know that a neutral atom by definition has an equal number of protons and electrons in its nucleus. However, the number of neutrons in a neutral atom can differ. Two atoms with the same number of protons but different numbers of neutrons are called **isotopes**.

isotopes atoms with the same number of protons but different numbers of neutrons

atomic number (*Z*) the number of protons in a nucleus

mass number (*A*) the total number of protons and neutrons in a nucleus

The nucleus of each carbon isotope in **Figure 10** has the same **atomic number (*Z*)** which is the number of protons. However, each nucleus has a different **mass number (*A*)** which is the total number of protons and neutrons. The symbols for these two isotopes are written as $^{12}_{6}C$ and $^{14}_{6}C$. Notice that the atomic number is written as a subscript and the mass number is written as a superscript. These carbon isotopes can also be written as carbon-12 or C-12, and carbon-14 or C-14. Isotopes have almost identical chemical properties because they have the same number of electrons and protons. In nature, most elements contain mixtures of isotopes. In addition to occurring in nature, radioisotopes can be synthesized from certain elements.

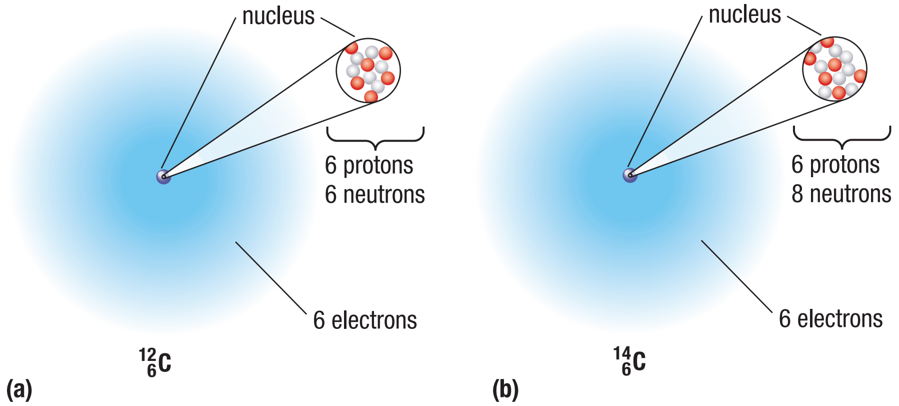


Figure 10 (a) Carbon-12 contains 6 protons and 6 neutrons. (b) Carbon-14 is an isotope of carbon that has 8 neutrons.

radioisotope an isotope that emits radioactive gamma rays and/or subatomic particles (for example, alpha and/or beta particles)

Recall that Henri Becquerel observed the spontaneous emission of radiation by uranium. When the nuclei of isotopes are unstable, as is the case for some uranium isotopes, they are radioactive and are called radioisotopes. A **radioisotope** is an isotope with an unstable nucleus, meaning that the nucleus decays and emits radioactive gamma rays and/or subatomic particles. Scientists and engineers use the radiation emitted by radioisotopes in many applications, including carbon dating, nuclear energy, and medicine. For example, carbon-14 is used in archaeological dating.

The Nature of Matter and Energy

During the first half of the twentieth century, scientists realized that the results of several key experiments were not consistent with the classical theories of physics developed by Isaac Newton and other scientists. To account for the observed behaviour of light and atoms, physicists developed a radical new idea called quantum theory. This new physics provided many surprises, but it also more accurately explains the behaviour of light and matter. WEB LINK

Classical Theories of Light

Light, or light energy, is electromagnetic radiation. Visible light is the portion of this spectrum that can be seen by the human eye. The nature and properties of light have been debated for centuries. Around 300 BCE, Greek philosophers proposed that light existed as a stream of particles. In the seventeenth century, Dutch scientist Christiaan Huygens conducted investigations that led him to theorize that light is a wave. Not all scientists agreed with Huygens. For example, Isaac Newton believed that light was composed of tiny particles, which he called "corpuscles." Investigations continued and new evidence from experiments with refraction, diffraction, and reflection provided a great deal of support for the wave hypothesis proposed by Huygens.

In the mid-nineteenth century, physicist James Maxwell proposed a theory regarding the properties of magnetism, light, and electricity. Maxwell theorized that light could act on charged particles because it existed as an electromagnetic wave made of magnetic and electric fields. Over time, Maxwell's electromagnetic wave theory gained wide acceptance and came to be the classical theory of light. According to Maxwell's theory, light is an electromagnetic wave composed of continuous wavelengths that form a spectrum (**Figure 11**).

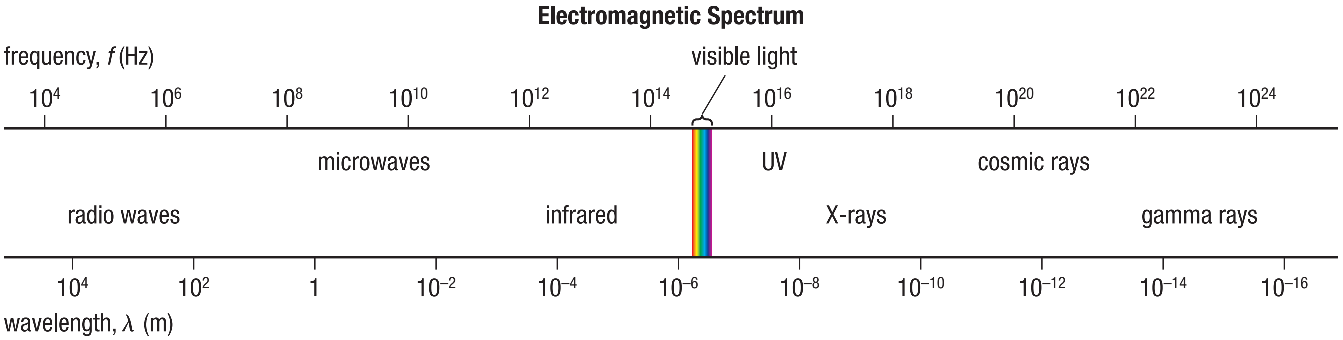


Figure 11 Visible light is only a very narrow band on the electromagnetic spectrum.

At the end of the nineteenth century, matter and energy were considered to be distinct, and unrelated, entities. Matter was thought to be composed of particles that had mass and a specific position in space at a particular time. Light energy was considered to be an electromagnetic wave that had no mass or specific position in space.

However, in 1887 German physicist Heinrich Hertz was attempting to generate electromagnetic waves using induction coils, and instead, discovered the **photoelectric effect**, in which light shining on a metal surface causes the emission of electrons from the metal. Hertz reported the photoelectric effect, but did not attempt to explain it. The discovery of the photoelectric effect had a major impact on the classical theories of light and matter. WEB LINK

photoelectric effect electrons are emitted by matter that absorbs energy from shortwave electromagnetic radiation (for example, visible or UV light)

According to the classical theory of light, the intensity (brightness) of the light shining on the metal should determine the kinetic energy of the electrons emitted. Therefore, the more intense the light, the more energy the emitted electrons should have. However, Hertz's experiments demonstrated that the *frequency* of the light was more important in determining the energy of the emitted electrons (**Figure 12**). Since the classical theory of light and matter could not explain these observations, it began to be viewed as flawed.

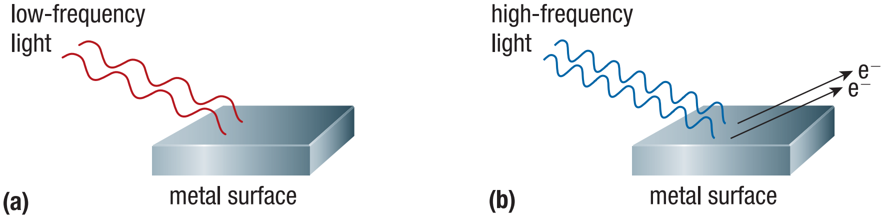


Figure 12 Hertz's experiments showed that light with frequency less than a certain frequency, called the threshold frequency, produces no electrons (a), whereas light with frequency higher than the threshold frequency causes electrons to be emitted from the metal (b).

Investigation **3.1.1**

The Photoelectric Effect (page 179)
Einstein was later able to explain the photoelectric effect through experimentation, for which he received a Nobel Prize. In this investigation, you will observe what Einstein observed, which ultimately led to the modern theory of light and atoms.

Planck's Quantum Hypothesis

Figure 13 Max Planck (1858–1947), at right, is regarded as the founder of quantum theory. He studied the light emitted by hot objects. His experiments led him to hypothesize that energy could be gained or transferred in whole-number multiples.

In 1900, German physicist Max Planck (**Figure 13**) was studying the spectra of the radiant energy emitted by solid bodies (called blackbodies) heated to incandescence (glowing). When a solid is heated to very high temperatures, it begins to glow, first red, then white, then blue. The changes in colour and the corresponding light spectra do not depend on the composition of the solid. The intensity of the light of different colours can be measured and plotted on a graph, to produce a curved line (or energy curve). WEB LINK

Classical physics predicted that the energy curve should go up continuously as temperature increases: physicists thought that matter could absorb or emit any quantity of energy. However, Planck's experiments showed that the curve reached a peak and then decreased. The position of the peak correlated to the temperature and moved toward higher light frequencies as an object became hotter. Compare the positions of the peaks for a red-hot and a white-hot object in **Figure 14**. Now compare these to the curved line that would result as predicted by the classical theory of light.

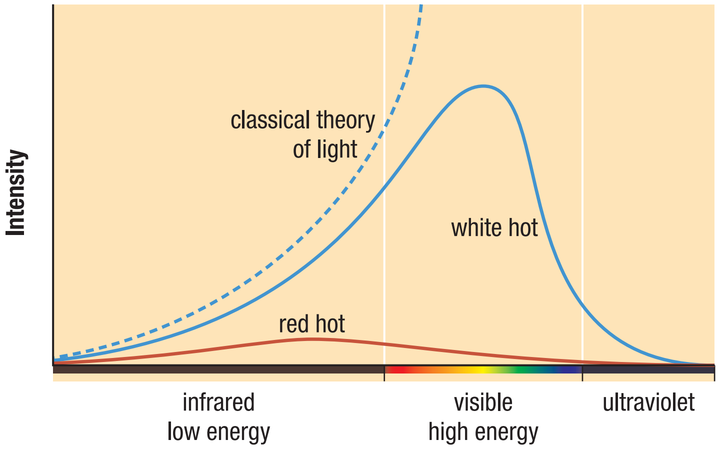


Figure 14 A white-hot wire and a red-hot wire emit light at different colours and intensities. The light emitted does not follow the expected results of the classical theory of light.

Planck accounted for the unexpected results of his heating experiments by postulating that matter can gain or lose energy, E, only in whole-number multiples, according to the equation

$$E = nhf$$

where n is an integer (1, 2, 3, ...), f is the frequency of the radiation and h is Planck's constant. Planck's constant is a constant of nature and has the value 6.63×10^{-34} J·s.

Planck knew that radiation was emitted as atoms vibrated back and forth (oscillated). He hypothesized that the energies from the oscillating atoms in the heated object were multiples of a small quantity of energy. Light was emitted in bursts of this discrete (separate and distinct) quantity of energy rather than as a continuous stream. Albert Einstein later brought Planck's hypothesis to its logical conclusion—the light emitted by a heated solid is quantized. One burst or packet of energy is now known as a **quantum** of energy.

quantum a unit or packet of energy (plural: quanta)

A quantum is a difficult concept. It may help to imagine a quantum of energy as a unit of money. Any value of money can be understood as equal to, for example, a number of pennies, the smallest unit of money. Similarly, that same value of money can be described in terms of other units of money. For example, $2.00 is equal to 200 pennies, but it is also equal to 8 quarters or 20 dimes or 40 nickels. Quanta of light are similar to units of money in that the colours of light emitted are analogous to the value of a particular coin. Infrared light may be thought of as being analogous to a penny, red light to a nickel, blue light to a dime, and ultraviolet light to a quarter.

Heating a solid until it glows in the infrared range is analogous to it emitting pennies of light energy. Similarly, a red-hot solid emits quantities of light energy analogous to nickels, a white-hot solid emits quantities of light energy analogous to dimes, and so on. It is important to keep in mind that there are no intermediate quantities of light energy, just as there are no seven-and-a-half-cent coins.

Planck's results were a surprise to the scientific community. It was now clear that energy can occur only in discrete quanta and, therefore, a system can transfer energy only in whole quanta. Planck's observations (for example, the bell-shaped curves shown in Figure 14) revealed that as the temperature of an object increases, more of the larger quanta and fewer of the smaller quanta of energy are emitted. Also, the colour of the light emitted by a hot object depends on the proportion of the quanta of different energies that are emitted. In this way, light energy seems to have properties similar to particles.

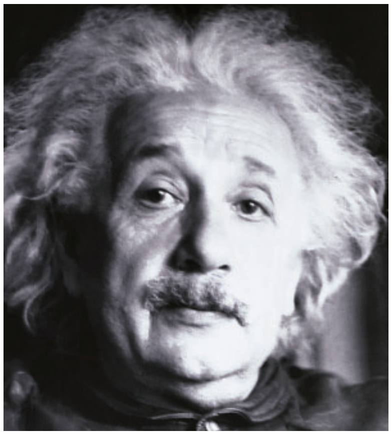


Figure 15 Albert Einstein (1879–1955) received a Nobel Prize in 1921 for a paper explaining the photoelectric effect in terms of quantum theory.

Photons

Investigation and discovery of the photoelectric effect was critical to the development of quantum theory. In 1905, Albert Einstein explained the photoelectric effect by applying Planck's idea of a quantum of energy (**Figure 15**). Einstein suggested that electromagnetic radiation could be viewed as a stream of particles called photons. A **photon** is a unit of light energy. Einstein proposed that an electron was emitted from the surface of the metal because a photon collided with the electron. During the collision, the energy of the photon transferred to the electron. Some of the transferred energy caused the electron to break away from the atom, and the rest was converted to kinetic energy. To free an electron from the atom requires the energy from a minimum of one photon.

photon a unit of light energy

An electron stays in place because of electrostatic forces. If a single electron absorbs a single photon with the right quantity of energy, the electron can escape the metal surface. If a photon does not have enough energy, no electrons can escape the metal no matter how many photons strike it. The kinetic energy of the ejected electrons depends on the frequency of the light used. When the frequency is below a certain level, called the threshold frequency, no electrons are ejected.

Quantum theory has provided explanations for observations, namely, the photoelectric effect and blackbody radiation, that no other theory could explain. For this reason, quantum theory is one of the greatest achievements in modern science. In upcoming sections you will learn about other observations that only quantum theory has been able to explain.

Research This

The Large Hadron Collider—A Smashing Success

Skills: Researching, Analyzing, Communicating, Defining the Issue, Defending a Decision

SKILLS HANDBOOK A5.1

The Large Hadron Collider (LHC) at CERN in Geneva, Switzerland, is the world's most powerful particle accelerator (**Figure 16**). Scientists are using it to investigate how atomic and subatomic particles are structured. A Toroidal LHC ApparatuS (ATLAS) was built to detect the particles and energy present after protons collide. Canadian scientists, including University of Alberta professor James Pinfold, have been working on the ATLAS project alongside scientists from across the globe.

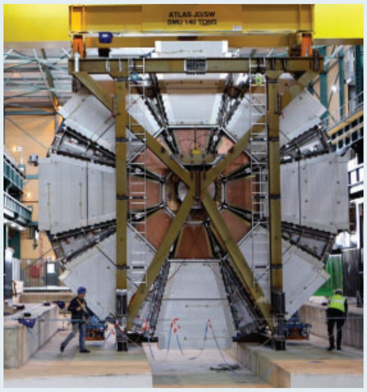


Figure 16

1. Research Canada's participation in the ATLAS project.
2. Research string theory and the grand unified theory.

A. Briefly outline the premises of string theory and the grand unified theory. K/U
B. An enormous amount of money has been spent on LHC and ATLAS projects. Do you think it is worth it? What are the benefits to science and society? T/I A
C. Summarize your research and choose an appropriate, interesting presentation format to share what you learned. T/I C A
D. Should further investments in these projects and this type of research continue? Explain your reasoning. T/I A

WEB LINK

3.1 Review

Summary

- According to modern atomic theory, the atom has a small, dense nucleus containing protons and neutrons. Electrons reside outside the nucleus in the relatively large remaining atomic volume.
- The atomic number, *Z*, is the number of protons in an atom's nucleus. The mass number, *A*, is the total number of protons and neutrons in an atom's nucleus.
- Isotopes of an element have the same atomic number but different mass numbers. Radioisotopes have unstable nuclei that decay and emit radiation.
- According to quantum theory, electromagnetic energy is not continuous; instead, energy exists as packets or quanta, called photons.

Questions

1. For each of the following atoms, identify
   (a) the number of protons and neutrons in the nucleus
   (b) the number of electrons present in the neutral atom for that element K/U
   (i) ^{79}Br (iv) ^{133}Cs
   (ii) ^{81}Br (v) ^{3}H
   (iii) ^{239}Pu (vi) ^{56}Fe
2. Write the atomic symbol ($^{A}_{Z}\text{X}$) for each of the following isotopes: K/U
   (a) $Z = 8$; number of neutrons $= 9$
   (b) the isotope of chlorine in which $A = 37$
   (c) $Z = 27$; $A = 60$
   (d) number of protons $= 26$; number of neutrons $= 31$
   (e) the isotope of I with a mass number of 131
   (f) $Z = 3$; number of neutrons $= 4$
3. For each of the following ions, indicate the number of protons and electrons the ion contains: K/U
   (a) Ba^{2+} (d) Rb^{+}
   (b) Zn^{2+} (e) Co^{3+}
   (c) N^{3-} (f) Te^{2-}
4. What is the atomic symbol of an ion with
   (a) 16 protons, 18 neutrons, and 18 electrons?
   (b) 16 protons, 16 neutrons, and 18 electrons? K/U
5. Explain the photoelectric effect. K/U
6. Use a series of diagrams and a few point-form notes to create a flow chart that summarizes the history of atomic theory, beginning with Dalton and ending with Einstein. K/U C
7. Copy **Table 3** in your notebook and complete it. K/U C

Table 3

Symbol	Protons	Neutrons	Electrons	Net charge
$^{238}_{92}\text{U}$				0
	20	20		+2
	23	28	20	
$^{89}_{39}\text{Y}$				0
	35	44	36	
	26	33		+3
	13	14	10	

8. Scientists record their experimental observations and conclusions in a lab book or journal. Write a journal entry that would reflect the results of Rutherford's gold foil experiment. K/U T/I C
9. According to the latest developments in nuclear theory, protons and neutrons are composed of smaller subatomic particles called quarks. Research quarks and their properties K/U T/I A
   (a) How are quarks named?
   (b) Describe the composition of a proton, and explain how its composition accounts for its charge.
   (c) Which Canadian scientist provided some of the first supporting evidence for the existence of quarks and received a share of the Nobel Prize?
10. The newly updated periodic table includes pie charts for each element. Each pie chart represents the isotopes of that element found in nature, and each pie segment represents the abundance of that isotope in nature. Evaluate the usefulness of this new format compared to the classic table format. K/U T/I A

WEB LINK

Bohr's Model of the Atom

3.2

If you have seen a fireworks display, then you have experienced a fantastic example of chemistry in action. The different colours that appear in fireworks arise when electrons in the atoms of various chemicals become excited by absorbing electrical or thermal energy, and then emit that energy at various wavelengths. This seemingly simple explanation comes from decades of work on the structure of the atom by some of the world's most talented scientists.

Limits of the Rutherford Model of the Atom

In the previous section you read about some of the experiments that led to the discovery of the electron, proton, and neutron, and to Ernest Rutherford's model of the atom. The model of the atom proposed by Rutherford predicted that electrons move around the nucleus of the atom, much like planets orbit the Sun. This idea seemed reasonable because even though the Sun's gravity pulls planets toward it, this pull is counteracted by the planets' movement. It seemed reasonable that electrons orbiting an atomic nucleus would behave in the same way.

However, it became apparent that there was a problem with this idea. A body that is moving in an orbit is constantly changing direction, and a body that is changing direction or speed is accelerating. Physicists had demonstrated that when a charged particle accelerates, it continuously produces electromagnetic radiation (emitted as photons). According to classical light theory, an electron travelling in an orbit emits energy as photons and, therefore, loses energy. If an electron loses energy as it orbits, it should spiral in toward the positively charged nucleus (**Figure 1**). Since the electron is negatively charged and opposite charges attract, the atom would eventually collapse. However, this prediction is not supported by evidence. Generally, most atoms are stable and do not appear to be collapsing. This suggests that, although electrons are constantly moving, they do not lose energy. Rutherford's model, therefore, is not able to explain the stability of atoms.

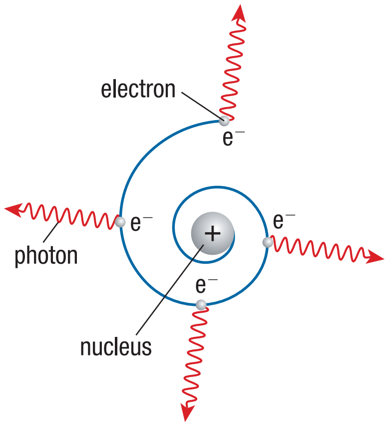


Figure 1 An electron accelerating around the nucleus would continuously emit electromagnetic radiation and lose energy. Therefore, it would eventually fall into the nucleus and the atom would collapse. However, this is not consistent with real-world observations.

Atomic Spectra

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spectroscopy the analysis of spectra to determine properties of their source

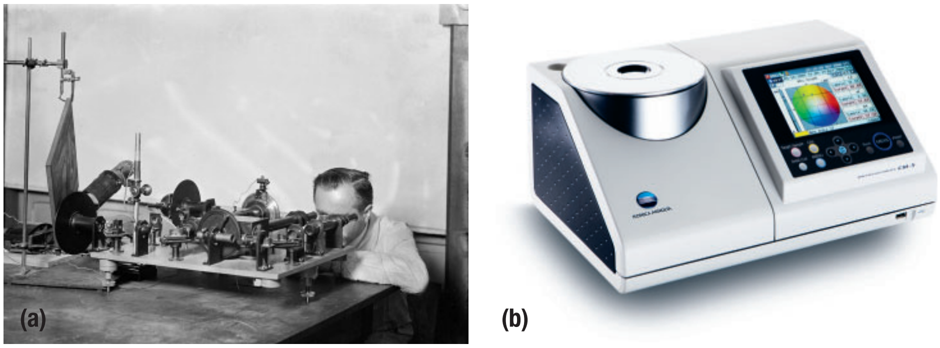

Figure 2 (a) Early spectroscopes used a candle and a gas lamp as light sources and focused light using a prism. (b) Modern spectrophotometers have a sealed area for the sample that does not allow interfering light to enter the unit, and can be adjusted to allow analysis at different wavelengths.

The earliest analytical instrument invented expressly for spectroscopy was a spectroscope similar to the one shown in Figure 2(a). Robert Bunsen and Gustav Kirchhoff invented the spectroscope to use in the first spectroscopy investigations, which they conducted in 1859. They viewed and analyzed the spectra produced by emission of energy by various substances, especially elements. As with most fields of scientific study, advances in spectroscopy dovetailed with advances in technology. Investigations of light emitted from excited substances led to further developments in atomic theory.

The Atomic Spectrum of the Hydrogen Atom

The atomic spectrum of the hydrogen atom played an important role in advancing atomic theory. Hydrogen gas, $H_2(g)$, is a molecular element. When a high-energy spark is applied to a sample of hydrogen gas, the hydrogen molecules absorb energy, which breaks some of the H–H bonds. The resulting hydrogen atoms are excited: they contain excess energy. The excited hydrogen atoms release this excess energy by emitting light of various wavelengths. When this light is passed through a spectroscope, it forms an emission spectrum. An **emission spectrum** is the spectrum (or pattern of bright lines) seen when the electromagnetic radiation of a substance is passed through a spectrometer.

Two types of emission spectra can be produced, depending on the nature of the source. A **continuous spectrum** contains every wavelength in a particular region of the electromagenetic spectrum. For example, when white light passes through a prism, a continuous spectrum appears (**Figure 3(a)**) containing all the wavelengths of visible light. In contrast, a **line spectrum** contains only particular wavelengths, and arises when excited electrons emit energy. **Figure 3(b)** shows the line spectrum of the hydrogen atom. Each coloured band corresponds to a discrete wavelength.

emission spectrum the spectrum of electromagnetic radiation emitted by an atom; results when an atom is returned to a lower energy state from a higher energy state

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line spectrum an emission spectrum that contains only those wavelengths characteristic of the element being studied

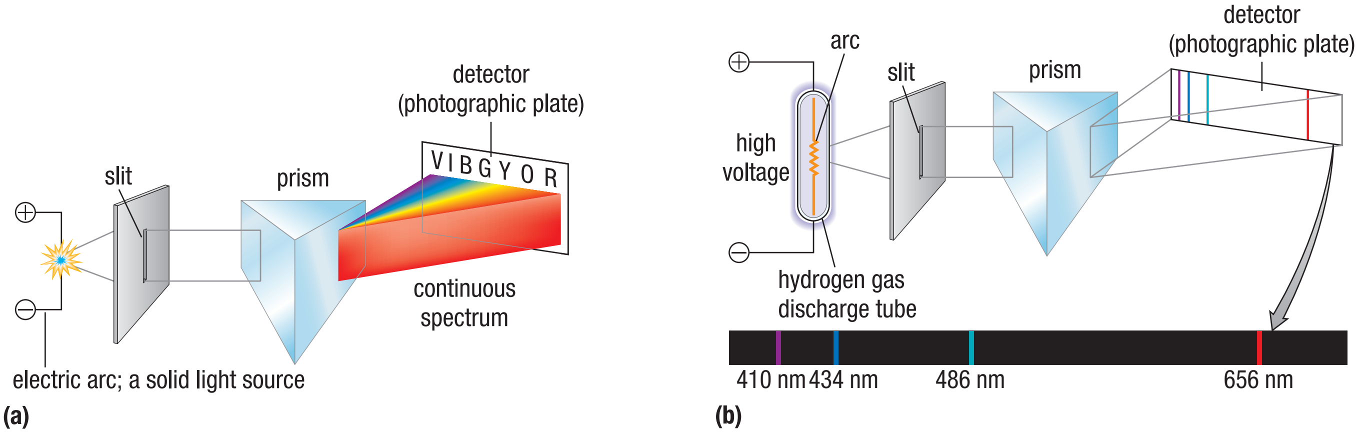

Figure 3 (a) A continuous spectrum contains all wavelengths of visible light (indicated by the initial letters of the colours of the rainbow). (b) The line spectrum for the hydrogen atom contains only a few discrete wavelengths.

Investigation **3.2.1**

Bright-Line Spectra (page 180)
All atoms absorb and emit electromagnetic radiation. In this investigation, you will observe the visible spectra of various substances.

The investigations of Bunsen, Kirchhoff, and other scientists in the late nineteenth century revealed that each element has its own unique line spectrum. The spectra of the known elements were quickly catalogued. The line spectrum is like a fingerprint of a specific element. If a new spectrum was found, it provided evidence of a new element. In fact, the elements cesium and rubidium were discovered within a year of the invention of spectroscopy. There are many applications of line spectra. For example, astronomers use line spectra to identify the composition of stars.

The unique line spectrum of the hydrogen atom is significant to atomic theory because it indicates that the electron of the hydrogen atom can exist only at discrete energy levels. In other words, the energy of the electron in the hydrogen atom is quantized. This observation is consistent with Planck's quantum theory. The particular wavelengths of light emitted by the electrons of hydrogen atoms are produced by changes in energy. When excited electrons in hydrogen atoms move to a lower energy level, they emit a photon of light. This is true of excited electrons in other atoms as well.

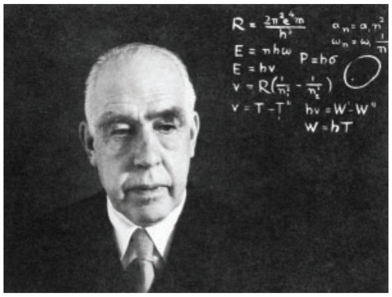

Figure 4 Niels Bohr (1885–1962) developed a quantum model for the hydrogen atom and, even though his model was later proved to be incorrect, Bohr was awarded the Nobel Prize in Physics in 1922.

The Bohr Model of the Atom

Niels Bohr was a Danish physicist who studied under J.J. Thomson at Cambridge University in the United Kingdom (**Figure 4**). In 1913, Bohr used the emission spectrum of the hydrogen atom to develop a quantum model for the hydrogen atom. He knew that his model had to account for the experimental evidence provided by spectroscopy: that electrons could have only particular discrete energy levels. Bohr accounted for this data by proposing that electrons could move only in specific orbits around the nucleus. He assigned each orbit a specific energy level, and postulated that the energy level of an orbit increased with its distance from the nucleus. When an electron gained more energy (for example, became excited), it could move into an orbit farther from the nucleus. Although Bohr's atomic model did not explain *why* electrons behaved this way, it was consistent with the observed line spectrum of the hydrogen atom. **Figures 5(a)** and **5(b)** show electron transitions in the Bohr model for the hydrogen atom. Compare these to the line spectrum of the hydrogen atom, shown in **Figure 5(c)**.

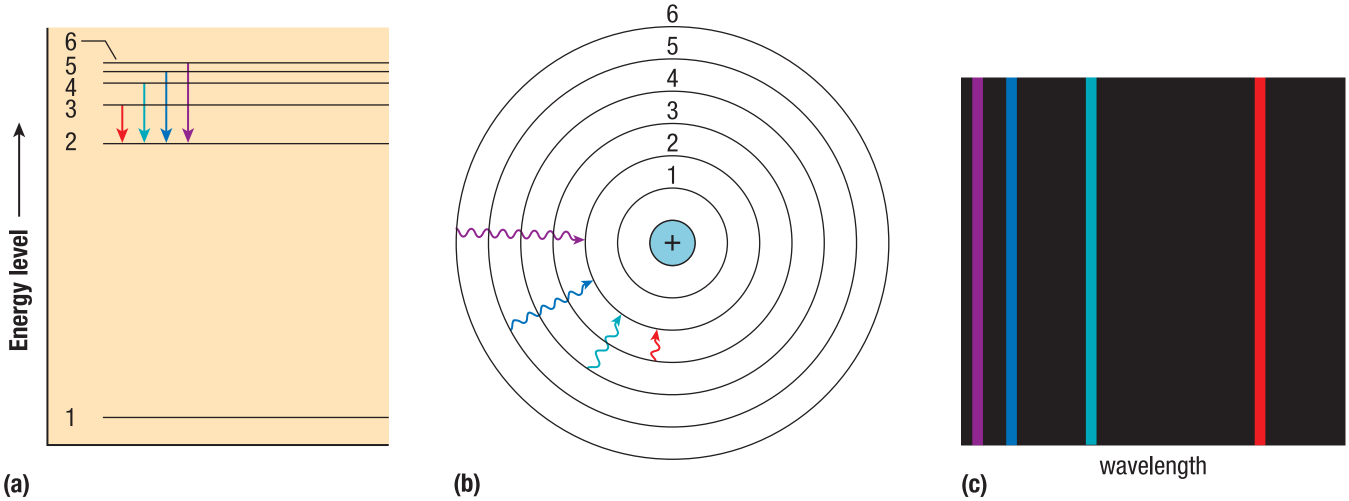

Figure 5 Electron transitions in the Bohr model for the hydrogen atom. An energy-level diagram (a) and an orbit-transition diagram (b), each showing electron transitions in the Bohr model for the hydrogen atom. Both of these account for the observed line spectrum of the hydrogen atom (c). The orbits are not drawn to scale. The lines in the visible region of the spectrum correspond to transitions from higher levels to level 2.

To help you envision how the orbits in Bohr's model relate to the line spectrum of the hydrogen atom, imagine a ball sitting on a staircase. Since the ball can only be positioned on a stair, it can only ever be found at specific distances from the ground. Applying Bohr's theory to this analogy, the higher up the staircase the ball is, the more potential energy it has. If the ball moves up the staircase (that is, to a higher energy level), it gains potential energy. If it moves down the staircase (that is, to a lower energy level), it loses potential energy. The ball in **Figure 6** is moving down the staircase, so it is losing potential energy.

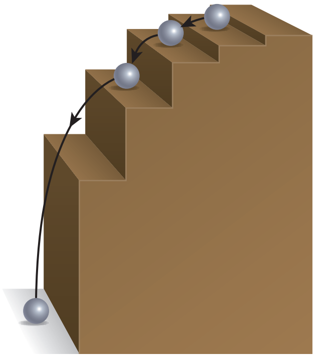

Figure 6 The position of the ball on the stairs determines its quantity of potential energy.

In the Bohr model of the atom, the electron is analogous to the ball in Figure 6 and the orbits are analogous to the different stairs. As with the ball on the stairs, electrons can only be at specific positions (energy levels or orbits) in relation to the nucleus of the atom. In **Figure 7**, the radius, r_x, of each orbit is analogous to the height of a stair from the floor in Figure 6. The electron gains or loses potential energy by moving from one position (orbit) to another.

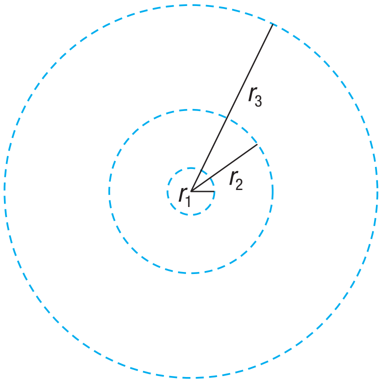

Figure 7 The position of an electron relative to the nucleus of an atom determines its quantity of potential energy.

transition the movement of an electron from one energy level to another

ground state the lowest energy state for an atom

The movement of an electron from one energy level to another is called a **transition**. During a transition to a higher energy level, an electron absorbs a specific quantity of energy, such as when it is struck by a photon. During a transition to a lower energy level, an electron emits a photon of a particular quantity of energy. The lowest possible energy state for an atom is called the **ground state**. There are no excited electrons in the ground state.

Successes and Failures of the Bohr Model

Recall that in a Bohr-Rutherford diagram, the numbers of protons, p^+, and neutrons, n^0, are noted in the nucleus. The concentric circles represent the different energy levels of electrons, and each contains a specific number of electrons. In an attempt to be consistent with observations related to the quantization of energy in atoms, Bohr's model assumes that each energy level can hold a maximum number of electrons. For the first 18 elements in the periodic table, the Bohr model predicts that the first, second, and third orbits can contain a maximum of 2, 8, and 18 electrons, respectively, and that the lower energy levels must fill first. The corresponding Bohr–Rutherford diagrams are especially useful for the first 20 elements of the periodic table, in which atoms of all the elements are arranged according to the number of protons and electrons in a neutral atom. Beyond the first 20 elements, however, Bohr–Rutherford diagrams become too cumbersome to be useful.

Bohr's model of the atom initially appeared to be very promising for understanding the behaviour of atoms because it appeared to be consistent with observed chemical and physical properties. For example, the energy levels Bohr calculated for the electron in the hydrogen atom were very similar to values obtained from the hydrogen atom's emission spectrum by spectroscopy. However, the electron energies predicted by Bohr's model were not consistent with observed data for atoms with more than one electron (**Figure 8**). Scientists eventually concluded that Bohr's model did not fully describe the structure of an atom. Still, the Bohr model is of great historic importance because it included the quantization of energy in atoms and paved the way for later theories. Bohr–Rutherford diagrams are so widely recognized, however, that it can be easy to forget that according to current theories of the atom, electrons do not actually orbit the nucleus.

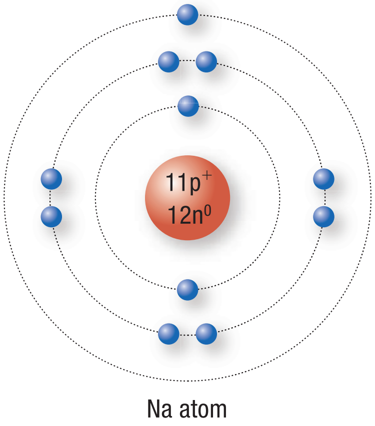

Figure 8 Electron energies for a neutral sodium atom, as predicted by the Bohr–Rutherford model. Current atomic theories do not support this arrangement of electron energies.

3.2 Review

Summary

- Spectroscopy is the study of light emitted by excited sources.
- Spectroscopy of excited gaseous elements led to the discovery of line spectra, which are unique to specific atoms and elements.
- Line spectra are consistent with Planck's quantum theory.
- Niels Bohr proposed a model of the atom that was consistent with experimental observations of the line spectrum of the hydrogen atom.
- In the Bohr model of the atom, electrons travel in circular orbits of quantized energy around the atomic nucleus.

Questions

1. Explain the main weakness with the Rutherford model of the atom and how Bohr addressed it. K/U
2. Describe what happens when atoms or molecules absorb light. K/U
3. Scientists use emission spectra to confirm the presence of an element in materials. Explain why this is possible. K/U
4. Using a series of diagrams, show what happens to the electrons of an atom when they are excited and how they can produce spectra that can be viewed in a spectroscope. K/U C
5. Explain why the emission spectrum of an atom or molecule depends on its arrangement of electrons. K/U
6. The emission spectrum of an element is unique. K/U A
   (a) Explain why the emission spectrum is sometimes referred to as an element's fingerprint.
   (b) Give a real-life example of how the emission spectrum could be used to help determine the nature of an unknown chemical.
   (c) Would using an emission spectrum be considered qualitative or quantitative analysis? Explain your answer.
7. In both ground-state sodium and magnesium atoms, the electrons are found in the first, second, and third energy levels. These electrons will jump to higher energy levels when energy is applied, and then fall back down, releasing their energy and giving off a spectrum. Why do you think the spectra for sodium and magnesium are not the same? Why might you think they would be the same? K/U T/I
8. (a) What is spectroscopy?
   (b) Discuss how spectroscopy was useful to the development of early atomic theory. K/U
9. (a) Describe the Bohr model of the atom, including quantization and emission spectra.
   (b) Discuss the successes and failures of the Bohr model. K/U
10. Why is the work of Bohr and Rutherford on atomic theory sometimes referred to collectively as the Bohr–Rutherford model? K/U
11. (a) What part of the original Bohr model still seems to be well supported by experimental evidence?
    (b) Identify one weakness in Bohr's atomic theory. K/U
12. When drawing the energy levels of an atom with one electron, your friend draws the diagram shown in **Figure 9**. Describe the line spectra that will be produced by an atom with this arrangement of energy levels. Provide evidence that this is not an accurate representation of the energy levels in an atom. K/U T/I

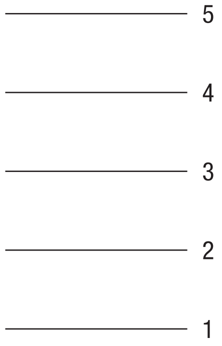

Figure 9

13. Using a graphic organizer or a chart,
    (a) compare and contrast Thomson's and Bohr's models of the atom
    (b) compare and contrast Bohr's and Rutherford's models of the atom K/U C
14. Summarize the evolution of atomic theory, starting with Thomson and ending with Bohr. Use a labelled diagram or a flow chart. (You may want to add this information to your answer to Question 6 in Section 3.1 to create a complete flow chart showing the development of atomic theory.) K/U C

Bohr's Model of the Atom

3.2

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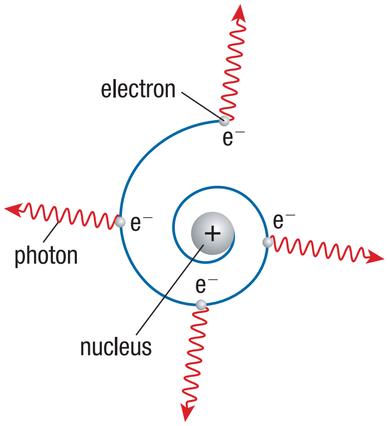

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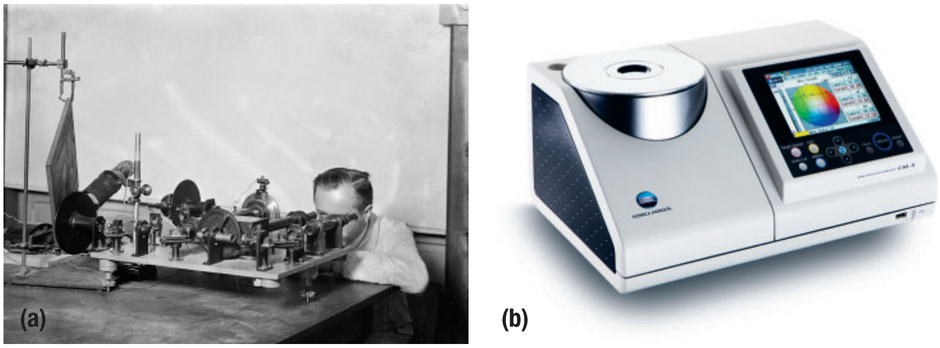

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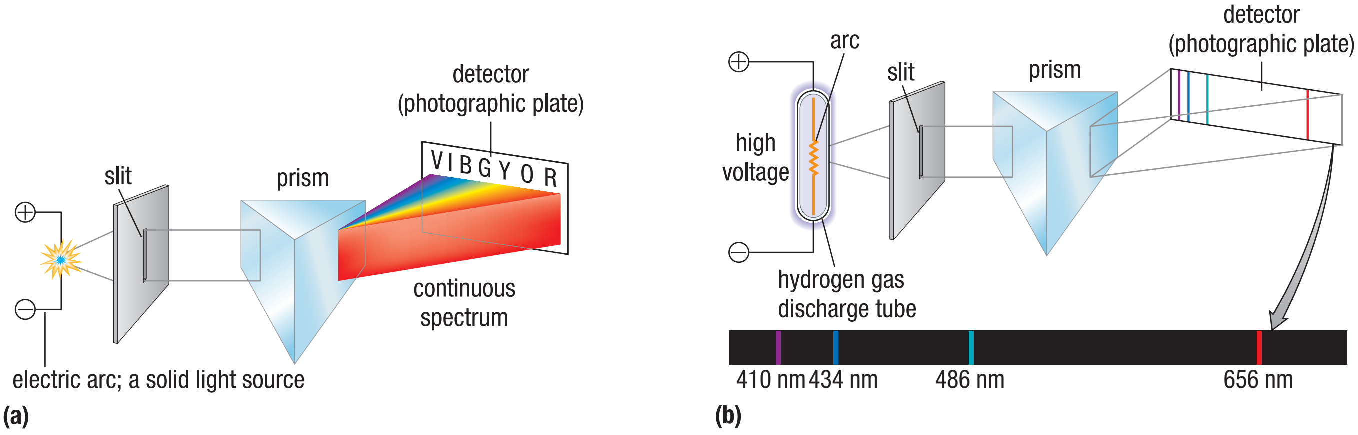

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Investigation **3.2.1**

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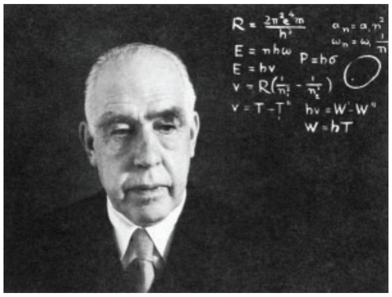

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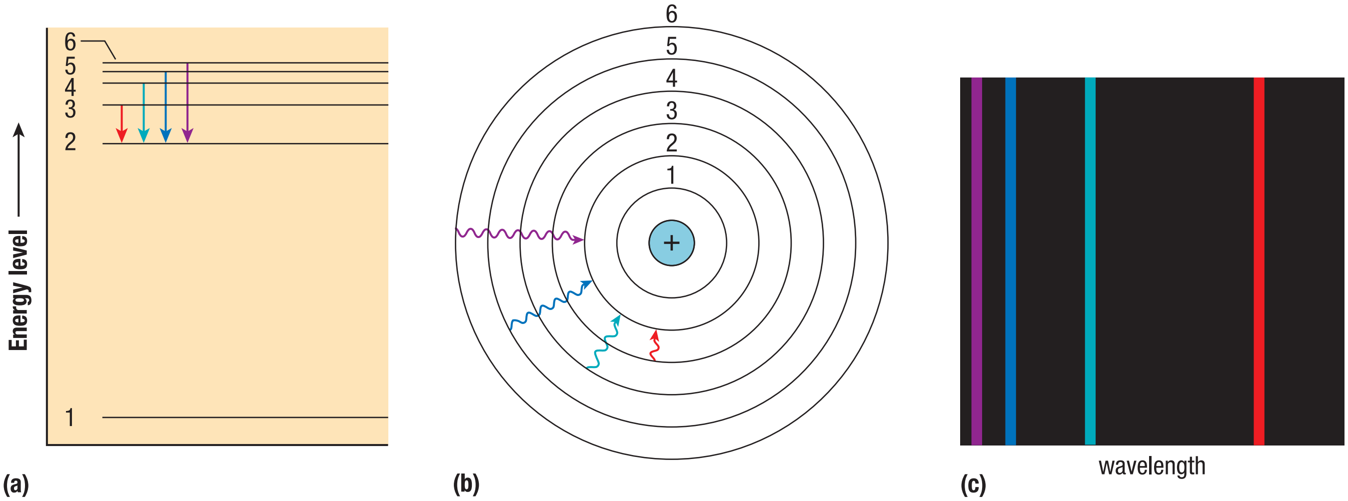

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To help you envision how the orbits in Bohr's model relate to the line spectrum of the hydrogen atom, imagine a ball sitting on a staircase. Since the ball can only be positioned on a stair, it can only ever be found at specific distances from the ground. Applying Bohr's theory to this analogy, the higher up the staircase the ball is, the more potential energy it has. If the ball moves up the staircase (that is, to a higher energy level), it gains potential energy. If it moves down the staircase (that is, to a lower energy level), it loses potential energy. The ball in **Figure 6** is moving down the staircase, so it is losing potential energy.

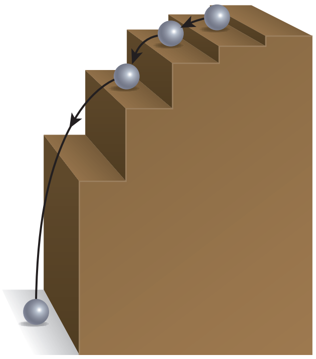
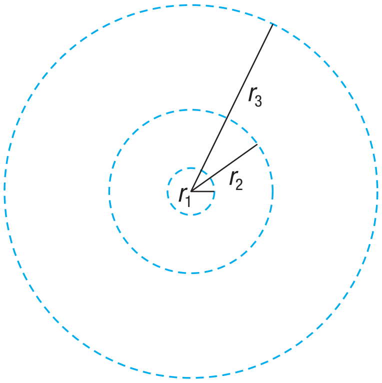


Figure 6 The position of the ball on the stairs determines its quantity of potential energy.

In the Bohr model of the atom, the electron is analogous to the ball in Figure 6 and the orbits are analogous to the different stairs. As with the ball on the stairs, electrons can only be at specific positions (energy levels or orbits) in relation to the nucleus of the atom. In **Figure 7**, the radius, r_x, of each orbit is analogous to the height of a stair from the floor in Figure 6. The electron gains or loses potential energy by moving from one position (orbit) to another.



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ground state the lowest energy state for an atom

The movement of an electron from one energy level to another is called a **transition**. During a transition to a higher energy level, an electron absorbs a specific quantity of energy, such as when it is struck by a photon. During a transition to a lower energy level, an electron emits a photon of a particular quantity of energy. The lowest possible energy state for an atom is called the **ground state**. There are no excited electrons in the ground state.

Successes and Failures of the Bohr Model

Recall that in a Bohr-Rutherford diagram, the numbers of protons, p^+, and neutrons, n^0, are noted in the nucleus. The concentric circles represent the different energy levels of electrons, and each contains a specific number of electrons. In an attempt to be consistent with observations related to the quantization of energy in atoms, Bohr's model assumes that each energy level can hold a maximum number of electrons. For the first 18 elements in the periodic table, the Bohr model predicts that the first, second, and third orbits can contain a maximum of 2, 8, and 18 electrons, respectively, and that the lower energy levels must fill first. The corresponding Bohr–Rutherford diagrams are especially useful for the first 20 elements of the periodic table, in which atoms of all the elements are arranged according to the number of protons and electrons in a neutral atom. Beyond the first 20 elements, however, Bohr–Rutherford diagrams become too cumbersome to be useful.

Bohr's model of the atom initially appeared to be very promising for understanding the behaviour of atoms because it appeared to be consistent with observed chemical and physical properties. For example, the energy levels Bohr calculated for the electron in the hydrogen atom were very similar to values obtained from the hydrogen atom's emission spectrum by spectroscopy. However, the electron energies predicted by Bohr's model were not consistent with observed data for atoms with more than one electron (**Figure 8**). Scientists eventually concluded that Bohr's model did not fully describe the structure of an atom. Still, the Bohr model is of great historic importance because it included the quantization of energy in atoms and paved the way for later theories. Bohr–Rutherford diagrams are so widely recognized, however, that it can be easy to forget that according to current theories of the atom, electrons do not actually orbit the nucleus.

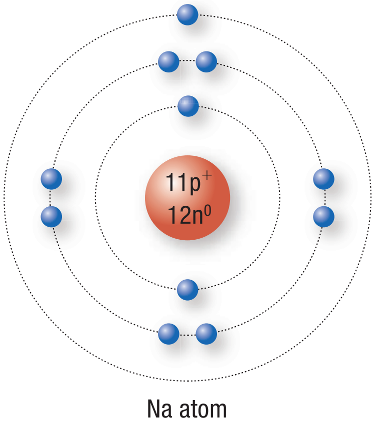

Figure 8 Electron energies for a neutral sodium atom, as predicted by the Bohr–Rutherford model. Current atomic theories do not support this arrangement of electron energies.

3.2 Review

Summary

- Spectroscopy is the study of light emitted by excited sources.
- Spectroscopy of excited gaseous elements led to the discovery of line spectra, which are unique to specific atoms and elements.
- Line spectra are consistent with Planck's quantum theory.
- Niels Bohr proposed a model of the atom that was consistent with experimental observations of the line spectrum of the hydrogen atom.
- In the Bohr model of the atom, electrons travel in circular orbits of quantized energy around the atomic nucleus.

Questions

1. Explain the main weakness with the Rutherford model of the atom and how Bohr addressed it. K/U
2. Describe what happens when atoms or molecules absorb light. K/U
3. Scientists use emission spectra to confirm the presence of an element in materials. Explain why this is possible. K/U
4. Using a series of diagrams, show what happens to the electrons of an atom when they are excited and how they can produce spectra that can be viewed in a spectroscope. K/U C
5. Explain why the emission spectrum of an atom or molecule depends on its arrangement of electrons. K/U
6. The emission spectrum of an element is unique. K/U A
   (a) Explain why the emission spectrum is sometimes referred to as an element's fingerprint.
   (b) Give a real-life example of how the emission spectrum could be used to help determine the nature of an unknown chemical.
   (c) Would using an emission spectrum be considered qualitative or quantitative analysis? Explain your answer.
7. In both ground-state sodium and magnesium atoms, the electrons are found in the first, second, and third energy levels. These electrons will jump to higher energy levels when energy is applied, and then fall back down, releasing their energy and giving off a spectrum. Why do you think the spectra for sodium and magnesium are not the same? Why might you think they would be the same? K/U T/I
8. (a) What is spectroscopy?
   (b) Discuss how spectroscopy was useful to the development of early atomic theory. K/U
9. (a) Describe the Bohr model of the atom, including quantization and emission spectra.
   (b) Discuss the successes and failures of the Bohr model. K/U
10. Why is the work of Bohr and Rutherford on atomic theory sometimes referred to collectively as the Bohr–Rutherford model? K/U
11. (a) What part of the original Bohr model still seems to be well supported by experimental evidence?
    (b) Identify one weakness in Bohr's atomic theory. K/U
12. When drawing the energy levels of an atom with one electron, your friend draws the diagram shown in **Figure 9**. Describe the line spectra that will be produced by an atom with this arrangement of energy levels. Provide evidence that this is not an accurate representation of the energy levels in an atom. K/U T/I

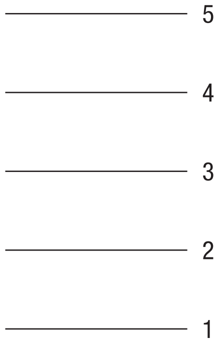

Figure 9

13. Using a graphic organizer or a chart,
    (a) compare and contrast Thomson's and Bohr's models of the atom
    (b) compare and contrast Bohr's and Rutherford's models of the atom K/U C
14. Summarize the evolution of atomic theory, starting with Thomson and ending with Bohr. Use a labelled diagram or a flow chart. (You may want to add this information to your answer to Question 6 in Section 3.1 to create a complete flow chart showing the development of atomic theory.) K/U C

3.3

The Quantum Mechanical Model of the Atom

LEARNING **TIP**

What Is Quantum Mechanics?
Classical mechanics is the branch of physics that studies the motion of macroscopic objects. Quantum mechanics is the study of motion at the atomic level, where the laws of classical mechanics do not apply because particles behave like waves.

Weaknesses in theories and models provide opportunities for science to improve. It is impossible to devise a perfect theory or model the first time around. Instead, science usually involves years and years of revisions and new discoveries. Science is constantly changing by identifying and improving on weaknesses. The success of the Bohr atomic model was important because it showed that electrons exist in discrete energy levels. Also, it explained experimental observations of line spectra in terms of quantum theory. But there were weaknesses in this model that other scientists identified, which paved the way for the complete development of the quantum model of the atom.

By the mid-1920s, it had become apparent that the Bohr model could not explain and make predictions about multi-electron atoms. A new approach was needed. Three physicists were at the forefront of this effort: Erwin Schrödinger, Louis de Broglie, and Werner Heisenberg. The approach they developed to explain properties of matter is called wave mechanics or, more commonly, **quantum mechanics**. CAREER LINK

quantum mechanics the application of quantum theory to explain the properties of matter, particularly electrons in atoms

Schrödinger's Standing Wave

Louis de Broglie, a French physicist, originated the idea that the electron, previously considered just a particle, has wave properties. Pursuing this line of reasoning, Erwin Schrödinger, an Austrian physicist, decided to approach the problem of atomic structure by focusing on the wave properties of the electron. To Schrödinger and de Broglie, an electron bound to a nucleus in an atom resembled a standing wave, so they began research on a description of the atom based on wave behaviour instead of particle behaviour.

The strings on instruments such as guitars and violins are attached at both ends. When you pluck the string, it vibrates and produces a musical tone. The waves produced by the plucking are standing waves. They are called "standing" because they appear to be stationary. The motions of the string are a combination of simple waves of the type shown in **Figure 1**.

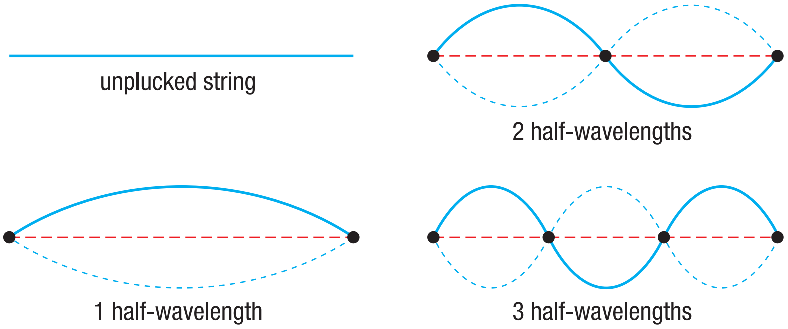

Figure 1 The standing waves caused by the vibration of a guitar string fastened at both ends. Each black dot represents a node (a point of zero displacement), which never moves.

The black dots in Figure 1 represent the nodes, or points, of zero lateral (sideways) displacement for a given wave. Between two nodes, at the point where the amplitude of the wave is at its maximum, is the antinode. Note that there are limitations on the allowed wavelengths of the standing wave. Each end of the string is fixed, so there is always a node at each end. This means that there must be a whole number of half-wavelengths in any of the allowed motions of the string.

Figure 2 shows how standing waves can be produced by a wave generator.

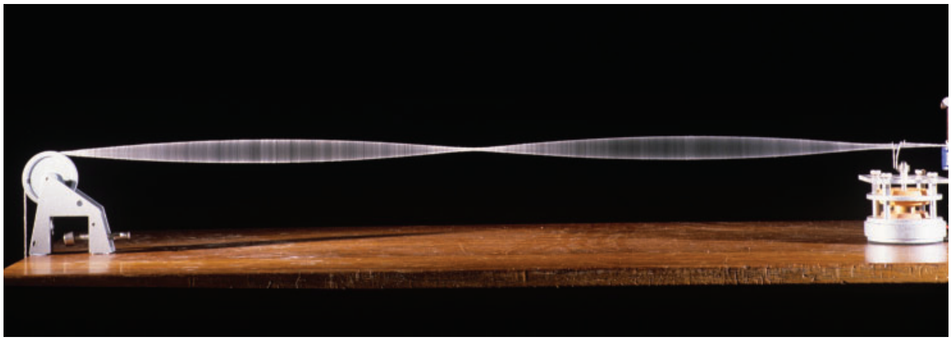

Figure 2 This wave generator is set to produce standing waves that are two half-wavelengths (one wavelength) long.

Mini **Investigation**

Modelling Standing Electron Waves

Skills: Performing, Observing, Analyzing, Evaluating, Communicating

SKILLS HANDBOOK A2.3

Schrödinger's standing waves can be simulated with a mechanical model. A mechanical oscillator causes a loop of wire to vibrate at varying frequencies. Creating vibrations at one point along the wire causes waves throughout the remainder of the wire. This activity is like holding the edge of a stretched Slinky and moving it up and down to produce waves along it. When waves return toward the original direction, they encounter other waves: If they meet constructively, there will be an increase in amplitude. If they meet destructively, there will be a decrease in amplitude. Standing waves result in stationary nodes (no amplitude) and antinodes (at maximum amplitude).

Equipment and Materials: oscillator; stand; loop of wire

When unplugging the oscillator, pull on the plug, not the cord.

Ask your teacher to check the attachment of the wire to the oscillator.

1. Position the oscillator on a laboratory stand. Attach the wire. Position the wire so that its loop is horizontal.
2. Turn the frequency as low as it will go. Plug in the oscillator, then turn it on.
3. Increase the frequency a little. Observe the changes in the waves on the wire.
4. Increase the frequency setting slowly until you can no longer see the nodes and antinodes.
5. Decrease the frequency slowly to the starting point. Observe the simulation in reverse order.
6. Repeat this procedure as necessary.

A. Describe what the nodes and antinodes look like. K/U T/I

B. Do all frequencies result in standing wave patterns? Explain. K/U T/I

C. List the number of nodes and antinodes you were able to observe. K/U T/I

D. How do the waves produced by the oscillator compare with waves in an atom? What are some limitations of the standing wave model of the atom? K/U T/I A

Schrödinger and de Broglie took the idea of standing waves and applied it to the electron in a hydrogen atom. In their model, the electron is a circular standing wave around the nucleus (**Figure 3**). This circular standing wave consists of wavelengths that are multiples of whole numbers ($n = 1, 2, 3, 4, \ldots$). Only certain circular orbits have a circumference into which a whole number of wavelengths can fit.

Any other orbits of the standing electron wave are not allowed because they would cause the standing wave to cancel out or collapse, that is, undergo destructive interference (Figure 3(c)). This model seemed like a possible explanation for the observed quantization of the hydrogen atom: the whole-number multiples of wavelengths correspond to multiples of fixed quanta of energy that the electron can have in the hydrogen atom. However, the new question that this model raised was this: where is the electron located in the hydrogen atom?

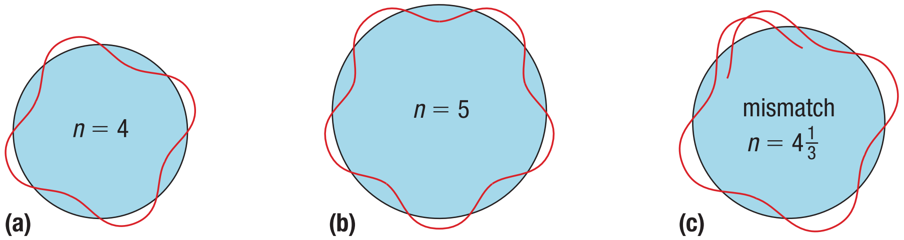

Figure 3 The hydrogen electron visualized as a standing wave around the nucleus. In (a) and (b), the circumference of a particular circular orbit corresponds to a whole number of wavelengths. (c) Otherwise, destructive interference occurs. This model is consistent with the idea that only certain electron energies are allowed, because the atom is quantized. Although this idea encouraged scientists to use a wave theory, it does not mean that the electron travels in circular orbits around the nucleus.

Orbitals and Probability Distributions

Schrödinger's work on quantum mechanics led to his development of a mathematical equation, called the Schrödinger wave equation, that could be used to calculate electron energy levels. If an electron has a definable energy, then it can be localized in an **orbital**, which is the region around the nucleus where there is a high probability of finding an electron. But how can you locate something as small as an electron?

orbital the region around the nucleus where an electron has a high probability of being found

Werner Heisenberg, who studied with Bohr, came up with a statistical approach for locating electrons. To measure the location and speed of an object, you must be able to observe it. Life-sized objects are easy to locate because you can see them. You can determine both the speed and the location of a moving car using a radar gun and a GPS unit. For atomic-sized particles and smaller, any attempt to probe them changes their position, direction of travel, or both. This idea formed the basis of Heisenberg's uncertainty principle. Heisenberg demonstrated using mathematics that there are limits to knowing both where a subatomic particle is and its speed at a given time. According to **Heisenberg's uncertainty principle**, it is therefore impossible to simultaneously know the exact position and speed of an electron. The best we can do is to describe the probability of finding an electron in a specific location.

Heisenberg's uncertainty principle the idea that it is impossible to know the exact position and speed of an electron at a given time

An electron orbital is analogous to students at school moving from classroom to classroom during a scheduled break. The students are like electrons, the school is like the atom, and the classrooms are like orbitals. Someone who does not know a student's exact schedule may be able to determine the probability of that student being in a particular classroom at a particular time, but it is not certain. Another analogy with more appropriate relative sizes is a bee in a closed stadium. You know that the bee is inside the stadium, and you can reason that it will most likely be near its nest. However, you cannot pinpoint its exact location.

A **wave function** is a mathematical description of an orbital in an atom where an electron of a certain energy is likely to be found. Note that an orbital is not a Bohr orbit—the electron is not moving around the nucleus in a circle. How, then, is the electron moving? The answer is surprising: we do not know. The wave function gives no information about the detailed pathway of the electron. This idea is somewhat disturbing. When we solve problems involving the motions of objects in the macroscopic world, we are able to predict their pathways. For example, when 2 billiard balls with known velocities collide, we can predict their motions after the collision. However, we cannot predict the electron's motion. It is a mystery what electrons do in the atom. Quantum mechanics does not describe how an electron moves or even if it moves. It only tells us the statistical probability of finding the electron in a given location in an atom. The area or region where we are likely to find an electron is an orbital.

wave function the mathematical probability of finding an electron in a certain region of space

Using wave functions, physicists have created a three-dimensional **electron probability density**, which is a plot that indicates regions around the nucleus with the greatest probability of finding an electron. The electron probability density plot for a hydrogen electron in the ground state (lowest energy state) is spherical and is called the 1*s* orbital (**Figure 4(a)**). The greatest probability of finding the electron occurs at a distance r_{max} from the nucleus (**Figure 4(b)**). This distance is the same as the distance Bohr calculated for the radius of the first circular orbit of hydrogen's electron.

electron probability density the probability of finding an electron at a given location, derived from wave equations and used to determine the shapes of orbitals; also called electron probability distribution

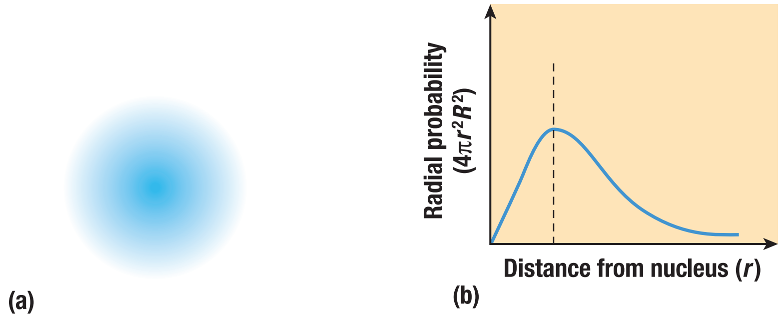

Figure 4 (a) The probability distribution for the hydrogen 1*s* orbital in three-dimensional space. (b) The radial probability distribution is a plot of the total probability of finding the electron as a function of distance from the nucleus.

Figure 5 illustrates different electron orbitals, or clouds. The electron can jump to any of these orbitals if it absorbs sufficient quanta of energy. Furthermore, these orbitals overlap, rather than being distinct levels as in the Bohr model. You will learn more about electron orbitals in the next sections. WEB LINK

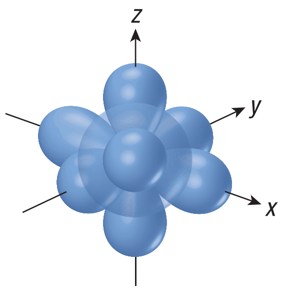

Figure 5 The electron probability density of various orbitals

LEARNING **TIP**

Orbitals versus Orbits

The table below outlines the main differences between orbitals and orbits.

Orbitals	Orbits
2 electrons	$2n^2$ electrons
three dimensions	two dimensions
distance from nucleus varies	distance from nucleus is fixed
no set path	path is elliptical or circular

The two main ideas of the **quantum mechanical model** of the atom are that electrons can be in different orbitals by absorbing or emitting quanta of energy, and that the location of electrons is given by a probability distribution. The quantum mechanical model is a radical departure from earlier atomic models because it is based on uncertainty—the uncertainty of an electron's location within the atom. According to this model, the structure of a tiny atom is much more complex than anyone would have thought possible, as you will see in the next section.

quantum mechanical model a model for the atom based on quantum theory and the calculation of probabilities for the location of electrons

3.3 Review

Summary

- Louis de Broglie originated the idea that the electron has both particle and wave properties.
- The quantum (wave) mechanical model describes an electron as a standing wave.
- The electron can occupy a series of orbitals. Each orbital has a prescribed possible energy value and spatial distribution.
- The exact position of the electron and how it is moving can never both be known. This is consistent with Heisenberg's uncertainty principle, which states that it is impossible to know both the position and the speed of a particle simultaneously.
- Orbitals are described as probability distributions and depicted as electron density plots.
- In the ground state, the single electron in a hydrogen atom resides in a low-energy orbital.
- The two main ideas of the quantum mechanical model of the atom are that electrons can move between orbitals by absorbing or emitting quanta of energy, and that the location of electrons is given by a probability distribution.

Questions

1. Define the following terms and provide an expanded description: K/U
   (a) orbital
   (b) electron probability density
   (c) quantum mechanics
   (d) wave function
   (e) quantum mechanical model
   (f) Heisenberg's uncertainty principle
2. (a) Draw a concept map illustrating the important aspects of the quantum mechanical model of the atom. Include a brief description of each point. Include the terms "wave function," "orbital," "probability density," and "uncertainty principle."
   (b) Expand on your concept map from (a) by including the contributions by Planck, Bohr, de Broglie, Schrödinger, and Heisenberg. K/U C
3. Explain how an electron orbital is not the same as an orbit. K/U
4. What information about the electron cannot be determined from quantum mechanics? K/U A
5. Explain the value of scientists working together and sharing information. How do you think this networking has contributed to current knowledge and understanding of major scientific principles? K/U T/I A
6. Heisenberg, de Broglie, and Schrödinger were all theoretical physicists. Explain why their work is studied in such detail in a chemistry course. K/U T/I A
7. Science is divided into the arbitrary groups of biology, chemistry, and physics. K/U T/I A
   (a) Why do you think science has been so divided?
   (b) This section highlights one area where physics and chemistry overlap. Identify three more areas where the different groups overlap.
   (c) Do you think it makes sense to divide up science into these groups? Explain your reasoning.
8. When most people visualize an atom, they use the Bohr–Rutherford model. K/U T/I A
   (a) Why do you think this is?
   (b) Do you think it is important for most people to understand exactly how the atom functions? Explain your reasoning.
9. Dr. Richard Bader and his research group at McMaster University, Hamilton, are well known for their work on the structure of chemical entities. Research Bader, and determine the nature of his group's work. Prepare a brief, general description of how it relates to quantum mechanics. K/U T/I A
10. Research Schrödinger's wave equation, and identify the different mathematical symbols in it. K/U T/I
11. Research the thought experiment called Schrödinger's cat. What does this thought experiment tell us about the quantum mechanical model of the atom? K/U T/I A

WEB LINK

3.3

The Quantum Mechanical Model of the Atom

LEARNING **TIP**

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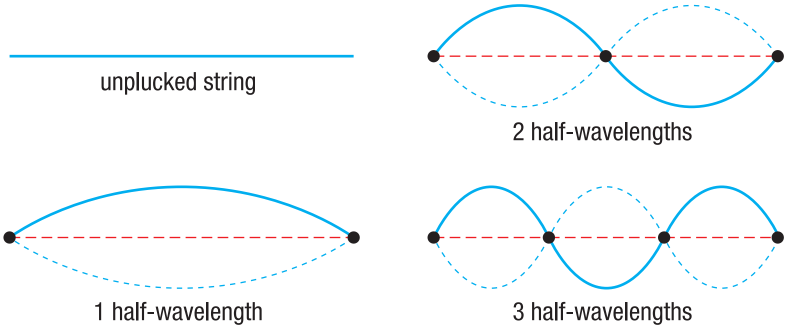

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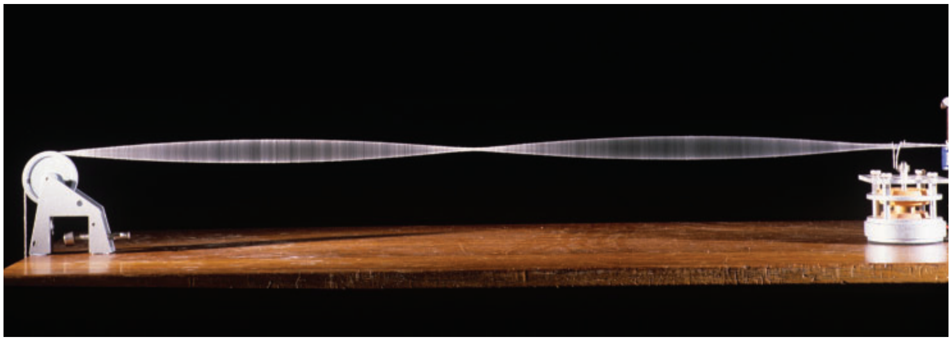

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Mini **Investigation**

Modelling Standing Electron Waves

Skills: Performing, Observing, Analyzing, Evaluating, Communicating

SKILLS HANDBOOK A2.3

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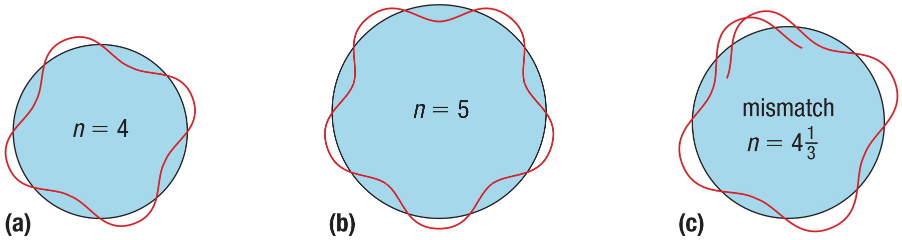

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Orbitals and Probability Distributions

orbital the region around the nucleus where an electron has a high probability of being found

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electron probability density the probability of finding an electron at a given location, derived from wave equations and used to determine the shapes of orbitals; also called electron probability distribution

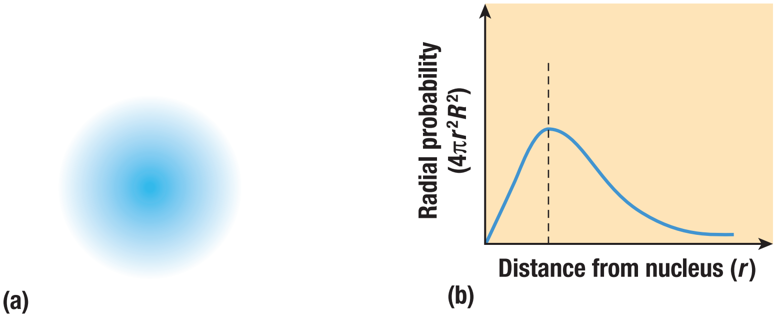


Figure 4 (a) The probability distribution for the hydrogen 1*s* orbital in three-dimensional space. (b) The radial probability distribution is a plot of the total probability of finding the electron as a function of distance from the nucleus.

Figure 5 illustrates different electron orbitals, or clouds. The electron can jump to any of these orbitals if it absorbs sufficient quanta of energy. Furthermore, these orbitals overlap, rather than being distinct levels as in the Bohr model. You will learn more about electron orbitals in the next sections. WEB LINK

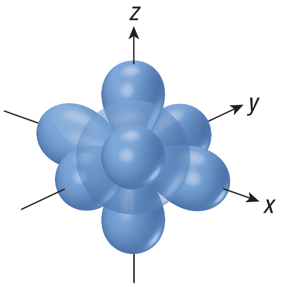


Figure 5 The electron probability density of various orbitals

LEARNING TIP

Orbitals versus Orbits

The table below outlines the main differences between orbitals and orbits.

Orbitals	Orbits
2 electrons	$2n^2$ electrons
three dimensions	two dimensions
distance from nucleus varies	distance from nucleus is fixed
no set path	path is elliptical or circular

The two main ideas of the **quantum mechanical model** of the atom are that electrons can be in different orbitals by absorbing or emitting quanta of energy, and that the location of electrons is given by a probability distribution. The quantum mechanical model is a radical departure from earlier atomic models because it is based on uncertainty—the uncertainty of an electron's location within the atom. According to this model, the structure of a tiny atom is much more complex than anyone would have thought possible, as you will see in the next section.

quantum mechanical model a model for the atom based on quantum theory and the calculation of probabilities for the location of electrons

3.3 Review

Summary

- Louis de Broglie originated the idea that the electron has both particle and wave properties.
- The quantum (wave) mechanical model describes an electron as a standing wave.
- The electron can occupy a series of orbitals. Each orbital has a prescribed possible energy value and spatial distribution.
- The exact position of the electron and how it is moving can never both be known. This is consistent with Heisenberg's uncertainty principle, which states that it is impossible to know both the position and the speed of a particle simultaneously.
- Orbitals are described as probability distributions and depicted as electron density plots.
- In the ground state, the single electron in a hydrogen atom resides in a low-energy orbital.
- The two main ideas of the quantum mechanical model of the atom are that electrons can move between orbitals by absorbing or emitting quanta of energy, and that the location of electrons is given by a probability distribution.

Questions

1. Define the following terms and provide an expanded description: K/U
   (a) orbital
   (b) electron probability density
   (c) quantum mechanics
   (d) wave function
   (e) quantum mechanical model
   (f) Heisenberg's uncertainty principle
2. (a) Draw a concept map illustrating the important aspects of the quantum mechanical model of the atom. Include a brief description of each point. Include the terms "wave function," "orbital," "probability density," and "uncertainty principle."
   (b) Expand on your concept map from (a) by including the contributions by Planck, Bohr, de Broglie, Schrödinger, and Heisenberg. K/U C
3. Explain how an electron orbital is not the same as an orbit. K/U
4. What information about the electron cannot be determined from quantum mechanics? K/U A
5. Explain the value of scientists working together and sharing information. How do you think this networking has contributed to current knowledge and understanding of major scientific principles? K/U T/I A
6. Heisenberg, de Broglie, and Schrödinger were all theoretical physicists. Explain why their work is studied in such detail in a chemistry course. K/U T/I A
7. Science is divided into the arbitrary groups of biology, chemistry, and physics. K/U T/I A
   (a) Why do you think science has been so divided?
   (b) This section highlights one area where physics and chemistry overlap. Identify three more areas where the different groups overlap.
   (c) Do you think it makes sense to divide up science into these groups? Explain your reasoning.
8. When most people visualize an atom, they use the Bohr–Rutherford model. K/U T/I A
   (a) Why do you think this is?
   (b) Do you think it is important for most people to understand exactly how the atom functions? Explain your reasoning.
9. Dr. Richard Bader and his research group at McMaster University, Hamilton, are well known for their work on the structure of chemical entities. Research Bader, and determine the nature of his group's work. Prepare a brief, general description of how it relates to quantum mechanics. 🌐 K/U T/I A
10. Research Schrödinger's wave equation, and identify the different mathematical symbols in it. 🌐 K/U T/I
11. Research the thought experiment called Schrödinger's cat. What does this thought experiment tell us about the quantum mechanical model of the atom? 🌐 K/U T/I A

🌐 WEB LINK

Quantum Numbers

3.4

Mathematical equations are the language of scientists as they try to model natural phenomena. Schrödinger's wave equation is a very complex equation. It describes the quantized energies of the electron in an atom as well as wave functions that determine the probability of finding electrons in various regions in an atom. In this section, you will explore the results of Schrödinger's equations.

The Four Quantum Numbers

Solutions to Schrödinger's equation for the hydrogen atom give many wave functions that describe various types of orbitals. Each of these types of orbitals has a set of four numbers called **quantum numbers**, which describe various properties of the orbital. These numbers are like addresses for locating the position of an electron by its city, street, number, and apartment number. In this subsection, you will learn about the four quantum numbers and what each quantum number represents.

quantum numbers numbers that describe the quantum mechanical properties of orbitals; from the solutions to Schrödinger's wave equation

The Principal Quantum Number (*n*)

Energy levels in an atom are sometimes called **shells**. Bohr devised this numbering system and called the shell number the principal quantum number. The **principal quantum number (*n*)** is the quantum number that describes the size and energy of an atomic orbital. It has whole-number values (1, 2, 3, and so on). It is important to note that the spaces between atomic shells are not equal (**Figure 1**). As n increases, the energy required for an electron to occupy that orbital increases. Each successive orbital is larger, meaning that an electron occupying that orbit spends more time farther from the nucleus. This also means that electrons with higher energy are less tightly bound to the nucleus.

shell an atom's main energy level, where the shell number is given by the principal quantum number, $n = 1, 2, 3, \ldots$

principal quantum number (*n*) the quantum number that describes the size and energy of an atomic orbital

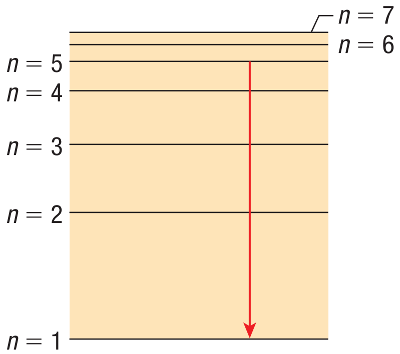


Figure 1 The principal quantum number, n, represents the position of an electron in an atom. If an electron moves from a higher shell, such as $n = 5$, to a lower shell, such as $n = 1$, the energy difference between the shells is released as a photon.

Recall that Bohr took up the challenge of explaining the line spectrum of the hydrogen atom. Bohr's success led other scientists to pursue the investigation of line spectra in detail because there were observations that still required explanation. In 1891, Albert Michelson discovered that the distinct lines in the hydrogen atom's spectrum actually consisted of many smaller lines. These smaller lines were difficult to see and were unexplained for many years. In 1915, a German physicist, Arnold Sommerfeld, studied the hydrogen atom's spectrum in detail. To explain the extra lines, Sommerfeld proposed the secondary quantum number as a way to describe electron energy sublevels, or **subshells**.

subshells orbitals of different shapes and energies, as given by the secondary quantum number; often referred to as *s*, *p*, *d*, and *f*

Subshells are part of the primary energy level. If an energy level is described as a staircase, one regular step actually represents a group of several smaller energy steps (**Figure 2**).

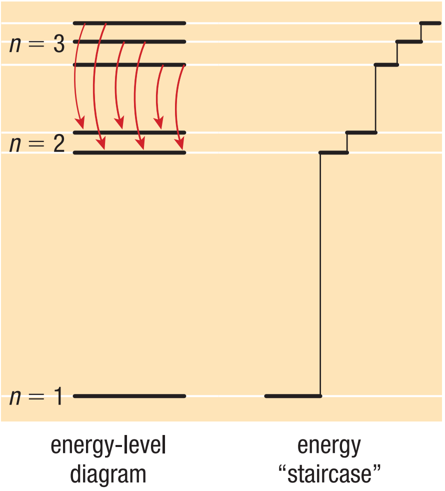


Figure 2 Sommerfeld's atomic model includes multiple energy levels within shells, called subshells, except when $n = 1$.

The Secondary Quantum Number (l)

secondary quantum number (l) the quantum number that describes the shape and energy of an atomic orbital, with whole-number values from 0 to $n - 1$ for each value of n

The **secondary quantum number (l)** describes the shape of an atomic orbital. It has whole-number values from 0 to $n - 1$ for each value of n. This quantum number also describes the energy of atomic orbitals. When $n = 1, l = 0$. When $n = 3, l = 0, 1$, and 2. The numbers used to describe l are usually replaced by letters to avoid confusion with n. These letters are given in **Table 1**.

Table 1 Secondary Quantum Numbers and Corresponding Letters Used to Designate Atomic Orbitals

Value of l	0	1	2	3	4
Letter used	*s*	*p*	*d*	*f*	*g*
Name	sharp	principal	diffuse	fundamental	

In other words, at an energy level of $n = 1$, only an *s* orbital exists. However, at the third energy level ($n = 3$), there can be *s*, *p*, and *d* orbitals. Each of these orbital types is a subshell. Higher-energy subshell symbols follow the alphabet (*g*, *h*, *i*), but no stable element in its ground state has electrons in subshells higher than *f*. This system of using letters to identify the various subshells arises from early spectral studies.

Compared to different values of n, different values of l represent smaller differences in the amount of energy an electron requires to occupy any of the orbitals.

The Magnetic Quantum Number (m_l)

magnetic quantum number (m_l) the quantum number that describes the orientation of an atomic orbital in space relative to the other orbitals in the atom, with whole-number values between $+l$ and $-l$, including 0

The **magnetic quantum number (m_l)** is the quantum number that describes the orientation of an atomic orbital in space relative to the other orbitals in the atom. It has whole-number values between $+l$ and $-l$, including 0. The value of m_l is related to the orientation of an orbital in space relative to the other orbitals in the atom. The number of different values that m_l can have equals the number of orbitals that are possible.

For example, when $l = 1$, there are three possible orbitals: $+1$, 0, and -1 (**Table 2**). These three types of orbital are all *p* orbitals, but they differ from each other by their orientation in space. Think about an *xyz* coordinate system (**Figure 3**).

Table 2 Quantum Numbers for the First Four Levels of Orbitals of Hydrogen

n	*l*	Sublevel designation	m_l	Number of orbitals	Number of electrons in each energy level ($2n^2$)
1	0	1*s*	0	1	2
2	0	2*s*	0	1	8
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	18
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	32
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

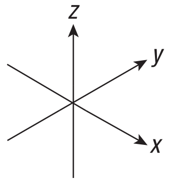


Figure 3 The magnetic quantum number describes an orbital's orientation in three-dimensional space.

Figure 4 shows the relative energies of the *s*, *p*, and *d* orbitals in their respective energy levels.

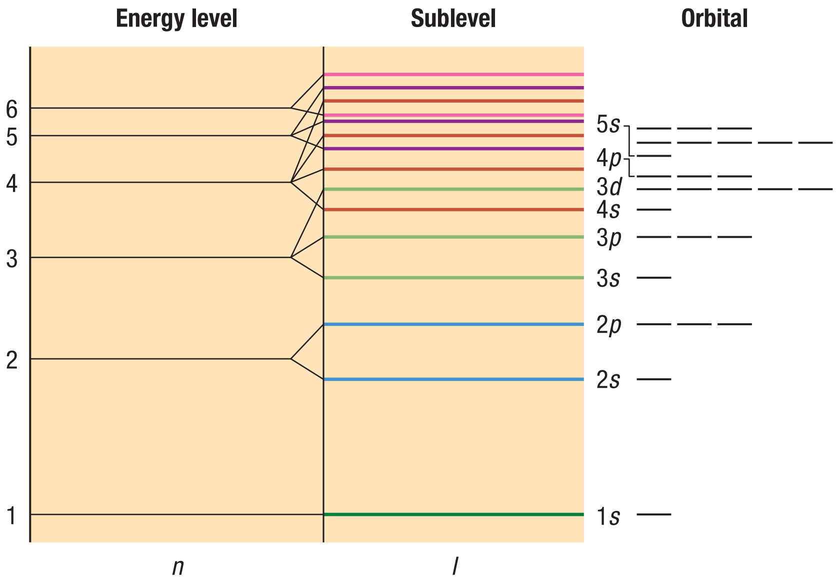


Figure 4 The energies of orbitals relative to each other. The farther the orbitals are from the nucleus, the closer together they are, and the subshells "overlap."

Shapes and Orientations of Orbitals

You have read that orbitals represent electron probability distributions and that each orbital has a unique probability distribution, shape, and orientation. Note that the 2*s* and 3*s* orbitals contain areas of high probability separated by areas of zero probability (**Figure 5(a)**, top). These areas of zero probability are called nodes. For simplicity, you can think of *s* orbitals in terms of their overall spherical shape, which becomes larger as the value of *n* increases. **Figure 5(a)**, bottom, illustrates the characteristic spherical shape of each of the *s* orbitals.

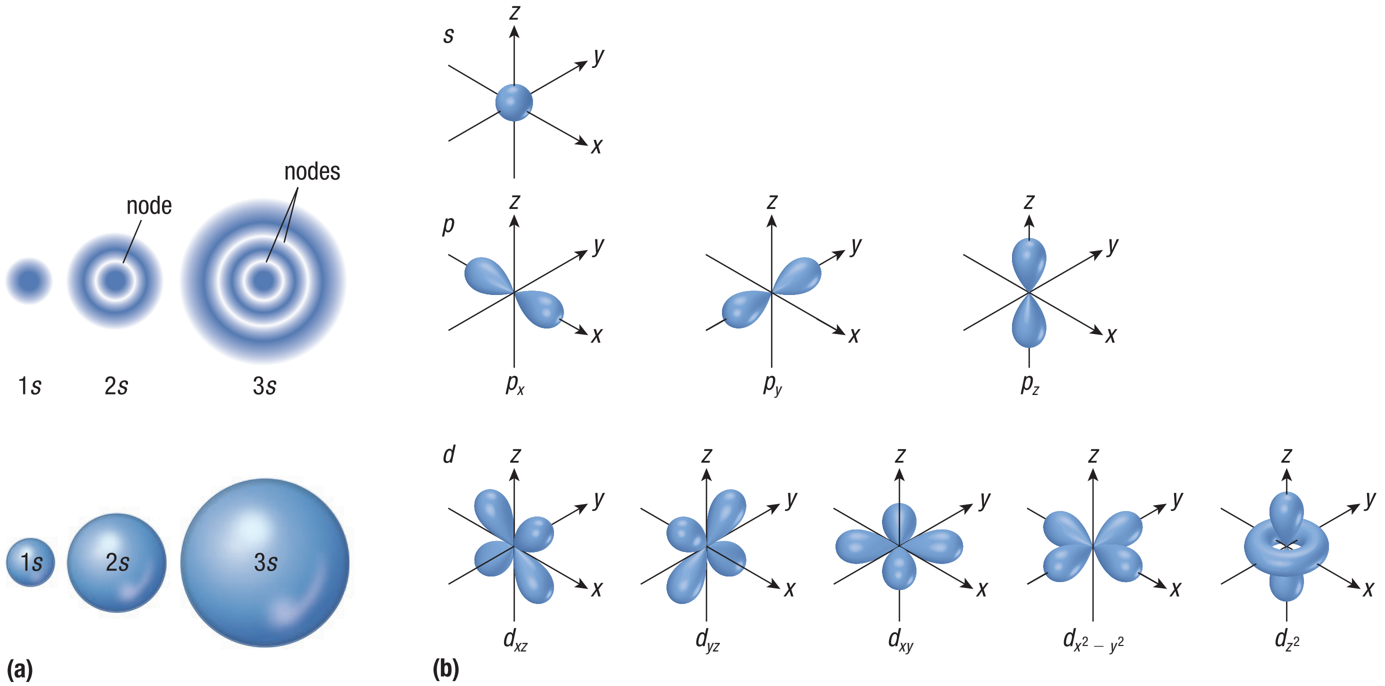


Figure 5 (a) In these representations of the hydrogen 1*s*, 2*s*, and 3*s* orbitals, the nodes are the areas of zero probability. The top diagram is a cross section of the electron probability distribution; the nodes are spherical, too. Bottom: the surface contains 90 % of the total electron probability (the size of the orbital, by definition). (b) Shapes and orientations of *s*, *p*, and *d* orbitals

The *p* orbitals are not spherical like *s* orbitals, but have two *lobes* separated by a node at the nucleus (**Figure 5(b)**). The *p* orbitals can exist in any of the three dimensions and are labelled using the *xyz* coordinate system along which the lobes lie. For example, the 2*p* orbital with its lobes centred along the *x*-axis is the $2p_x$ orbital.

Figure 6 shows how the $2p_x$ orbital is identified using the first three quantum numbers.

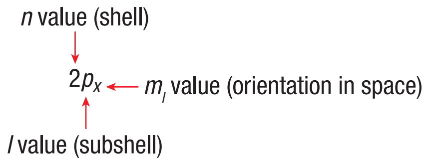


Figure 6

Investigation 3.4.1

Simulation of Electron Orbitals (page 181)

You have learned about the first three quantum numbers related to the model of the atom. This observational study will give you an opportunity to use the numbers to simulate electron orbitals.

The 3*p* orbitals have the same boundary surface shapes shown in Figure 5(b), except that they are larger because the value of *n* is greater.

The *d* orbitals ($l = 2$) first occur in level $n = 3$. The five 3*d* orbitals have the shapes shown in Figure 5(b). Four of the orbitals (d_{xz}, d_{yz}, d_{xy}, and $d_{x^2-y^2}$) have four lobes centred in the plane indicated in the orbital label. Note that d_{xy} and $d_{x^2-y^2}$ are both centred in the *xy* plane, but the lobes of $d_{x^2-y^2}$ lie *along* the *x*- and *y*-axes, whereas the lobes of d_{xy} lie *between* the axes. The fifth orbital, d_{z^2}, has a unique shape with two lobes along the *z*-axis and a belt centred in the *xy* plane. The *d* orbitals for levels $n > 3$ look like the 3*d* orbitals but have larger lobes.

The Spin Quantum Number (m_s)

Samuel Goudsmit and George Uhlenbeck, graduate students at the University of Leiden in the Netherlands, found that a fourth quantum number (in addition to n, l, and m_l) was necessary to account for the details of the emission spectra of atoms. The spectral data indicated that the atom has a magnetic property, called a magnetic moment, when the atom is placed in an external magnetic field. The magnetic moment of an atom has two orientations. Since they knew from classical physics that a spinning charge produces a magnetic moment, it seemed reasonable to assume that the electron could have two oppositely directed "spin states" (**Figure 7**). The new quantum number related to the spin of an electron, called the electron **spin quantum number (m_s)**, can have one of two values: $+\frac{1}{2}$ and $-\frac{1}{2}$. These two values mean that the electron can spin in one of two opposite directions, although other interpretations have been suggested.

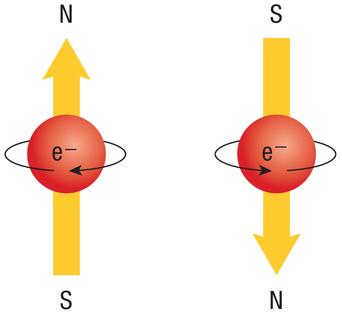


Figure 7 (a) By spinning in one direction, the electron produces a magnetic field oriented toward north. (b) By spinning in the opposite direction, the electron produces a magnetic field in the opposite orientation.

spin quantum number (m_s) the quantum number that relates to the spin of the electron; limited to $+\frac{1}{2}$ or $-\frac{1}{2}$

Research This

Magnetic Fields and Sunspots

Skills: Researching, Analyzing, Communicating, Identifying Alternatives SKILLS HANDBOOK A5.1

Sunspots are temporary dark spots on the surface of the Sun. They are areas of intense magnetic activity at a reduced temperature. Solar activity and sunspot cycles are important factors in forecasting space weather, which can affect satellite communications.

Energy levels in atoms, transitions between energy levels, and associated spectral lines of energy levels are assumed not to be under the influence of any magnetic field. However, when a magnetic force is present, the energy levels split into sublevels, and so do the spectral lines. This splitting is called the Zeeman effect. The idea of magnetic quantum numbers was developed to explain the Zeeman effect.

The Zeeman effect is a way to identify, explain, and measure characteristics of sunspots. Since the distance between the spectral lines produced by the split energy sublevels is proportional to the strength of the magnetic field, scientists can use the Zeeman effect to measure the magnetic fields of the Sun and other stars.

1. Research sunspots and their spectrographs. Find an image of a sunspot and its associated spectrograph.
2. Determine what the spectrograph shows and how it relates to the sunspot.
3. Research how scientists use this information and why it is important.

A. Summarize your research. Provide an image, and describe your sunspot and spectrograph. C A

B. What else do you think this technology could be used for? Are there any examples of this application? C A

WEB LINK

The Pauli Exclusion Principle

The Austrian physicist Wolfgang Pauli (1900–1958) formulated an important principle, the **Pauli exclusion principle**, which states the following:

Pauli Exclusion Principle

In a given atom, no two electrons can have the same set of four quantum numbers (n, l, m_l, and m_s).

Pauli exclusion principle the principle that no two electrons in the same atom can be in the same quantum state

Since electrons in the same orbital have the same values of n, l, and m_l, the Pauli exclusion principle implies that they must have different spin quantum numbers, m_s. Since only two values of m_s are allowed, *an orbital can hold only two electrons, which must have opposite spins*. This principle will have important implications when you apply the quantum mechanical atomic model to account for electron arrangements of the atoms in the periodic table.

UNIT TASK **BOOKMARK**

Refer to the Pauli exclusion principle as you work on the Unit Task on page 268.

Tutorial 1 Working with Quantum Numbers

By working with the quantum numbers in this Tutorial, you will better understand the rules that govern their use.

Sample Problem 1: Solving the Secondary Quantum Number

For principal quantum number $n = 5$, determine the value(s) of the secondary quantum number, l, and the types of orbitals in each case.

Solution

For $n = 5$, the allowed values of l are 0 to $n - 1$, or 0, 1, 2, 3, and 4. The types of orbitals in each case are shown in **Table 3**.

Table 3

$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$
5*s*	5*p*	5*d*	5*f*	5*g*

Sample Problem 2: Solving the Magnetic Quantum Number

How many possible values of m_l are there for $l = 0$, 1, 2, and 3? What pattern do you notice in these numbers?

Solution

The principal quantum number, n, determines the values of the secondary quantum number, l, which in turn determines the possible values of the magnetic quantum number, m_l.

The magnetic quantum number m_l is equal to whole numbers from l to $-l$.

For $l = 0$, 1, 2, and 3, the values of m_l are shown in **Table 4.**

Table 4

l	m_l
0	0
1	1, 0, −1
2	2, 1, 0, −1, −2
3	3, 2, 1, 0, −1, −2, −3

Practice

1. For $n = 7$, what are the possible values for the quantum numbers l and m_l? K/U T/I

   [ans: $l = 0$ to 6; $m_l = 6$ to -6]

2. Identify which of the following orbital designations do not exist: 1*s*, 1*p*, 7*d*, 3*f*, 4*f*, 2*d* K/U T/I

   [ans: 1*p*, 3*f*, 2*d*] CAREER LINK

3.4 Review

Summary

- Four quantum numbers, n, l, m_l, and m_s, define the electron's position in the atom.
- The principal quantum number, n, represents the main energy levels, or shells, the electrons can occupy in an atom and has whole-number values 1, 2, 3, ...
- The secondary quantum number, l, represents subshells, gives the shape of the orbital, has values 0 to $n - 1$, and letters *spdf*.
- The magnetic quantum number, m_l, represents the orientations of the subshells and has values $-l$ to $+l$.
- The spin quantum number, m_s, represents electron spin and has a value of either $+\frac{1}{2}$ or $-\frac{1}{2}$.
- The Pauli exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers (n, l, m_l, m_s).

Questions

1. What are quantum numbers? Create a chart showing the information you can obtain from the quantum numbers n, l, and m_l. K/U C
2. Suggest an analogy not mentioned in this section to help explain the four quantum numbers. Share it with a classmate and get his or her feedback. Revise your analogy if necessary. K/U T/I C A
3. How do $2p$ orbitals differ from each other? How do $2p$ and $3p$ orbitals differ from each other? K/U
4. Draw a sketch to compare the following orbitals. In a few words, highlight the similarities and differences. K/U C
   (a) $1s$ and $3s$
   (b) $2p_x$ and $3p_y$
   (c) $2s$ and $2p_z$
5. What are the possible values for the quantum numbers n, l, and m_l in the first three shells? K/U T/I A
6. List all the possible quantum numbers for an electron in the
   (a) $2s$ orbital
   (b) $6s$ orbital
   (c) $5f$ orbital K/U T/I A
7. Which of the following orbital designations do not exist? Explain your answer. K/U T/I
   (a) $1d$
   (b) $0p$
   (c) $4g$
   (d) $5s$
   (e) $2f$
8. Which of the following sets of quantum numbers are not allowed? For each set that is not allowed, explain why it is not allowed. K/U T/I A
   (a) $n = 3, l = 2, m_l = 2$
   (b) $n = 4, l = 3, m_l = 4$
   (c) $n = 0, l = 0, m_l = 0$
   (d) $n = 2, l = -1, m_l = 1$
   (e) $n = 1, l = 1, m_l = 2$
9. Which of the following sets of quantum numbers are not allowed? For each set that is not allowed, explain why it is not allowed. K/U T/I A
   (a) $n = 3, l = 3, m_l = 0, m_s = -\frac{1}{2}$
   (b) $n = 4, l = 3, m_l = 2, m_s = -\frac{1}{2}$
   (c) $n = 4, l = 1, m_l = 1, m_s = +\frac{1}{2}$
   (d) $n = 2, l = 1, m_l = -1, m_s = -1$
   (e) $n = 5, l = -4, m_l = 2, m_s = +\frac{1}{2}$
   (f) $n = 3, l = 1, m_l = 2, m_s = -\frac{1}{2}$
10. Science looks for ways to explain what is observed; theoretical knowledge forms the basis of these explanations. Explain the fourth quantum number. Why was it needed? K/U T/I A
11. The second energy shell ($n = 2$) in an atom can hold no more than 8 electrons. Explain this limitation. K/U
12. Every electron requires four unique quantum numbers. How many different sets of these numbers are there for $n = 1$ and $n = 2$? K/U T/I A

3.5 Atomic Structure and the Periodic Table

As the study of chemistry progressed from the seventeenth through the nineteenth centuries, it became evident to scientists that Earth is composed of a great many elements, each with very different properties. Scientists realized that the structure of matter is much more complicated than the simple model of earth, air, fire, and water suggested by ancient philosophers. As more elements were separated and identified, chemists learned more about their properties. Gradually, chemists began to notice patterns in the properties of elements.

The Periodic Table

UNIT TASK **BOOKMARK**

Use the information in this section as you work on the Unit Task on page 268.

Have you ever wondered why elements in the periodic table are arranged the way they are? (Refer to the periodic table in Appendix B1). The elements of the periodic table are arranged according to the way electrons arrange themselves around the nuclei of atoms. Electron arrangement determines the chemical behaviour of every element. After reading this section, you will be able to look at the position of an element in the periodic table and predict its electron arrangement. You will also be able to apply the quantum mechanical model of the atom to explain the periodicity of chemical properties.

Understanding how electrons are arranged in atoms has allowed engineers to make new products and develop new technologies. For example, lithium (**Figure 1(a)**) is a very reactive element found in Group 1 of the periodic table. Lithium's reactivity is due to the arrangement of its electrons and their location relative to the nucleus. When lithium is exposed to water, it reacts noticeably (**Figure 1(b)**). Scientists have learned to maximize the potential of lithium by using it in batteries for cellphones, MP3 players, laptop computers, radios, cameras, pacemakers, hybrid and electric cars, and many other devices (**Figure 1(c)**).

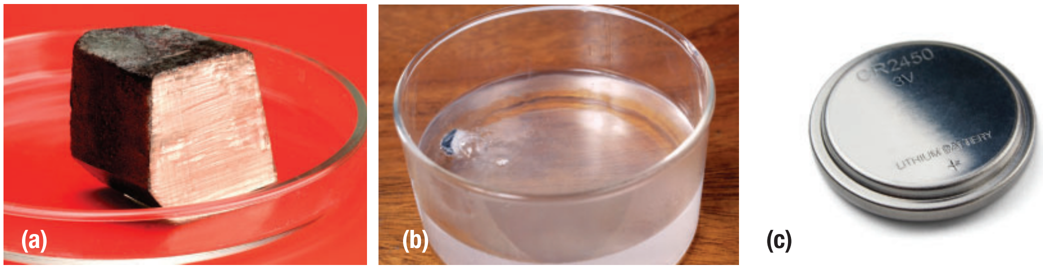


Figure 1 (a) The lithium atom is reactive. (b) Lithium reacts readily with water. (c) Lithium is used in many batteries because of its reactivity.

Multi-electronic Atoms

The Bohr–Rutherford model of the atom provides only a limited explanation of how electrons are configured in the atom. Bohr–Rutherford diagrams are useful for the first 20 elements, up to calcium. The quantum mechanical atomic model, with its four quantum numbers, not only describes all atoms in the periodic table, but also allows us to make theoretical predictions about atoms and their chemical properties.

To see how the quantum mechanical model applies to multi-electronic atoms (atoms with more than 1 electron), consider helium, which has 2 protons in its nucleus and 2 electrons in the 1*s* orbital.

Three energy contributions must be considered in the description of the helium atom: (1) the kinetic energy of the electrons as they move about the nucleus, (2) the potential energy of attraction between the nucleus and the electrons, and (3) the potential energy of repulsion between the 2 electrons. Even though the helium atom can be described in terms of the quantum mechanical model, the Schrödinger wave equation cannot be solved because the repulsions between electrons cannot be calculated exactly. This problem is called the electron correlation problem.

The electron correlation problem occurs with all multi-electronic atoms. To treat these systems using the quantum mechanical model, it is necessary to make approximations. The most common approximation is to treat each electron as if it were moving in a field of charge that is the net result of the nuclear attraction and the average repulsions of all the other electrons. For example, a sodium atom has 11 electrons: 10 electrons in the first and second energy shells and 1 electron in the third shell (**Figure 2**). Now consider the single outermost electron and the forces acting on it. The outermost electron is attracted to the positively charged nucleus, but it is also repelled by the 10 electrons in the first and second energy shells. The net effect is that the outer electron is not bound to the nucleus as tightly as it would be if the other electrons were not present. In essence, it is screened, or shielded, from the nuclear charge by the repulsions of the other electrons.

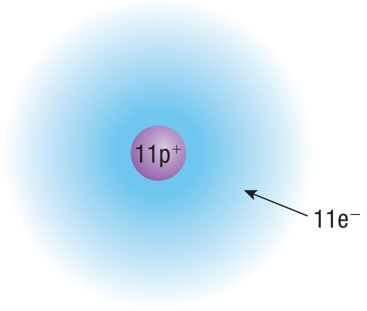


Figure 2 Sodium has 11 electrons and 11 protons.

The orbitals of multi-electronic atoms have the same general shapes as the orbitals for hydrogen, but their sizes and energy values are different. These differences occur because of the interplay between nuclear attraction and the repulsions from other electrons.

One important difference between multi-electronic atoms and the hydrogen atom is that, for hydrogen, all the orbitals of a given principal quantum level (shell) have the same energy. For example, in a hydrogen atom, electrons in the 2*s* and 2*p* orbitals possess the same energy. In multi-electronic atoms, for a given principal quantum level, *n*, the energies of electrons in the different orbitals vary as follows:

$$E_{ns} < E_{np} < E_{nd} < E_{nf}$$

In other words, electrons in a particular quantum shell fill orbitals in order of increasing energy: *s*, *p*, *d*, and then *f*. The reason for this has to do with the probability distributions of these orbitals. For example, notice in **Figure 3** that an electron in a 2*p* orbital has its maximum probability closer to the nucleus than does an electron in the 2*s* orbital. You might predict that a 2*p* orbital electron has lower energy than a 2*s* orbital electron. However, notice the small increase in electron density that occurs in the 2*s* orbital very near the nucleus. This means that for a small but very significant time, the 2*s* electron is closer to the nucleus than the 2*p* electron. This effect, called "penetration," causes an electron of a 2*s* orbital to be attracted to the nucleus more strongly than an electron of a 2*p* orbital. To summarize, electrons in the 2*s* orbital possess less energy than electrons in the 2*p* orbital of a multi-electronic atom. The probability distributions can also be represented by the probability profiles in **Figure 4**.

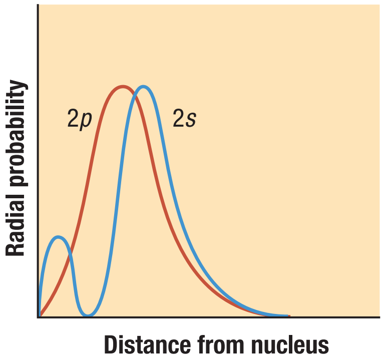


Figure 3 The probability profile of 2*s* orbital electrons and 2*p* orbital electrons

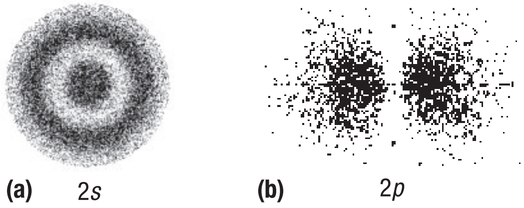


Figure 4 The probability profiles of (a) the 2*s* orbital and (b) the 2*p* orbital

The same rule applies to the other principal quantum levels. The relative energies of the electrons in the $n = 3$ orbitals are $E_{3s} < E_{3p} < E_{3d}$. In general, the more effectively electrons of an orbital penetrate the shielding electrons, the lower the energy of the electrons in that orbital.

The relative energies of the orbitals of the various sublevels are shown in **Figure 5**.

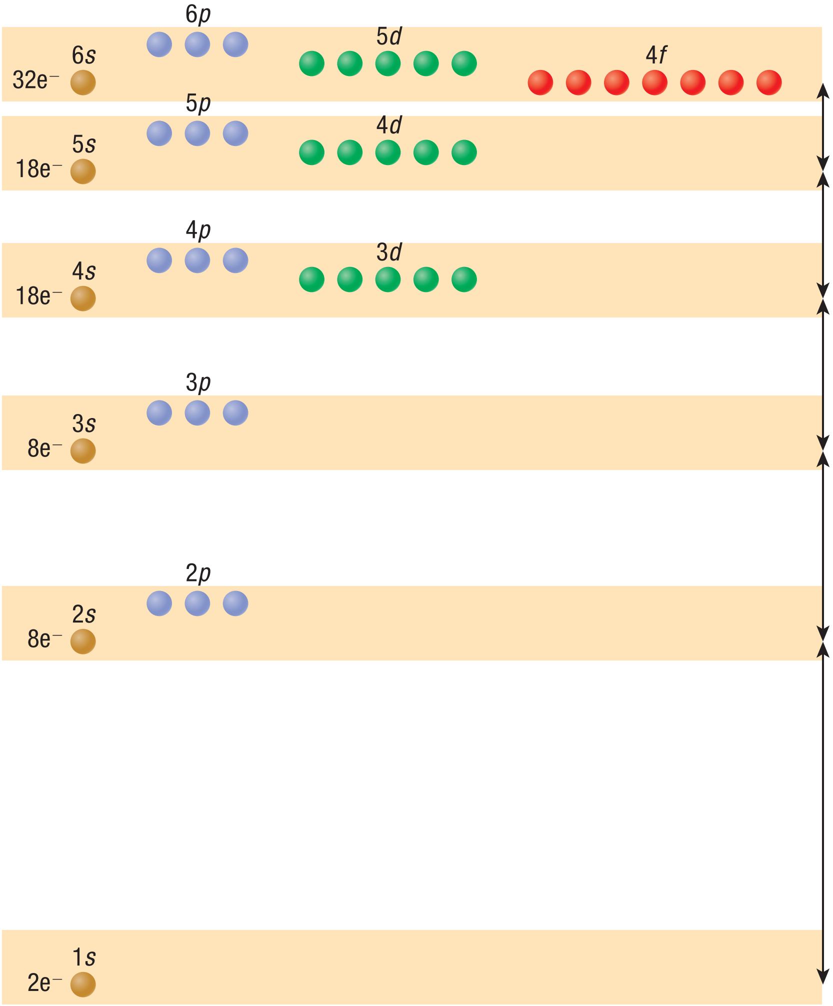


Figure 5 Relative energies of electron orbitals. Each orbital (dot) can contain up to 2 electrons.

electron configuration the location and number of electrons in the electron energy levels of an atom

aufbau principle the theory that an atom is "built up" by the addition of electrons, which fill orbitals starting at the lowest available energy orbital before filling higher energy orbitals (for example, 1*s* before 2*s*)

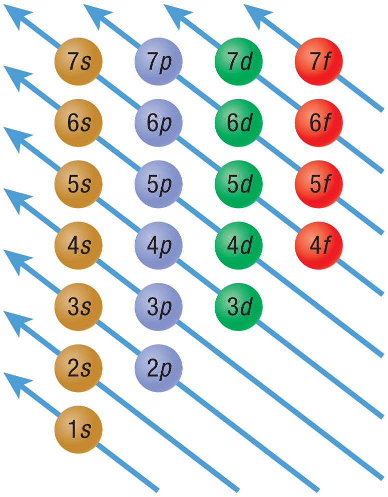


Figure 6 An aufbau diagram shows how electrons are added to each orbital, beginning with the 1*s* orbital (bottom left), until no electrons remain (top right).

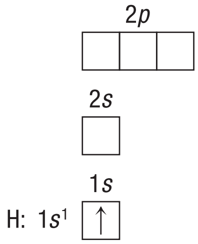
The Aufbau Principle and Writing Electron Configurations

You can apply the quantum mechanical model to show how the electron arrangements in atoms in the ground state account for the organization of the periodic table. The location and number of electrons in the energy levels of an atom or ion is called **electron configuration**.

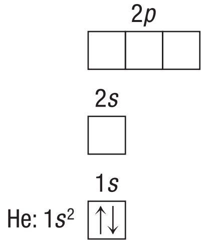
As you move across a row of the periodic table from left to right, atoms are arranged in order of increasing atomic number (proton number). Note that, in a neutral atom, the atomic number is also equal to the number of electrons. The result is that, as you move across the periodic table from left to right, the electron number of the elements also increases. The electron configuration of an atom can be determined using the **aufbau principle**, which hypothesizes that an atom is "built up" by progressively adding electrons. Furthermore, it states that as electrons are added, they assume their most stable condition (energy orbital) by filling the lowest available energy orbitals before filling higher energy orbitals. **Figure 6** shows how an aufbau diagram can be used as a tool for determining the electron configuration of an atom. The word *aufbau* is German for "building up."

The aufbau principle can be demonstrated by examining the electron configuration of the elements, moving from left to right along the periodic table. The following examples illustrate this. The hydrogen atom has 1 electron, which occupies the 1*s* orbital in its ground state. The electron configuration for hydrogen is written as $1s^1$, which can be represented by the following **energy-level diagram**, or **orbital diagram:**

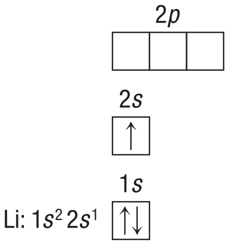
energy-level diagram (orbital diagram) a diagram that represents the relative energies of the electrons in an atom



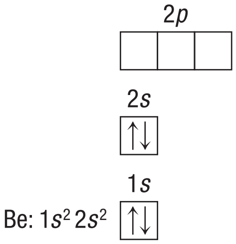
The next element, helium, has 2 electrons. According to the Pauli exclusion principle, since 2 electrons with opposite spins can occupy an orbital, the electrons in helium are in the 1*s* orbital with opposite spins. Helium therefore has a $1s^2$ configuration:



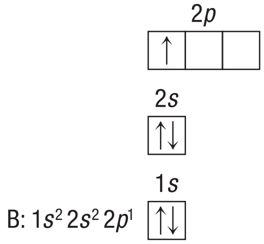
The atom of the element lithium has 3 electrons, 2 of which can go into the 1*s* orbital, which is now full. The third electron occupies the next lowest energy orbital ($n = 2$), the 2*s* orbital, so lithium has a $1s^22s^1$ configuration:



The atom of the next element, beryllium, has 4 electrons, which occupy the 1*s* and 2*s* orbitals:



The boron atom has 5 electrons, 4 of which occupy the 1*s* and 2*s* orbitals. The fifth electron goes into the second type of orbital with $n = 2$, the 2*p* orbital:

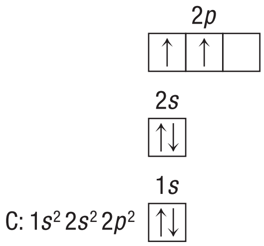


All the electrons in the 2*p* orbitals have the same energy, so it does not matter which 2*p* orbital the fifth electron occupies. By convention, we write it in the left-hand orbital.

For an atom with unfilled orbitals, the most stable energy level (lowest energy) is achieved when electrons occupy separate orbitals with parallel spins. An atom of carbon, the next element, has 6 electrons. Two electrons occupy the 1*s* orbital, 2 electrons occupy the 2*s* orbital, and 2 electrons occupy 2*p* orbitals. Since there are three 2*p* orbitals with the same energy, the electrons occupy separate 2*p* orbitals. This configuration is summarized by **Hund's rule,** which states that in a particular set of orbitals that have the same energy, the lowest energy configuration for an atom is the one with the maximum number of unpaired electrons allowed by the Pauli exclusion principle. In simple terms, this means that before any 2 electrons occupy an orbital in a subshell, other orbitals in the same subshell must first each contain 1 electron. Electrons filling a subshell will have parallel spin before the shell starts filling up with electrons having the (after the first orbital gains a second electron).

Hund's rule a rule stating that in a particular set of orbitals of the same energy, the lowest energy configuration for an atom is the one with the maximum number of unpaired electrons allowed by the Pauli exclusion principle; unpaired electrons are represented as having parallel spins

The electron configuration for the carbon atom could be written as $1s^22s^22p_x^12p_y^1$ to indicate that the electrons occupy separate 2*p* orbitals. However, the configuration is usually written as $1s^22s^22p^2$, and it is understood that the electrons are in different 2*p* orbitals. The energy-level diagram for carbon is



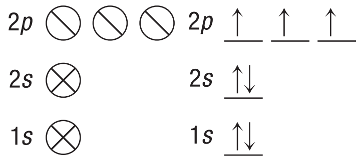
Note that the unpaired electrons in the 2*p* orbitals are shown with parallel spins.

The higher-energy orbitals have some anomalies in the order of filling orbitals. For example, in Figure 5 on page 162, the energy of the 4*s* orbital is lower than the energy of the 3*d* orbitals. Therefore, the 4*s* orbital must be filled before the 3*d* orbitals. When building the electron configuration of atoms, it is important to strictly follow this order. Use an aufbau diagram to write electron configurations in order of increasing energy. To do this you will also need to know the number of orbitals in each type of subshell: $s = 1$, $p = 3$, $d = 5$, and $f = 7$.

LEARNING **TIP**

Energy-level Diagrams

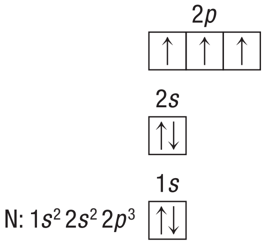
You may sometimes see energy-level diagrams expressed in different ways. The method used in this text (arrows in square boxes) is probably the most common. Two alternative ways to draw energy-level diagrams are shown below:



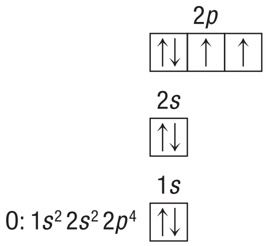
Procedure for Writing an Electron Configuration

1. Use the periodic table to determine the number of electrons in the atom or ion.
2. Assign electrons by main energy level and then by sublevel, using an energy-level diagram or an aufbau diagram.
3. Distribute electrons into orbitals that have the same energy according to Hund's rule.
4. Fill each sublevel before starting with the next sublevel. Continue until all electrons are assigned.
    - For anions (negatively charged ions), add an appropriate number of additional electrons.
    - For cations (positively charged ions), remove an appropriate number of electrons.

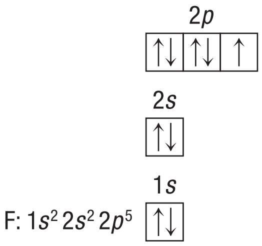
The electron configuration for the nitrogen atom (7 electrons) is $1s^22s^22p^3$. The 3 electrons in the 2*p* orbitals occupy separate orbitals with parallel spins:

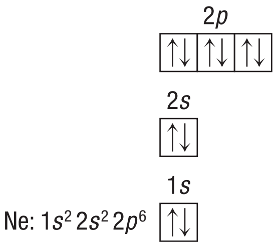


The configuration for the oxygen atom, which has 8 electrons, is $1s^2 2s^2 2p^4$. One of the $2p$ orbitals is now occupied by a pair of electrons with opposite spins, as required by the Pauli exclusion principle:



The energy-level diagrams and electron configurations for atoms of the elements fluorine (9 electrons) and neon (10 electrons) are as follows:





For neon, the orbitals $n = 1$ and $n = 2$ are now completely filled.

In atoms of sodium, Na(s), the first 10 electrons occupy the $1s$, $2s$, and $2p$ orbitals, so the eleventh electron must occupy the first orbital with $n = 3$, the $3s$ orbital. The electron configuration for sodium atoms is $1s^2 2s^2 2p^6 3s^1$. To avoid writing the increasing string of inner-level electrons, a shorthand using noble gas configurations is used. In this abbreviated form of the electron configuration, the nearest noble gas preceding the element is notated in brackets, and the electron configuration is continued from that point forward. For example, the noble gas configuration for sodium is $[\mathrm{Ne}]3s^1$, where [Ne] represents the electron configuration of neon, $1s^2 2s^2 2p^6$.

The atom of the next element, magnesium, has the electron configuration $1s^2 2s^2 2p^6 3s^2$, or $[\mathrm{Ne}]3s^2$. Atoms of the next 6 elements, aluminum through argon, have configurations obtained by filling the $3p$ orbitals one electron at a time.

Consider an analogy for the aufbau principle and the process of filling orbitals. Imagine that the atom is a concert hall (**Figure 7**). The stage is the nucleus, and the seating area represents the space where electrons most likely exist. The placement of electrons in orbitals in order of increasing energy follows a similar pattern to filling the seats closest to the stage first. The principal quantum number (which tells you the energy level) is like the seating section. The secondary quantum number (which tells you the subshell) is like the row. The magnetic quantum number (which gives specific information on the orientation of the orbital) is your seat. In this analogy, each seat is a loveseat. It can seat two people (left and right). The loveseat analogy is not totally appropriate, though. For the fourth quantum number—the spin quantum number—one person would have to be sitting on his or her head for the analogy to work completely.

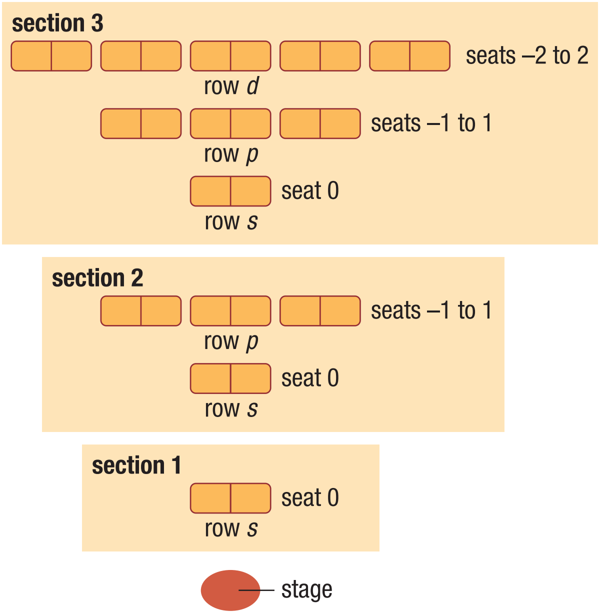


Figure 7 The atom can be thought of as analogous to a concert hall: the process of filling seats is similar to filling orbitals with electrons.

Tutorial 1 Writing Electron Configurations

In this tutorial, you will practise writing electron configurations of atoms and ions in different ways, and use electron configurations to identify an element.

Sample Problem 1: Writing a Full Electron Configuration

Write the full electron configuration for the sulfur atom.

Solution

Step 1. Determine the total number of electrons in the atom.

Sulfur has 16 electrons.

Step 2. Assign electrons in order of main energy levels and sublevels using the aufbau principle. Remember that each orbital can hold 2 electrons and the various subshells have specific numbers of orbitals (there is 1 *s* orbital, 3 *p* orbitals, 5 *d* orbitals, and so on).

1*s* has 2 electrons, 2*s* has 2 electrons, 2*p* has 6 electrons, 3*s* has 2 electrons, and 3*p* will fill 4 of 6 orbitals.

Statement: The electron configuration for sulfur is $1s^2 2s^2 2p^6 3s^2 3p^4$.

Sample Problem 2: Identifying an Element

Identify the element that has atoms with the following electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$

Solution

Count the number of electrons.

There are 28 electrons.

The number of electrons corresponds to the number of protons in a neutral atom. Therefore, the number of protons is 28 so the element is nickel (Ni).

Statement: The element with the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$ is nickel.

Sample Problem 3: Writing a Shorthand Electron Configuration

Write the shorthand electron configuration (noble gas configuration) for the chlorine atom.

Solution

Determine the noble gas immediately preceding chlorine, which is neon (Ne). Add the additional electrons to this noble gas.

$[Ne]3s^2 3p^5$

Statement: The shorthand electron configuration (noble gas configuration) for chlorine is $[Ne]3s^2 3p^5$.

Sample Problem 4: Electron Configurations for Ions

Write the electron configuration for the calcium ion Ca^{2+}.

Solution

Follow the same process as you did for a neutral atom, but add or remove electrons as required.

The electron configuration for a calcium atom is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. The calcium ion, Ca^{2+}, has a +2 charge, so remove 2 electrons. The electron configuration for the calcium ion is $1s^2 2s^2 2p^6 3s^2 3p^6$.

Statement: The electron configuration for the calcium ion Ca^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6$.

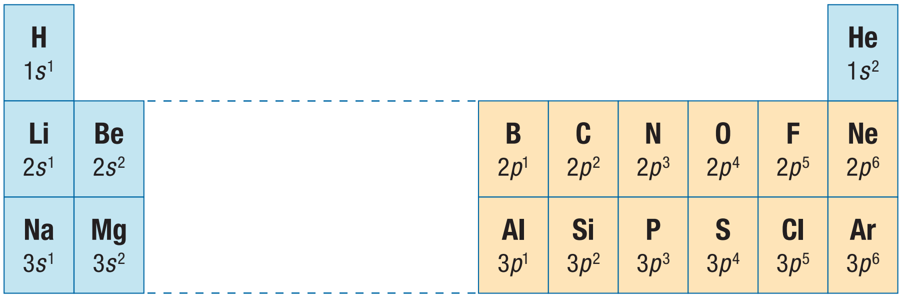
Practice

1. Write the full electron configuration for an atom of the element francium. T/I C
   [ans: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^3 5d^{10} 6s^2 6p^6 7s^1$]
2. Identify the element with the following electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ T/I C [ans: K]
3. Write the shorthand electron configuration (noble gas configuration) for an atom of silicon. T/I C [ans: $[Ne]3s^2 3p^2$]
4. Write the electron configuration for the magnesium ion Mg^{2+}. T/I C [ans: $1s^2 2s^2 2p^6$]

Explaining the Periodic Table

Electron configuration can help explain the structure of the periodic table and periodic trends. **Figure 8** summarizes the electron configurations of the first 18 elements by giving the number of electrons in the type of orbital occupied last. Note that an important pattern is developing: the elements in the same group have the same valence electron configuration. Recall that **valence electrons** are the electrons in the outermost shell (outermost principal quantum level) of an atom. For example, the valence electrons in a nitrogen atom are the 2*s* and 2*p* electrons, a total of 5 electrons. In a sodium atom, the valence electron is the electron in the 3*s* orbital, and so on. Valence electrons are the most important electrons to chemists because they are involved in bonding, as you will read in the next chapter. Remember that Mendeleev originally placed the elements in groups based on similarities in chemical properties. Now you know the reasons for these similarities. Elements with the same valence electron configuration show similar chemical behaviour. Chemical similarities allow you to draw conclusions about electron configurations. WEB LINK

valence electron an electron in the outermost principal quantum level of an atom



H $1s^1$							**He** $1s^2$
Li $2s^1$	**Be** $2s^2$	**B** $2p^1$	**C** $2p^2$	**N** $2p^3$	**O** $2p^4$	**F** $2p^5$	**Ne** $2p^6$
Na $3s^1$	**Mg** $3s^2$	**Al** $3p^1$	**Si** $3p^2$	**P** $3p^3$	**S** $3p^4$	**Cl** $3p^5$	**Ar** $3p^6$

Figure 8 The valence electron configurations for the first 18 elements

The nineteenth element of the periodic table is potassium. Recall that the 3*p* orbitals in an argon atom are fully occupied. Consequently, you might expect the additional electron in a potassium atom to occupy a 3*d* orbital, since for $n = 3$, the orbitals are 3*s*, 3*p*, and 3*d*. However, experimentation has shown that the properties of potassium are very similar to those of lithium and sodium. Potassium, like sodium, is very reactive with oxygen, so it must be carefully stored away from air. This property of potassium is evidence that the outermost electron in the potassium atom occupies the 4*s* orbital, rather than one of the 3*d* orbitals. The electron configuration of a potassium atom is shown below:

K: $1s^22s^22p^63s^23p^64s^1$ or $[\mathrm{Ar}]4s^1$.

The electron configuration of the atom of the next element, calcium, is Ca: $[\mathrm{Ar}]4s^2$.

The next element, scandium, begins a series of 10 elements (scandium through zinc) called the **transition metals**, which are elements whose highest-energy electrons are in *d* orbitals. The electron configuration of an atom of a transition metal is obtained by adding electrons to the five 3*d* orbitals. The configuration of an atom of scandium is Sc: $[\mathrm{Ar}]4s^23d^1$, that of titanium is Ti: $[\mathrm{Ar}]4s^23d^2$, and that of vanadium is V: $[\mathrm{Ar}]4s^23d^3$.

transition metal an element whose highest-energy electrons are in *d* orbitals

The expected electron configuration of atoms of the next element, chromium, is $[\mathrm{Ar}]4s^23d^4$. However, the observed configuration is Cr: $[\mathrm{Ar}]4s^13d^5$. The chromium atom is an exception to the aufbau principle. One explanation for this anomaly is provided by experimental evidence that indicates that unfilled subshells are less stable than half-filled and filled subshells, and that unfilled subshells have higher energy. It is less important for *s* orbitals to be filled or half-filled compared with *d* orbitals. In the chromium atom, an *s* electron moves to the *d* subshell and creates two half-filled *s* and *d* subshells: $4s^23d^4$ becomes $4s^13d^5$. This movement of electrons creates an overall energy state that is lower and therefore more stable.

The atoms of each of the next four elements, manganese through nickel, have the expected configurations:

Mn: [Ar]$4s^2 3d^5$ Co: [Ar]$4s^2 3d^7$

Fe: [Ar]$4s^2 3d^6$ Ni: [Ar]$4s^2 3d^8$

The electron configuration of the copper atom is expected to be [Ar]$4s^2 3d^9$. However, the observed configuration is Cu: [Ar]$4s^1 3d^{10}$. Copper is another exception to the aufbau principle. In the copper atom, an *s* electron moves to the *d* subshell and creates a half-filled *s* subshell and a filled *d* subshell, which makes it more stable.

The atom of the next element, zinc, has the expected configuration: Zn: [Ar]$4s^2 3d^{10}$.

The configurations of elements in the first row of the transition metals are shown in **Figure 9**. The elements gallium through krypton have configurations that correspond to filling the 4*p* orbitals.

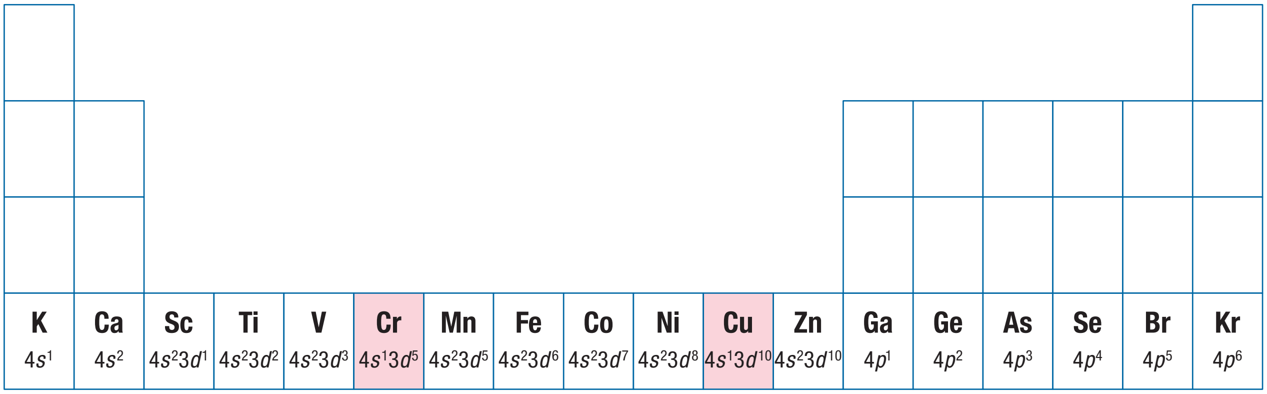


Figure 9 Valence electron configurations for potassium through krypton. The fourth period transition metals (scandium through zinc) have the general configuration [Ar]$4s^2 3d^n$, except for chromium and copper (highlighted in pink).

Figure 10 shows which orbitals in the periodic table are the last to be filled.

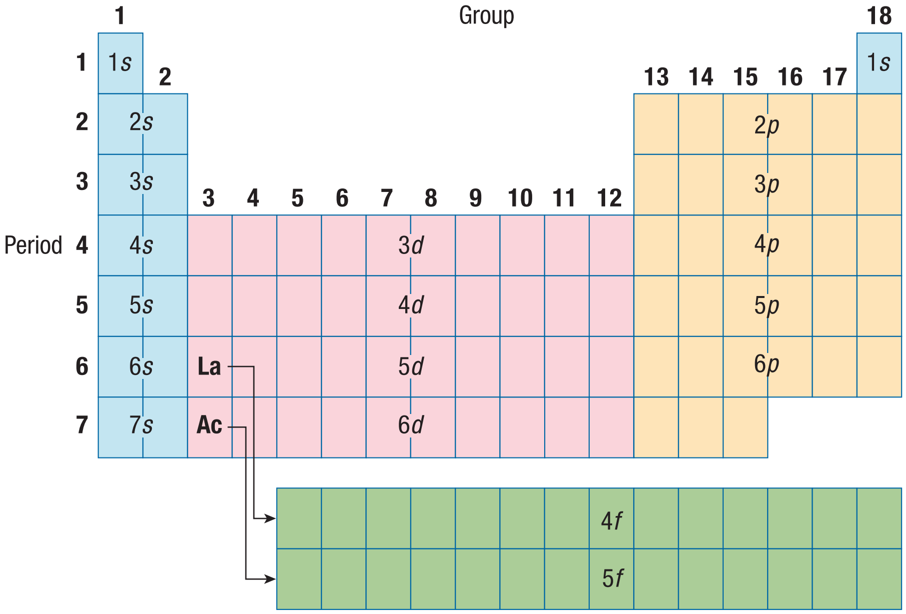


Figure 10 In the atoms of a period, the $(n + 1)s$ orbital fills before the *nd* orbital. The group labels indicate the number of valence electrons (*ns* plus *np* electrons) of atoms of the elements in each group.

Note the following additional points (with reference to Figure 10):

1. The ($n + 1$)*s* orbitals always fill before the *nd* orbitals. For example, the 5*s* orbitals fill before the 4*d* orbitals in atoms of the period 5 transition metals (yttrium through cadmium). This order of filling can be explained by the penetration effect: the 4*s* orbital penetrates closer to the nucleus, so it has a lower energy than the 4*d* orbital (see Figure 5, p. 162).
2. After lanthanum ([Xe]$6s^2 5d^1$), there is a group of 14 elements called the lanthanide series, or the lanthanides. This series of elements corresponds to filling the seven 4*f* orbitals in their atoms. Similarly, after actinium ([Rn]$7s^2 6d^1$), there are the 14 elements that make up the actinide series.
3. In the lanthanide and actinide series, since the 5*d* and 4*f*, and the 6*d* and 5*f* orbitals are close in energy, the increased stability associated with empty, half-filled and fully filled orbitals affects the electron configurations.
4. The group labels 1 to 18 indicate the total number of valence electrons for the atoms in these groups. For example, atoms of all the elements in Group 15 have the configuration ns^2np^3. (The *d* electrons fill one period later and are usually not counted as valence electrons.) The elements in Groups 1 to 18 are often called the main group, or **representative elements**. The atom of every member in each group has the same valence electron configuration.

representative elements those elements in the main blocks of the periodic table, which are Groups 1 to 18 (the *s* and *p* blocks)

The quantum mechanical model explains the arrangement of elements in the periodic table. This model allows you to understand why the elements in a group have similar chemistry: they all have atoms with the same valence electron configuration. Only the principal quantum number of the valence orbitals changes in a particular group.

In this text, when an electron configuration is given, the orbitals are listed in the order in which they fill. It is important to be able to write the electron configuration of atoms of each of the main group elements. If you understand how the periodic table is organized, it is not necessary to memorize the order in which the orbitals fill. Review Figure 10 to ensure you understand the correspondence between the orbitals and the periods and groups.

Predicting the electron configurations of the atoms of the transition metals (3*d*, 4*d*, and 5*d* elements), the lanthanides (4*f* elements), and the actinides (5*f* elements) is more difficult because there are many exceptions. Familiarize yourself with the electron configurations of the atoms chromium and copper, the two exceptions in the first-row transition metals, because these elements are often encountered: Cr: $[Ar]4s^1 3d^5$ and Cu: $[Ar]4s^1 3d^{10}$.

UNIT TASK **BOOKMARK**

Use the information in this section as you work on the Unit Task on page 268.

Tutorial 2 Writing Electron Configurations Using the Periodic Table

In this tutorial, you will practise writing electron configurations using the periodic table instead of the energy-filling order.

Sample Problem 1: Writing Electron Configurations

Give the electron configurations for the atoms of sulfur, S; cadmium, Cd; hafnium, Hf; and radium, Ra, using the periodic table (Appendix B1). Use Figure 10 on page 168 as an aid.

Solution

Sulfur is element 16 and resides in period 3, where the 3*p* orbitals of the atoms are being filled. Since sulfur is the fourth of the 3*p* elements in Figure 10, its atom must have 4 3*p* electrons. Its configuration is

S: $1s^2 2s^2 2p^6 3s^2 3p^4$ or [Ne]$3s^2 3p^4$

Cadmium is element 48 and is located in period 5 at the end of the 4*d* transition series. Since it is the tenth element in the series, the cadmium atom has 10 electrons in the 4*d* orbitals, in addition to the 2 electrons in the 5*s* orbital. Its electron configuration is

Cd: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$ or [Kr]$5s^2 4d^{10}$

Hafnium is element 72 and is found in period 6. Note that it occurs just after the lanthanide series. Thus, the 4*f* orbitals are already filled in the hafnium atom. Hafnium is the second member of the 5*d* transition series and its atom has two 5*d* electrons. The electron configuration of the hafnium atom is

Hf: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^2$

or [Xe]$6s^2 4f^{14} 5d^2$

Radium is element 88 and is in period 7. Thus, the radium atom has 2 electrons in the 7*s* orbital. Its electron configuration is

Ra: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2$

or [Rn]$7s^2$

Practice

1. Give the full electron configurations for the elements titanium, Ti(s), and aluminum, Al(s), using the periodic table in Appendix B1. Modify these configurations to show the shorthand noble gas form. T/I C

   [ans: Ti: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ or [Ar]$4s^2 3d^2$; Al: $1s^2 2s^2 2p^6 3s^2 3p^1$ or [Ne]$3s^2 3p^1$]

2. Write the shorthand configuration for the following: $_{35}$Br; $_{43}$Tc; $_{83}$Bi, $_{59}$Pr; $_{96}$Cm T/I C

   [ans: $_{35}$Br: [Ar]$4s^2 3d^{10} 4p^5$; $_{43}$Tc: [Kr]$5s^2 4d^5$; $_{83}$Bi: [Xe]$6s^2 4f^{14} 5d^{10} 6p^3$; $_{59}$Pr: [Xe]$6s^2 5d^1 4f^2$; $_{96}$Cm: [Rn]$7s^2 6d^1 5f^7$]

Explaining Ion Charges

The ability of transition metals to form multiple ions can now be explained. The electron configuration for the neutral cadmium atom is Cd: [Kr]$5s^2 4d^{10}$. It shows that the cadmium atom has 12 electrons in its outer orbitals. Cadmium forms a 2+ ion. If the outer two 5*s* electrons were removed, the neutral cadmium atom would be left with a full 4*d* orbital and would be relatively stable: Cd^{2+}: [Kr]$4d^{10}$. Alternatively, the cadmium atom could give up 10 electrons and leave filled 5*s* orbitals. (However, this possibility is very unlikely.)

Lead, Pb, is an example of how 2+ and 4+ ions form. The neutral electron configuration for the lead atom is Pb: [Xe]$6s^2 4f^{14} 5d^{10} 6p^2$. It shows full 6*s*, 4*f*, and 5*d* orbitals and a partially filled 6*p* orbital (2 out of 6 electrons). The lead atom could lose these two 6*p* electrons fairly easily, forming a 2+ lead ion. To form a 4+ ion, the lead atom would have to lose 4 electrons from its 6*s* and 6*p* orbitals.

Explaining Magnetism

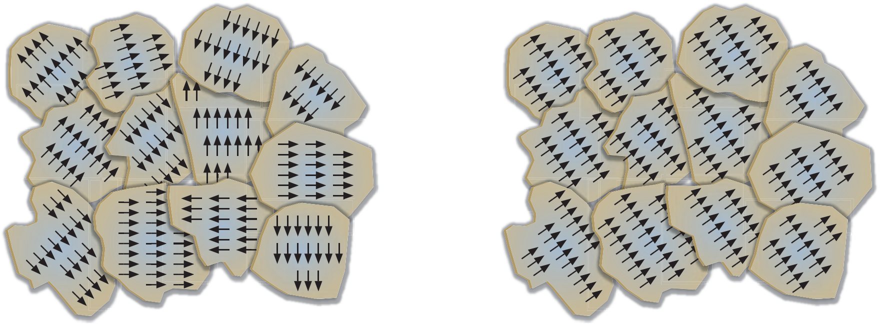
Table 1 shows three strongly magnetic elements and the electron configurations of their atoms. Based on the evidence in Table 1, you might speculate that magnetism is caused by the presence of several unpaired electrons in an atom. However, if you examine the periodic table more closely, you will notice that the elements ruthenium, rhodium, and palladium—which are in the same group as iron, nickel, and cobalt—are only weakly magnetic. These elements also have several unpaired electrons. Therefore, having several unpaired electrons only partially explains the strong magnetic properties of iron, nickel, and cobalt. There must be other properties that can explain why these metals are so strongly magnetic.

Table 1 Electron Configurations of Ferromagnetic Elements

Ferromagnetic element	Electron configuration	*d*-orbital filling	Pairing of *d* electrons
Fe	[Ar]$4s^2 3d^6$	↑↓ | ↑ | ↑ | ↑ | ↑	1 pair; 4 unpaired
Co	[Ar]$4s^2 3d^7$	↑↓ | ↑↓ | ↑ | ↑ | ↑	2 pairs; 3 unpaired
Ni	[Ar]$4s^2 3d^8$	↑↓ | ↑↓ | ↑↓ | ↑ | ↑	3 pairs; 2 unpaired

Scientists have found that iron, nickel, and cobalt consist of small, dense packs of atoms called domains. The magnetic fields of atoms in a domain align in the same direction, even though the domains themselves align randomly (**Figure 11(a)**). However, in the presence of an outside magnetic field, the magnetic fields of most of the domains become aligned with the outside field and, hence, with one another (**Figure 11(b)**). As a result, many groups of atoms become aligned in the same direction and the metal becomes a permanent magnet. They stay magnetized even when the external magnetic field is removed. This is because their magnetic properties are based on the alignment of their atoms. The mechanism by which elements form permanent magnets is called **ferromagnetism**. Iron, nickel, and cobalt are the most well-known ferromagnetic elements.

ferromagnetism the very strong magnetism commonly exhibited by materials that contain nickel, iron, and cobalt; applies to a collection of atoms



(a) no external magnetic field

(b) external magnetic field present

Figure 11 (a) In the absence of an external magnetic field, the magnetic domains are randomly aligned. (b) In the presence of a magnetic field, the domains align with the field. Once aligned, these domains stay aligned until they are disturbed.

Iron, cobalt, and nickel display strong magnetic properties, but there are other elements, such as aluminum and platinum, that display weak but measurable magnetic fields. These fields arise due to the presence of unpaired electrons in the atom. Hund's rule tells us that unpaired electrons in an atom all have the same spin. This spinning generates a weak magnetic field, a property called **paramagnetism**. This magnetic field is not usually noticed but is detectable when the element interacts with a strong magnetic field.

paramagnetism the weak attraction of a substance to a magnet; applies to individual atoms

Investigation 3.5.1

Paramagnetism (page 182)
Some elements exhibit magnetic properties, whereas some elements display magnetic properties only when exposed to a magnetic field. This controlled experiment will give you an opportunity to identify paramagnetic materials.

3.5 Review

Summary

- The electron configuration of an atom describes the energies and locations of the electrons in the atom.
- The aufbau principle states that each successive electron added to an atom occupies the lowest-energy orbital available to it.
- Hund's rule states that orbitals of equal energy fill with 1 unpaired electron each before electrons begin to pair up.
- Valence electrons—the electrons in the outermost principal quantum level of an atom—determine many of the chemical properties of elements.
- Electron configurations can be simplified by writing shorthand configurations.
- The characteristic properties and positions of elements in each of the *s*, *p*, and *d* sections of the periodic table are related to their electron configurations.

Questions

1. (a) Four blocks of elements in a periodic table refer to various subshells being filled. What are the four blocks and the corresponding orbitals?
   (b) What information from the periodic table helps you derive an electron configuration from the position of an element in the periodic table?
   (c) State the aufbau principle and Hund's rule.
   (d) Explain how the aufbau principle and Hund's rule help us determine the order of orbital filling. K/U
2. Draw an outline of the periodic table. Shade the *s* block in red, the *p* block in blue, the *d* block in green, and the *f* block in yellow. Include a key. K/U C
3. For elements 1 to 36, there are two exceptions to the filling order predicted by the periodic table. K/U T/I
   (a) Write the electron configurations for these two elements, and indicate how many unpaired electrons are present.
   (b) Briefly explain why these unpredicted electron configurations form.
4. The elements Si, Ga, As, Ge, Al, Cd, S, and Se are all used in the manufacture of various semiconductor devices. Write the expected full electron configurations for the atom of each of these elements. T/I C
5. The elements Cu, O, La, Y, Ba, Tl, and Bi are all found in high-temperature ceramic superconductors. Write the shorthand noble gas configurations for the atom of each of these elements. T/I C
6. Use the periodic table to predict which orbital the last electron enters for each of the following atoms: T/I
   (a) Zn
   (b) I
   (c) Ba
7. Using only the periodic table, write the expected ground-state electron configuration for the atom of
   (a) the third element in Group 15
   (b) element number 116
   (c) an element with 3 unpaired 5*d* electrons
   (d) the halogen with electrons in the 6*p* atomic orbitals K/U T/I C
8. Write the full electron configuration for the atom of each of the following: K/U T/I C
   (a) the lightest halogen
   (b) an alkali metal with a full 3*p* orbital
   (c) the Group 13 element in the same period as Sn
   (d) the non-metallic elements in Group 14
9. Draw the energy-level diagram for the atom of each of the following elements: T/I C
   (a) boron
   (b) silicon
   (c) mercury
10. Use electron configurations to explain
    (a) why arsenic can acquire charges of −3 and +3 but not +2
    (b) the +2 charge on the lead(II) ion
    (c) the +1 charge of the silver ion K/U T/I C

Applications of Quantum Mechanics

3.6

Quantum technologies are more common than you may think. They are used in lasers in DVD players (**Figure 1**), microchips in cellphones, and MRI machines in hospitals. All of these technologies operate at the nanoscale level, where the effects of quantum mechanics are significant.

Quantum mechanics and quantum theory are not science fiction. They are at the core of each of the above technologies, and are also the foundation of many cutting-edge scientific research projects. The effects of these technologies can be beneficial, but it is always important to recognize that there may also be associated risks that can be detrimental to society and the environment. The risks and benefits and/or application must be considered carefully.

While there are numerous applications, this section explores three specific applications of quantum theory: lasers, Bose–Einstein condensates, and quantum analysis and diagnostic technologies (MRI). **Figure 2** shows some additional applications of quantum theory.

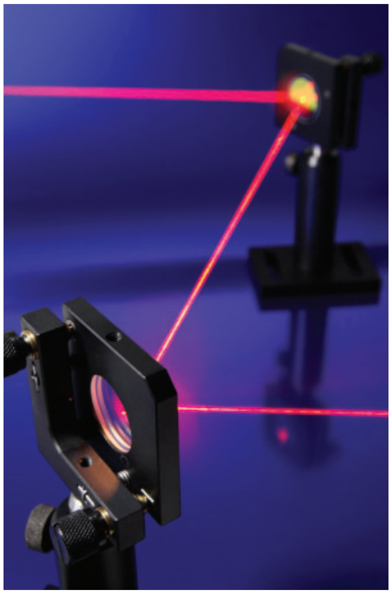


Figure 1 Lasers are possible because of an understanding of quantum mechanics.

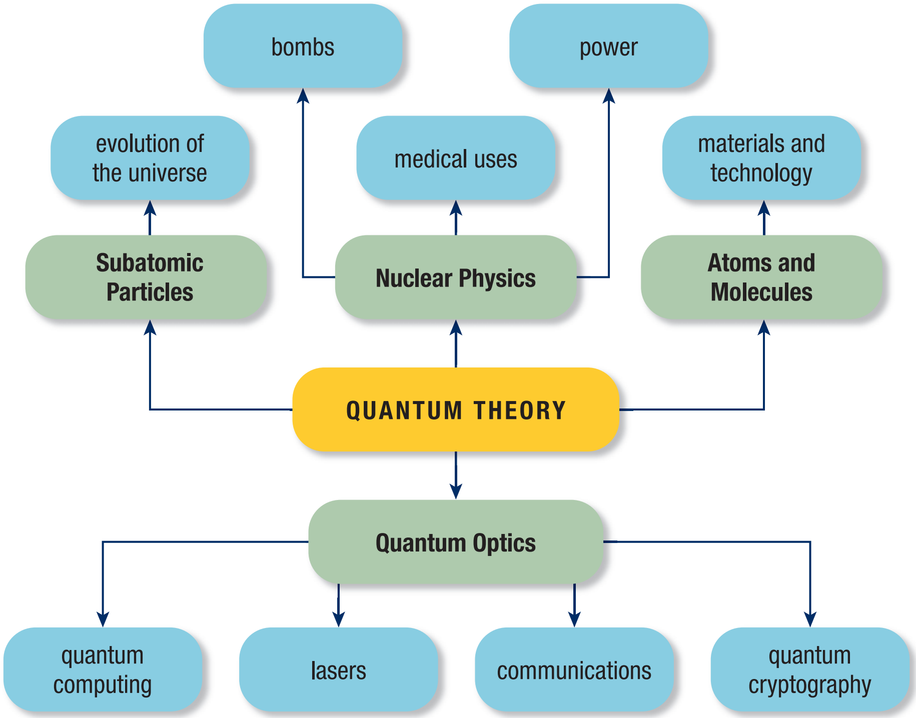


Figure 2 Quantum theory has many applications (shown in blue) across many industries (shown in green).

Laser Technology

Applied science occurs when science theory or knowledge is used for practical purposes. Often, a technology develops first and then scientific theory is used to explain how it works. However, in some cases, the technology is theorized and then science is used to develop the technology. To illustrate this point, consider the development of laser technology. In 1917, Einstein established the theoretical foundations for the laser. He proposed the theory that electrons can be stimulated to higher energy states and then release radiation when they return to the ground state. In order to develop the laser, scientists first had to understand quantum theory, especially the way electrons make quantum leaps from one energy level to another.

The race to develop the first laser devices had its share of controversy. Many research labs were working on developing the laser at the same time, and there were arguments about who could lay claim to the first series of patents. Theodore Maiman

laser (**l**ight **a**mplification by **s**timulated **e**mission of **r**adiation) a device that produces light of a single colour with all waves travelling parallel to each other

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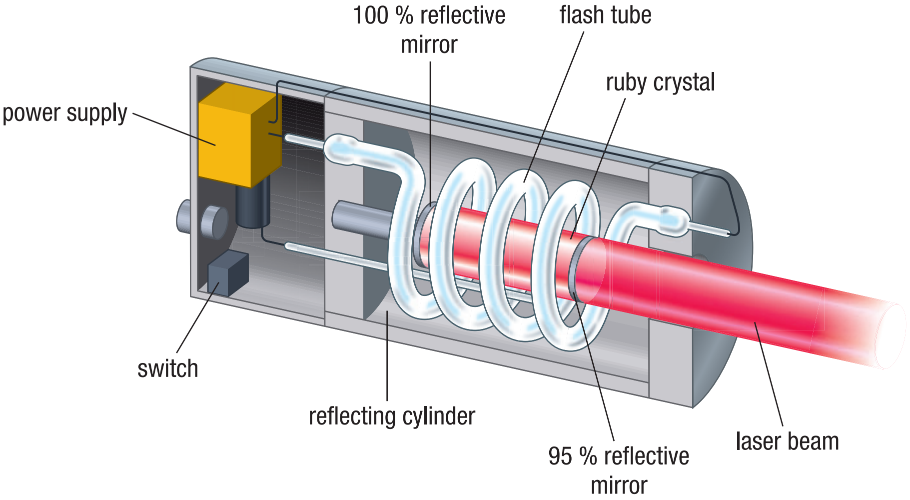

Figure 3 Lasers contain an electric flash tube that emits a series of bright flashes of light. Electrons in atoms of the ruby rod absorb photons from the flash tube and move into higher energy levels. When these excited electrons drop back to a lower energy level, they emit photons with a specific wavelength. The release of photons by a few atoms triggers other atoms to do the same. This action increases the intensity of the laser light. Mirrors reflect the photons back and forth between the ends of the ruby rod, and the laser beam eventually passes through the mirror at the right end of the rod.

The operation of lasers is based on quantum theory. An electron requires a photon of specific energy to excite it to a higher energy level. An excited electron hit by a photon of specific energy will return to its original energy level after releasing a photon with the same energy. Some of the photons released collide with other atoms in the ruby rod in Figure 3, causing other photons to be released. Some photons reflect from the mirrors at the ends of the rod, and then collide with atoms, which releases more photons. This effect is called the amplification of photons. Some of the photons that travel along the axis of the ruby rod eventually exit through the 95 % reflective mirror and form the laser beam. These photons all have the same wavelength and travel in parallel, continuous waves along the same path.

Figure 4 Satyendra Bose of India collaborated with Albert Einstein to predict the existence of the Bose–Einstein condensate.

Bose–Einstein Condensate: Another State of Matter

In the 1920s, Satyendra Nath Bose of India (**Figure 4**) and Albert Einstein together predicted the existence of another state of matter, sometimes referred to as the fifth state of matter. They hypothesized that if a collection of atoms were cold enough, all the atoms would be in the lowest possible quantum energy state and would therefore have identical energy. As a result, the atoms could effectively all occupy the same space at the same time—a very strange idea. Scientists called this state a condensate, sometimes referred to as the Bose–Einstein condensate. **Bose–Einstein condensate (BEC)** is a state of matter that consists of a pile of atoms all in the same place at the same time (**Figure 5**). It exists only at temperatures within a few billionths of a degree of absolute zero, which is 0 K or −273.15 °C. WEB LINK

It was not until 1995 that scientists were able to create the first condensate in a laboratory. The cooling technology necessary for producing condensates was not available until this time. No one yet knows how Bose–Einstein condensates can be put to practical use, but not every scientific discovery yields a practical application. The purpose of science is to learn about the universe. The BEC is another example of quantum theory predicting an actual material result.

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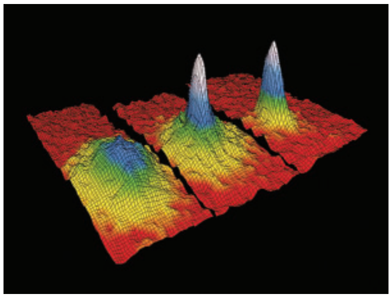

Figure 5 A Bose–Einstein condensate is beginning to form on the left and reaches completion on the far right.

Quantum Analysis and Diagnostic Technologies

At the beginning of this chapter, you saw an example of quantum analysis in a diagnostic technology called magnetic resonance imaging. **Magnetic resonance imaging (MRI)** uses a strong magnetic field to cause the magnetic fields of the hydrogen atoms to align in the same direction as the outside magnetic field. A radio transmitter then applies varying radio waves. Certain frequencies of the radio waves are absorbed when the radio-frequency photons cause the magnetic fields of the molecules to "flip" to the opposite direction. A scanner detects the changes in the spectrum of radio waves, and a computer converts these changes into an image. Today's scanning techniques can produce a three-dimensional image that can be rotated on a computer screen (**Figure 6**). The MRI is an option for scanning soft tissues, such as muscles, internal organs, and the brain. WEB LINK

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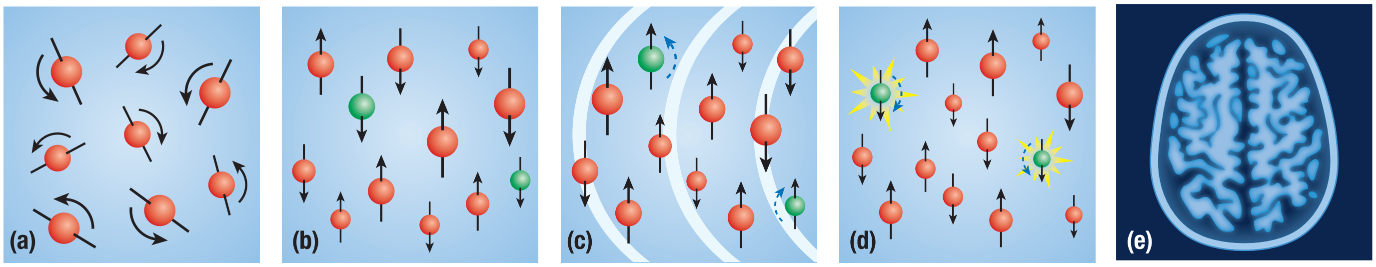

Figure 6 (a) Hydrogen atoms in water molecules in the body spin in random directions. (b) When the MRI machine produces a magnetic spin, the hydrogen atom's spin will line up in the direction of the magnetic field. About half will spin up, and the rest will spin down. But the balance is not exactly equal. There will be a few atoms (green atoms) that have a spin that does not cancel. This produces a measurable magnetic field. (c) A radio pulse is then applied, causing these unmatched atoms to reverse their spin. (d) When the pulse is removed, these atoms will flip back to their original spin and release energy. (e) Detectors in the machine register the energy released, and a computer program interprets the energy patterns to create an image.

One advantage that MRI has over X-ray and CAT (computerized axial tomography or CT) scans is that MRI does not use ionizing radiation. There is virtually no risk to patients who receive an MRI scan. Patients who receive an X-ray or CAT scan are exposed to low levels of radiation, which is a known risk for cancer, although the levels are so low that this is not a major concern for most patients and the benefits outweigh the risks. CAREER LINK

The application of quantum theory to common, everyday technologies is still in its infancy. Quantum technologies allow scientists to obtain increasingly sensitive measurements in their analyses. This increased precision in measurement will allow the development of new technologies that have even greater precision. The application of these technologies will range from quantum imaging and photography to smaller computer chips. Quantum computers may become possible as scientists learn more about creating and maintaining certain quantum energy states in atoms and ways of detecting changes in those states. Computing speed and memory capacity could be increased to amazing levels. As more and more technologies emerge that operate at the atomic or molecular level, the implications of quantum theory will only become more important. WEB LINK

3.6 Review

Summary

- The applications of quantum mechanics are extensive, and the technology is advancing at a very fast rate.
- Advances in quantum technology are generating cutting-edge materials, improved medical diagnostic capabilities (such as MRI), new sources of power, and revolutionary computing power.
- Laser technology is based on electrons being stimulated to release photons.
- The Bose–Einstein condensate is a gas-like state of matter that exists at extremely cold temperatures. It was predicted around 1925 and confirmed in 1995.
- Magnetic resonance imaging technology is possible due to an understanding of how hydrogen atoms in water react in magnetic fields.
- Quantum theory will become increasingly important as new atomic-scale technologies are developed.

Questions

1. Explain how an element's absorption and emission spectra could be used to predict the colour of light it might produce if it were used in a laser. K/U A
2. What would most likely happen to the intensity of a laser beam if the mirrors in the device were misaligned? Explain your answer. K/U A
3. Create a poster or other presentation format summarizing four everyday applications of lasers. Include a brief description of how lasers are used in each device. K/U C A
4. Explain why Bose–Einstein condensates were only theoretical until the mid-1990s. K/U A
5. Both the magnetic field and the radio pulse are important in the function of MRI. Use a flow chart with diagrams to describe how an image is produced in MRI. K/U C A
6. What is the primary advantage of MRI over X-rays and CT scans? K/U
7. Research quantum computing. 🌐 T/I C A
    (a) Explain what quantum computing is and how it works.
    (b) Outline the differences between a quantum computer and a modern traditional computer.
    (c) In what ways are quantum computers better than traditional computers?
    (d) Are there any drawbacks or disadvantages to quantum computers?
8. Cryptography is the study of codes. Research one type of traditional cryptography, along with the area of cryptography called quantum cryptography. Then answer the following: 🌐 K/U T/I A
    (a) Write a brief report to explain how your chosen traditional cryptography works. In your report, include the probability of decoding your chosen cryptography, as well as its weaknesses and strengths.
    (b) Where has quantum cryptography been used thus far?
    (c) How are photons and polarizations used in quantum cryptography?
    (d) Outline the steps involved in sending, receiving, and interpreting a quantum-encrypted message.
    (e) Compare the traditional cryptographic method to the quantum cryptographic method. What advantages does quantum cryptography have over traditional cryptography and vice versa?
9. Research the difference between gas and chemical lasers. Briefly explain the difference, and state where each is used. 🌐 K/U T/I A
10. The development of MRI technology has revolutionized medical research, especially the study of how the brain works. Research a neurological disorder, such as epilepsy, and find out how MRI technology has enhanced this field of study. Report on your findings in a format of your choosing. 🌐 K/U T/I C A

🌐 WEB LINK

Applications of Quantum Mechanics

3.6

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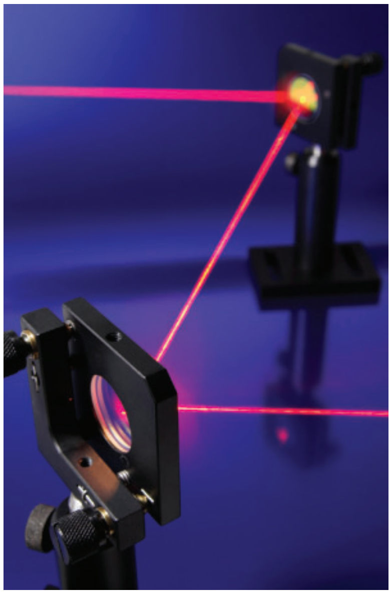

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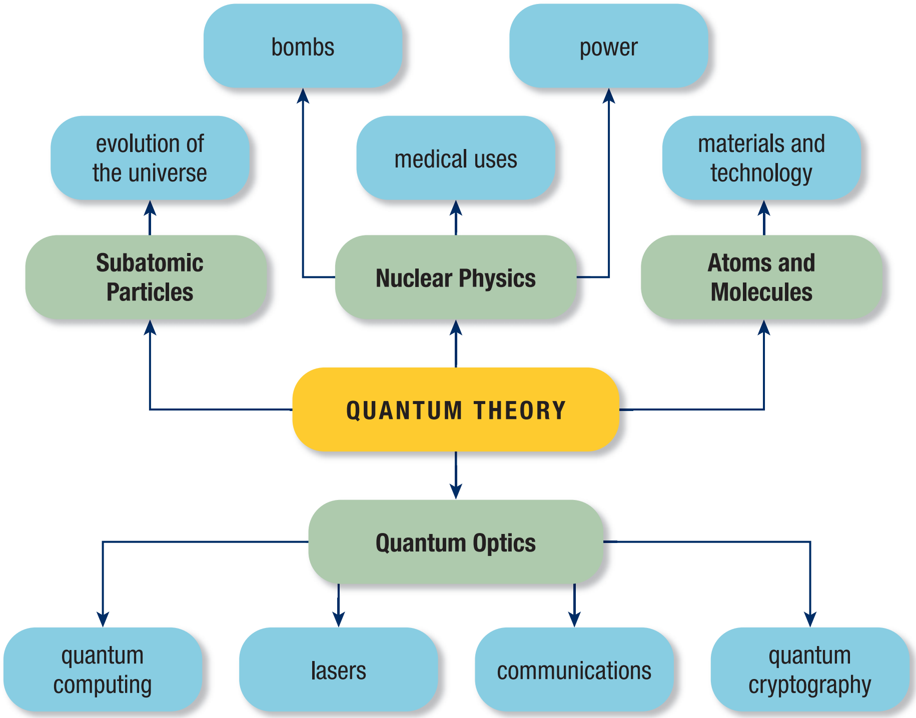

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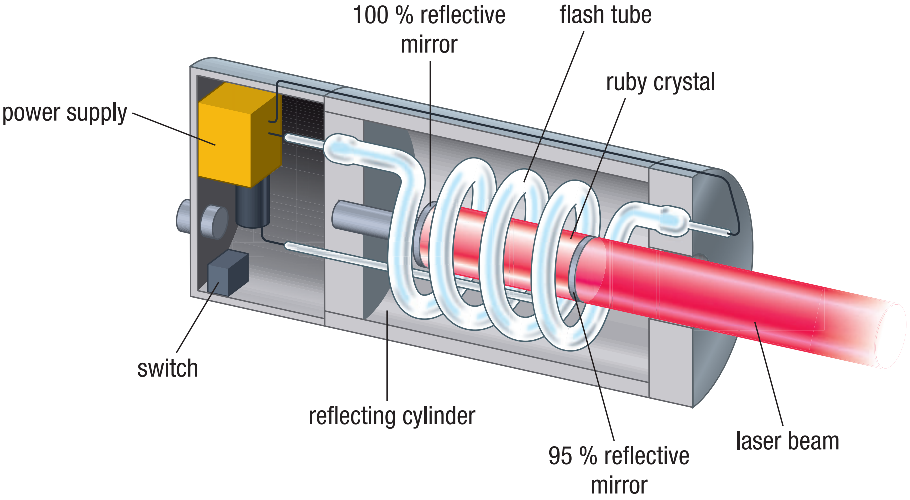

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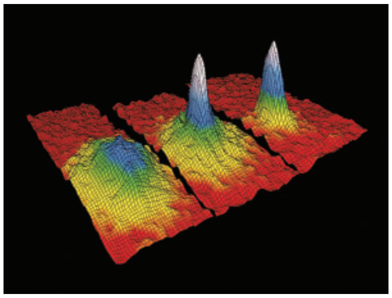

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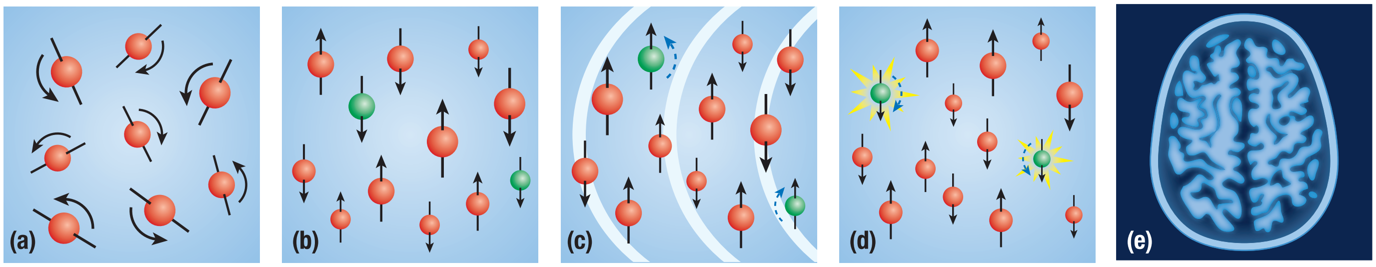

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- The applications of quantum mechanics are extensive, and the technology is advancing at a very fast rate.
- Advances in quantum technology are generating cutting-edge materials, improved medical diagnostic capabilities (such as MRI), new sources of power, and revolutionary computing power.
- Laser technology is based on electrons being stimulated to release photons.
- The Bose–Einstein condensate is a gas-like state of matter that exists at extremely cold temperatures. It was predicted around 1925 and confirmed in 1995.
- Magnetic resonance imaging technology is possible due to an understanding of how hydrogen atoms in water react in magnetic fields.
- Quantum theory will become increasingly important as new atomic-scale technologies are developed.

Questions

1. Explain how an element's absorption and emission spectra could be used to predict the colour of light it might produce if it were used in a laser. K/U A
2. What would most likely happen to the intensity of a laser beam if the mirrors in the device were misaligned? Explain your answer. K/U A
3. Create a poster or other presentation format summarizing four everyday applications of lasers. Include a brief description of how lasers are used in each device. K/U C A
4. Explain why Bose–Einstein condensates were only theoretical until the mid-1990s. K/U A
5. Both the magnetic field and the radio pulse are important in the function of MRI. Use a flow chart with diagrams to describe how an image is produced in MRI. K/U C A
6. What is the primary advantage of MRI over X-rays and CT scans? K/U
7. Research quantum computing. 🌐 T/I C A
   (a) Explain what quantum computing is and how it works.
   (b) Outline the differences between a quantum computer and a modern traditional computer.
   (c) In what ways are quantum computers better than traditional computers?
   (d) Are there any drawbacks or disadvantages to quantum computers?
8. Cryptography is the study of codes. Research one type of traditional cryptography, along with the area of cryptography called quantum cryptography. Then answer the following: 🌐 K/U T/I A
   (a) Write a brief report to explain how your chosen traditional cryptography works. In your report, include the probability of decoding your chosen cryptography, as well as its weaknesses and strengths.
   (b) Where has quantum cryptography been used thus far?
   (c) How are photons and polarizations used in quantum cryptography?
   (d) Outline the steps involved in sending, receiving, and interpreting a quantum-encrypted message.
   (e) Compare the traditional cryptographic method to the quantum cryptographic method. What advantages does quantum cryptography have over traditional cryptography and vice versa?
9. Research the difference between gas and chemical lasers. Briefly explain the difference, and state where each is used. 🌐 K/U T/I A
10. The development of MRI technology has revolutionized medical research, especially the study of how the brain works. Research a neurological disorder, such as epilepsy, and find out how MRI technology has enhanced this field of study. Report on your findings in a format of your choosing. 🌐 K/U T/I C A

🌐 WEB LINK

3.7 Explore an Application in Quantum Mechanics

The Tiny World of Nanotechnology

SKILLS MENU

- Researching
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating
- Identifying Alternatives

A nanometre is one billionth of a metre—the scale of atomic and molecular interactions. For perspective, a single hair from your head is about 100 000 nanometres in diameter. Nanotechology is the science of working with structures that are between 1 nm and 100 nm long in at least one dimension. The effects of quantum mechanics are very important when working at this scale. The invention of the scanning electron microscope contributed to nanotechnology because scientists could actually confirm the geometry of molecules they constructed.

Nanotechnology began with the development of carbon-based cage molecules such as the fullerenes (also known as buckyballs). Due to their electron configuration, carbon atoms can form three-dimensional soccer ball–shaped structures (**Figure 1**(**a**)). Carbon atoms can also bond in ways that form long, hollow nanotubes (**Figure 1**(**b**)). Carbon nanotubes exhibit extraordinary strength. One possible use being explored is adding carbon nanotubes to building materials to increase their strength. If nanotubes can be woven into fabric, they could be used to create bullet- and knife-proof clothing. Nanotubes are good conductors of electricity, so the production of ultra-thin batteries, electronic and computer devices, and solar cells from nanotubes is being explored. Nanoparticles of certain substances have already been added to textiles to produce fabric that resists stains and eliminates unwanted odours.

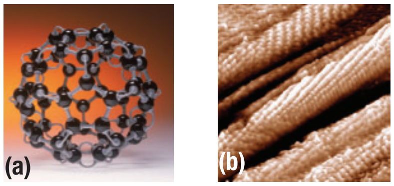


Figure 1 (a) A buckyball is a member of the fullerene family of carbon compounds. (b) Carbon nanotubes are extraordinarily strong.

Nanotechnology has led to the possibility of molecule-sized nanomachines that could one day work inside cells and tissues to treat diseases. For example, nanobots could be used to remove plaque from arterial walls in an effort to treat heart disease (**Figure 2**).

Scientists are working to construct molecular assemblers—nanomachines that can assemble atoms into designer molecules. Such machines may be able to synthesize molecules that are nearly impossible to make by ordinary chemical reactions. These molecules could be the wonder drugs of the future. In addition, nanomachines could repair genetic defects by modifying the DNA in cells or targeting the RNA of cancerous cells (**Figure 3**). On the other hand, science-fiction stories have been written on the theme of out-of-control molecular machines.

Figure 2 Someday, nanobots could help treat heart disease. (Artist's rendition)

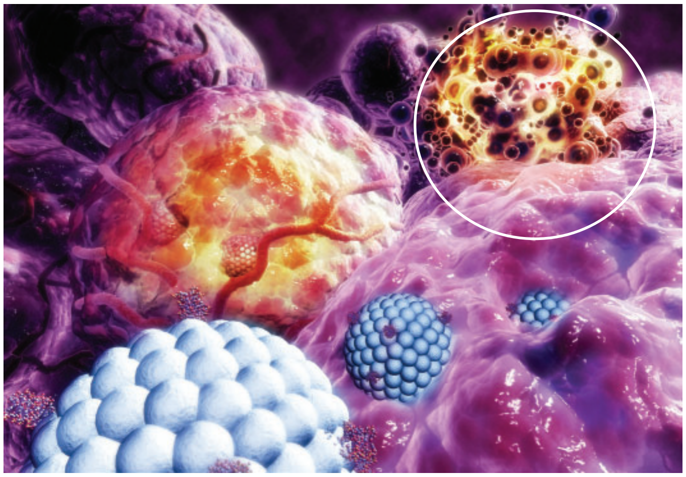


Figure 3 This image highlights nanoparticles (dark spots) attacking a tumour in the body (circled). (Artist's rendition)

Nanotechnology is poised to become the fastest-growing field of technology. For this reason, scientists have been considering the possible disadvantages of nanotechnology. For example, what if a targeted cancer drug attacked the wrong cells? These tiny particles are too small for existing air and water filtration systems. An accumulation of nanoparticles in the air could contribute to air pollution, just as any other airborne particles can, and possibly trigger inflammatory diseases of the lungs, such as asthma. Experts are debating these issues at international conferences and proposing regulations for the application of nanotechnology.

The Application

You are the CEO of a healthcare and medical diagnostic centre in southern Ontario. You must decide what types of nanotechnology-based services to offer to patients who visit your centre.

Your Goal

To learn about the risks and benefits of a specific application of nanotechnology, and to determine whether this application is or needs to be regulated by the government

Research

SKILLS HANDBOOK A5.1

Explore one specific application of nanotechnology. Choose from the following topics, or choose your own topic with your teacher's approval:

- nanoparticles for drug delivery systems in the human body
- nanobots for internal surgery purposes
- nanotechnology in medical diagnostic equipment

Possible Solutions

SKILLS HANDBOOK A5.1, A5.2

Set selection criteria for the nanotechnology you are considering. These criteria could include costs of the technology, current status of the research, availability of the technology, professional training or certification required, health concerns, environmental impact, status of regulation elsewhere if it exists, and customer acceptance.

- Include other criteria as well.
- Develop a rating system for your criteria.
- Based on your research, evaluate the different alternatives according to your selection criteria.

Decision

Extract the main points of your research and be prepared to defend your decision.

Communicate

Create an Advisory Report in a format of your choice based on your findings. It should include

- an overview of the technology
- a risk–benefit analysis for the technology
- current and future applications of the technology
- regulations or guidelines currently in place, and suggestions for future regulations
- health and safety precautions (if any) that need to be taken by people who work with nanoparticles
- any other risks associated with the use of the technology, such as environmental risks WEB LINK

Investigation 3.1.1 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

The Photoelectric Effect

An electroscope detects and measures electrical activity. What will happen to a charged metal plate when light shines on it? In this investigation, you will charge a zinc plate by touching it with a charged object. You will then observe the effects of shining white and ultraviolet light on the plate.

Purpose

SKILLS HANDBOOK A2.3

To develop a basic understanding of photoelectric effect theory

Equipment and Materials

- ultraviolet light source
- electroscope (with a flat top)
- vinyl strip
- paper towel
- square zinc plate (3 cm to 5 cm)
- steel wool
- lamp (100 W bulb or more)

When unplugging the lamp or the ultraviolet source, pull on the plug, not the cord.

Do not touch the bulb after using it. It could be very hot. Do not look into an ultraviolet light source. It can damage your eyes.

Procedure

1. Position the electroscope so that it is on a level surface. Be sure the leaves move freely.
2. Rub the paper towel and vinyl together several times to create a negative charge on the vinyl.
3. Touch the vinyl to the top of the electroscope until the leaves open and remain open.
4. Observe the leaves for a minute or two.
5. Neutralize the electroscope by placing your finger on the top where you placed the vinyl. Observe the leaves.
6. Polish the zinc with steel wool until the zinc shines. Ensure that the zinc plate is very clean. Place the plate on the electroscope.
7. Repeat Steps 2 and 3 to charge the electroscope once more.
8. Plug in the lamp, and turn it on. Position the light bulb about 10 cm from the zinc plate.
9. Observe the electroscope for a minute or two.
10. Repeat Steps 2 and 3 as necessary to charge the electroscope. Repeat Steps 8 and 9 using ultraviolet light.

Analyze and Evaluate

(a) What was the effect of the lamp on the charged zinc plate compared with the control? T/I

(b) What was the effect of the ultraviolet light on the charged zinc plate compared with the control? T/I

(c) Should a greater intensity of ultraviolet or white light have a different effect? Explain. K/U

(d) Describe what was happening to the protons and electrons in the zinc plate during the investigation. T/I

(e) When lit with white light, was the electroscope more or less charged than when lit with ultraviolet light? T/I

(f) Use your observations from this investigation to explain the effect of ultraviolet light on the charged zinc plate. T/I

(g) What could you do, using the electroscope and zinc plate, to test your explanation above? T/I

(h) What changes could you make to the materials, equipment, and/or procedure to improve this investigation and the quality of data collected? T/I

Apply and Extend

(i) Some materials, such as glass, absorb ultraviolet light. What would happen if you positioned a glass plate between the charged zinc plate and the source of ultraviolet light? K/U T/I

(j) Would direct sunlight or sunlight through a window discharge the electroscope? Explain. K/U T/I A

(k) How do you think the results would change if the charge added to the zinc plate were positive instead of negative? T/I A

(l) Research a use or effect of this phenomenon. Write a short paragraph explaining what you learned. T/I A

WEB LINK

Investigation 3.2.1 OBSERVATIONAL STUDY

Bright-Line Spectra

All atoms can absorb and emit electromagnetic radiation. Some atoms absorb radiation in the range of the visible spectrum, and other atoms can absorb radiation in the ultraviolet or infrared ranges. When atoms absorb light, they produce a dark-line spectrum. Since atoms absorb and emit the same wavelengths of light, the absorption spectrum can be thought of as the "negative" of an emission spectrum. The emission spectrum is called a bright-line spectrum. This investigation will demonstrate dark-line and bright-line spectra.

Purpose

SKILLS HANDBOOK A2.3

To observe dark-line and bright-line spectra

Equipment and Materials

- spectrum tube power supply
- hydrogen gas spectrum tube
- spectroscope
- overhead projector
- heavy paper
- diffraction grating (600 lines/mm)
- tape
- beakers
- glass plate cover for beaker
- fume hood
- distilled water
- crystals of potassium permanganate and iodine

The spectrum tube power supply poses a serious potential shock hazard.

Procedure

1. Use the overhead projector to shine light on a white wall. Place sheets of heavy paper about 5 mm apart on the glass stage of the projector so all of the light is blocked except for a thin strip.
2. Suspend a diffraction grating in the middle of the vertical projection lens with tape.
3. Place a clean beaker on the thin strip of light. Shut off the room lights so the continuous visible spectrum can be observed.
4. Add distilled water to the beaker and observe the spectrum.
5. Add 4–6 crystals of potassium permanganate to the beaker and stir and observe the spectrum.

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

6. Gently heat the solid iodine in a covered beaker in a fume hood. Place this covered beaker of iodine vapour on the screen of the overhead projector over the light strip and observe the spectrum.
7. Observe the spectrum produced by sunlight using a spectroscope (**Figure 1**).

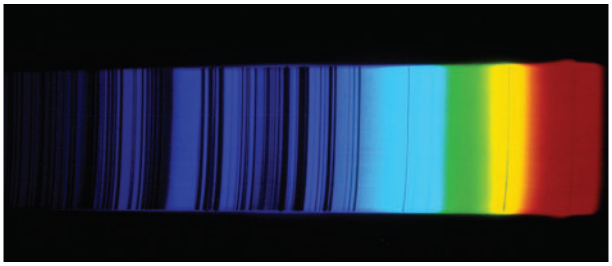


Figure 1 The dark-line spectrum of sunlight

8. Connect a spectrum tube filled with hydrogen gas to a spectrum tube power supply. Turn it on and observe the spectrum using a spectroscope. Draw and label the spectrum.

Analyze and Evaluate

(a) How does the visible spectrum change between the empty beaker and the beaker of water? Do either of these beakers and their contents absorb light? T/I

(b) Explain the difference between absorption spectra (Steps 5 and 6) and emission spectra (Step 8). What do you think the emission spectrum of iodine would look like? What do you think the absorption spectrum of hydrogen would look like? T/I

(c) How did adding potassium permanganate to water affect what you saw through the spectroscope? T/I

(d) What effect does iodine have on the spectrum? T/I

(e) Compare the spectrum for potassium permanganate with the spectrum of iodine. T/I

(f) Do gases absorb electromagnetic radiation? Describe the spectrum of hydrogen and any other gases you tested. T/I

(g) What evidence indicates that light from the Sun is being absorbed by gases? T/I

Apply and Extend

(h) Under what circumstances will a sample of gas produce visible light? T/I

(i) Is the hydrogen spectrum produced in this investigation a continuous spectrum or a bright-line spectrum? T/I

(j) How do scientists use line spectra? T/I A

(k) Describe a continuous spectrum, and explain how you could produce one in the lab. T/I

(l) Explain what is happening at the atomic level to produce (i) an absorption spectrum and (ii) an emission spectrum. K/U

(m) Research the uses of gas tubes in lighting. What colours are the most common? What gases are used? T/I A

(n) Research fluorescent light bulbs. How is the concept of emission spectra used in fluorescent light bulbs? T/I A

WEB LINK

Investigation 3.4.1

OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- **Performing**
- **Observing**
- **Analyzing**
- **Evaluating**
- **Communicating**

Simulation of Electron Orbitals

Atomic orbitals are regions of space in an atom where there is a high probability of finding an electron of a certain energy. In this investigation, you will use an orbital simulator to study the properties of orbitals.

Purpose

SKILLS HANDBOOK A2.3

To illustrate atomic models, demonstrate principles of quantum theory, and examine energy levels

Equipment and Materials

- computer with access to the Internet

Procedure

1. Go to the Nelson Science website, and run the simulation.

Analyze and Evaluate

(a) Describe and draw the shapes of *s*, *p*, *d*, and *f* orbitals. T/I C

(b) How many electrons does it take to fill the first energy level? How many does it take to fill the second energy level? T/I

(c) How many electrons, protons, and neutrons are in a stable neon atom? T/I

(d) Which quantum number determines the shape of the orbital? Which quantum number determines the size of the orbital? T/I

(e) Copy and complete **Table 1** in your notebook. T/I C

Table 1

	n	l	m_l
3*d*			
6*s*			
7*p*			
5*f*			

(f) Draw each of the following orbitals: T/I C

(i) 3*s*

(ii) 3*d*

(iii) 5*f*

(iv) 4*p*

(g) (i) How do the sizes of 1*s* and 2*s* orbitals compare?

(ii) How does the energy of an electron in the 1*s* orbital compare with the energy of an electron in the 2*s* orbital? T/I

(h) (i) How do the 2*s* and 2*p* orbitals compare?

(ii) How do the $2p_x$ and $2p_y$ orbitals compare? T/I

(i) Which atom has full 1*s* and 2*s* orbitals with half-filled $2p_x$ and $2p_y$ orbitals? T/I

Apply and Extend

(j) What happens to an atom when it is ionized? K/U

(k) What happens to an atom when it is radioactive? K/U

(l) What is a node? What is the probability of finding an electron at a node? K/U

(m) Which elements do not follow the electron configuration rules? K/U

(n) Does an electron in a 2*s* orbital have more energy than in a 2*p* orbital for a hydrogen atom? How do you know? K/U

(o) Does an electron in a 2*s* orbital have more energy than in a 2*p* orbital for a helium atom? How do you know? K/U

(p) Compare two orbitals with different principal quantum numbers (n) but the same secondary quantum number (l) and magnetic quantum number (m_l). What are two specific differences between them? K/U

(q) As the central charge of the nucleus increases for higher atomic weight atoms, the actual size of the nucleus is still much smaller than the size of the orbitals containing the electrons. Compare a 2*s* electron and a 4*s* electron in lithium and potassium. Give two reasons why it is easier to remove the 4*s* electron than the 2*s* electron from the atom. Use the simulation to help with your explanation. Remember to change the number of protons in the nucleus to account for the effect of the nuclear charge on the orbital. T/I C

(r) Draw 2 carbon atoms separated from one another by 120 pm along the *x*-axis, with the *y*-axis in the same plane as the *x*-axis and the *z*-axis perpendicular to the plane. It is possible for the 2*s* orbitals of the carbon atoms to overlap and form a bond between them. What other orbitals can form a bond between the carbon atoms along the *x*-axis? Can any other bonds form? Illustrate using the simulation. T/I C

WEB LINK

Investigation 3.5.1 CONTROLLED EXPERIMENT

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Paramagnetism

Michael Faraday first investigated paramagnetism in the mid-1800s. At that time, no one knew what caused paramagnetism because electrons had not yet been discovered. Scientists now think that there is a connection between unpaired electrons and magnetism. This investigation will test this hypothesis.

Testable Questions

SKILLS HANDBOOK A2.2

(a) Which solids are paramagnetic?
(b) How does the number of unpaired electrons affect the paramagnetic strength of metal salts?

Hypothesis

Formulate a hypothesis based on the testable questions.

Variables

Identify all major variables that will be measured and/or controlled in this investigation. Identify the manipulated and responding variables.

Experimental Design

In this investigation, you will determine which solids being tested are paramagnetic, both qualitatively and quantitatively, by using a magnet and a balance.

Equipment and Materials

- electronic balance
- chemical safety goggles
- 5 small test tubes with rims
- stirring rod
- thread
- laboratory stand
- clamp
- horizontal bar
- a very strong magnet, such as a neodymium magnet
- small wooden block
- 3.00 g each of the following solids:
  - calcium sulfate
  - aluminum sulfate Ⓣ
  - copper(II) sulfate pentahydrate Ⓣ
  - iron(II) sulfate heptahydrate
  - iron(III) chloride hexahydrate

Ⓣ Aluminum sulfate and copper(II) sulfate pentahydrate are both toxic and irritants. Avoid skin and eye contact. If you spill these chemicals on your skin, wash the affected area with plenty of cool water and inform your teacher.

People who have allergies to any of the chemicals may have irritations of the eyes or skin.

Procedure

Part A

1. Put on your safety goggles.
2. Place 3.00 g of each solid into different test tubes. Label each test tube.
3. Tie a thread around each test tube so that each may be suspended from a clamp on a laboratory stand. You will use this setup to measure any attraction each solid has toward a strong magnet.

Part B

4. Copy **Table 1** into your notebook, including the given data. You will use the given data and data you collect in your analysis.
5. An electronic balance will help you quantify the attraction of the metal salts to a strong magnet. Place the magnet on the wooden block, then place both objects on the balance. Set the balance to 0.00 g.

6. Clamp the test tube containing calcium sulfate to the laboratory stand 10 cm or higher above the magnet.
7. Slowly lower the test tube and observe the mass reading on the balance. Record the mass on the balance just before the magnet makes contact with the test tube. Record your data.
8. Repeat Steps 6 and 7 for the remaining test tubes containing metal salt samples.

Observations

Table 1 Mass Change in Magnetic Field

Ionic compound	Δm (g)
$CaSO_4(s)$	
$Al_2(SO_4)_3(s)$	
$CuCl(s)$	0.00
$CuSO_4 \cdot 5H_2O(s)$	
$NiSO_4 \cdot 7H_2O(s)$	−0.22
$CoCl_2 \cdot 6H_2O(s)$	−0.47
$FeSO_4 \cdot 7H_2O(s)$	
$FeCl_3 \cdot 6H_2O(s)$	
$MnSO_4 \cdot H_2O(s)$	−1.26

Analyze and Evaluate

(a) What variables were measured, recorded, and/or manipulated in this investigation? T/I

(b) Which solids are paramagnetic? T/I

(c) How certain are you about the data obtained? Identify possible error sources or areas of uncertainty. T/I

(d) Explain why some solids cause a zero change in the magnet's mass while other solids cause a negative change in the magnet's mass. T/I

(e) Create and complete another table with the following headings: Metal ion, Electron configuration of ion, Number of unpaired electrons, Molar mass of metal salt, Number of moles of metal salt, Mass reading decrease per mole. T/I C

(f) Use your data in (e) to draw a graph with the number of unpaired electrons on the *x*-axis and the decrease in mass per mole on the *y*-axis. Connect the points, and draw a single line of best fit. T/I C

Apply and Extend

(g) What are some ways you could improve the quantity and quality of data you collected? T/I A

CHAPTER 3 SUMMARY

Summary Questions

1. Create a study guide based on the points listed in the margin on page 132. For each point, create three or four sub-points that provide further information, relevant examples, explanatory diagrams, or general equations.
2. Look back at the Starting Points questions on page 132. Answer these questions using what you have learned in this chapter. Compare your latest answers with the answers that you wrote at the beginning of the chapter. Note how your answers have changed.

Vocabulary

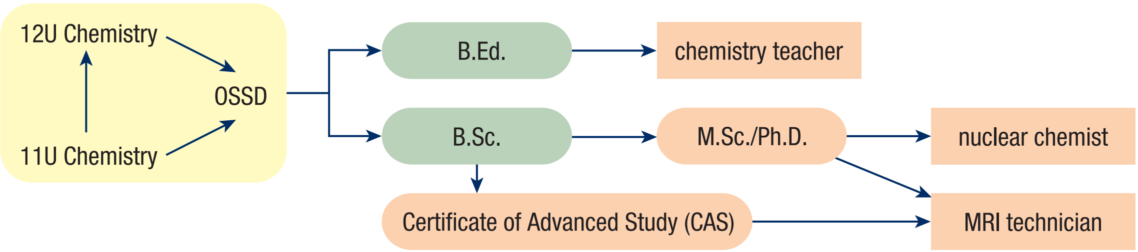
electron (p. 134)
radioactivity (p. 136)
nucleus (p. 137)
proton (p. 137)
neutron (p. 137)
isotopes (p. 138)
atomic number (Z) (p. 138)
mass number (A) (p. 138)
radioisotope (p. 138)
photoelectric effect (p. 139)
quantum (p. 140)
photon (p. 141)
spectroscopy (p. 143)
emission spectrum (p. 144)
continuous spectrum (p. 144)
line spectrum (p. 144)
transition (p. 146)
ground state (p. 146)
quantum mechanics (p. 148)
orbital (p. 150)
Heisenberg's uncertainty principle (p. 150)
wave function (p. 151)
electron probability density (p. 151)
quantum mechanical model (p. 151)
quantum numbers (p. 153)
shell (p. 153)
principal quantum number (n) (p. 153)
subshells (p. 153)
secondary quantum number (l) (p. 154)
magnetic quantum number (m_l) (p. 154)
spin quantum number (m_s) (p. 157)
Pauli exclusion principle (p. 157)
electron configuration (p. 162)
aufbau principle (p. 162)
energy-level diagram (orbital diagram) (p. 163)
Hund's rule (p. 164)
valence electron (p. 167)
transition metal (p. 167)
representative elements (p. 169)
ferromagnetism (p. 171)
paramagnetism (p. 171)
laser (p. 174)
Bose–Einstein condensate (BEC) (p. 175)
magnetic resonance imaging (MRI) (p. 175)

CAREER PATHWAYS

SKILLS HANDBOOK A7

Grade 12 Chemistry can lead to a wide range of careers. Some require a college diploma or a B.Sc. degree. Others require specialized or postgraduate degrees. This graphic organizer shows a few pathways to careers mentioned in this chapter.

1. Select two careers related to Atoms that you find interesting. Research the educational pathways that you would need to follow to pursue these careers. What is involved in the required educational programs? Prepare a brief report of your findings.
2. For one of the two careers that you chose above, describe the career, main duties and responsibilities, working conditions, and setting. Also outline how the career benefits society and the environment.



CAREER LINK

CHAPTER 3 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Rutherford's classic experiment provided evidence for a nuclear atomic model when atoms in a thin sheet of gold foil scattered a beam of
   (a) cathode rays
   (b) alpha particles
   (c) X-rays
   (d) electrons (3.1) K/U
2. Max Planck's mathematical explanation of blackbody radiation required that he assume that
   (a) most of the atom's mass is in a tiny part of its volume
   (b) electrons orbit the nucleus as planets orbit a star
   (c) electrons have several different energy levels
   (d) the energy of the vibrating atoms is quantized (3.1) K/U
3. Which of the following statements is NOT part of Bohr's model of the hydrogen atom? (3.2) K/U
   (a) the energy of an electron is quantized
   (b) the electron in the orbit nearest to the nucleus has the lowest energy
   (c) the energy of the electron is not quantized
   (d) the electron orbits the nucleus
4. The contribution of Erwin Schrödinger to the quantum mechanical atomic model was
   (a) a theoretical prediction that particles exhibit wave properties
   (b) a theoretical principle that precision of measurement has an ultimate limit
   (c) an explanation of the photoelectric effect in terms of energy quanta
   (d) a mathematical description that treats electrons as standing waves (3.3) K/U
5. Which atom has the ground-state electron configuration of [Ne]$3s^2 3p^4$? (3.5) K/U
   (a) magnesium
   (b) silicon
   (c) sulfur
   (d) argon
6. Which of the following is NOT used to determine an electron configuration for an atom? (3.5) K/U
   (a) Hund's rule
   (b) Heisenberg's uncertainty principle
   (c) the Pauli exclusion principle
   (d) the aufbau principle
7. Which of the following does NOT have an electron configuration ending with $3s^2 3p^6$? (3.5) K/U
   (a) chloride ion
   (b) sulfide ion
   (c) aluminum ion
   (d) calcium ion
8. Quantum theory is used to explain
   (a) subatomic particles
   (b) nuclear physics
   (c) optics
   (d) all of the above (3.6) K/U
9. A nanometre is
   (a) one-billionth of a metre
   (b) one-billionth of a centimetre
   (c) one-millionth of a metre
   (d) one-millionth of a centimetre (3.7) K/U

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

10. A photon is a quantum of electromagnetic energy. (3.1) K/U
11. When a sample of hydrogen gas receives a high-energy spark, the hydrogen molecules absorb energy. This energy causes the breaking of bonds, which leads to excess energy that is released and can be seen in an emission spectrum. (3.2) K/U
12. The region in space where an electron is most likely to be found is called an energy level. (3.3) K/U
13. The quantum mechanical model describes an electron as a standing wave. (3.3) K/U
14. The secondary quantum number refers to the shape of the atomic orbitals. (3.4) K/U
15. The Pauli exclusion principle states that 2 electrons cannot occupy the same energy level. (3.4) K/U
16. Electron configurations are often condensed by writing them using the previous noble gas core as a starting point. In this system, [Ar]$3d^3 4s^2$ represents calcium. (3.5) K/U
17. The noble gas electron configuration for the bismuth atom is [Xe]$4f^{14} 5d^{10} 6p^5$. (3.5) K/U
18. Nanotechnology is poised to become the largest and fastest-growing field of scientific study because it has diverse applications. (3.7) K/U

Go to Nelson Science for an online self-quiz.
WEB LINK

CHAPTER 3 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Which of the following is a use of radioisotopes? (3.1) K/U
   (a) carbon dating
   (b) nuclear power
   (c) diagnosing medical conditions
   (d) all of the above
2. Which of the following describes the spectrum that contains all of the wavelengths of visible light? (3.2) K/U
   (a) hydrogen emission spectrum
   (b) continuous spectrum
   (c) line spectrum
   (d) none of the above
3. Which of the following models was developed to replace Bohr's atomic model? (3.3) K/U
   (a) quantum mechanics
   (b) theory of relativity
   (c) transition model
   (d) spectroscopy
4. The orientation of an orbital in space relative to the other orbitals in the atom is defined by the
   (a) primary quantum number
   (b) spin quantum number
   (c) secondary quantum number
   (d) magnetic quantum number (3.4) K/U
5. Which of the following describes the aufbau principle? (3.5) K/U
   (a) Each electron is added to the lowest energy orbital available.
   (b) The lowest energy configuration for an atom is the one with the maximum number of unpaired electrons.
   (c) No 2 electrons in the same atom can have the same set of four quantum numbers.
   (d) none of the above
6. Which of the following are applications of quantum theory? (3.6) K/U
   (a) improved medical diagnostic capabilities
   (b) new sources of power
   (c) cutting-edge materials
   (d) all of the above
7. Which of the following is an application of nanotechnology? (3.7) K/U
   (a) solar cells
   (b) surgical procedures
   (c) delivery of medicine to specific cells
   (d) all of the above

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

8. The chemical properties of an atom mainly results from its protons. (3.1) K/U
9. Energy is quantized and can only occur in discrete units. (3.1) K/U
10. Bohr's atomic model is supported because it accurately describes most atoms. (3.2) K/U
11. It is impossible to determine the exact position of an electron. (3.3) K/U
12. Each atom has a unique ability to combine and can only combine in one way. (3.5) K/U
13. The position of an element in the periodic table indicates its energy properties. (3.5) K/U
14. Laser-beam light is monochromatic because lasers are designed to emit light of a specific wavelength. (3.6) K/U
15. Nanoparticles can be harmful to living organisms because they are so small. (3.7) K/U

Understanding

Write a short answer to each question.

16. Explain the relationship between the atomic number and the mass number of an element. (3.1) K/U
17. Explain what radioactivity means. (3.1) K/U C
18. What is the significance of the photoelectric effect? (3.1) K/U
19. Explain how experimental observations and influences made by Rutherford and Bohr contributed to the development of the planetary model of the hydrogen atom. (3.1, 3.2) K/U
20. Explain the difference between a continuous spectrum and a line spectrum. (3.2) K/U
21. What was the main flaw in Bohr's atomic model? (3.2) K/U

22. The line spectrum for helium is shown in **Figure 1(a)**, and the line spectrum for xenon is shown in **Figure 1(b)**. Explain why there are so many more lines in the xenon spectrum than in the helium spectrum. Relate your answer to the quantum mechanical model of the atom. (3.2) K/U T/I

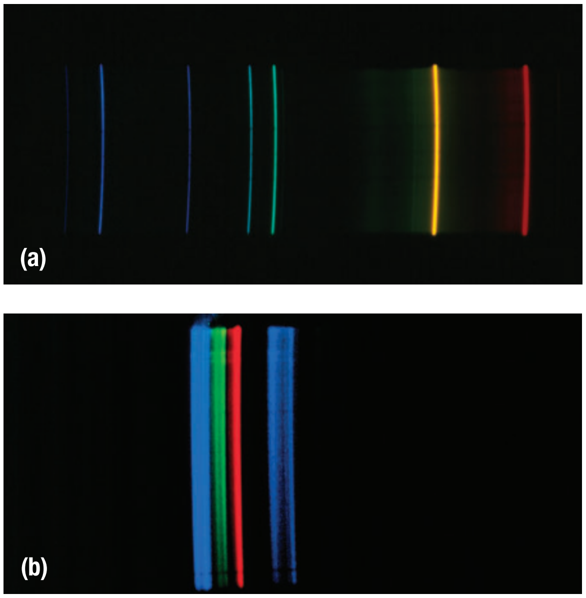


Figure 1

23. Are the line spectra in Question 22 absorption or emission spectra? How can you tell? (3.2) K/U
24. Draw a timeline showing the development of atomic theory from Democritus to the quantum mechanical model. Include the main scientists involved, and a brief statement of their contribution. (3.1, 3.2, 3.3) K/U C
25. Compare and contrast an atomic orbit and an atomic orbital. Identify the atomic model(s) that used each of these terms. (3.3) K/U
26. Compare and contrast energy levels in the Bohr model of the atom and in the quantum mechanical model. (3.2, 3.3) K/U
27. (a) What is the lowest energy level that can have an *s* orbital?
    (b) What region of the periodic table is designated as the *s* region?
    (c) What groups of elements make up this region? (3.3) K/U
28. Completely describe the orbitals found in the fourth energy level. How many electrons can be found in a full fourth energy level? Give an example of an element that has its valence electrons in the fourth energy level. (3.3) K/U
29. Calculate the maximum number of electrons in the energy levels with the following principal quantum numbers, n: (3.4) K/U T/I
    (a) 1
    (b) 2
    (c) 3
    (d) 4
30. According to quantum mechanics, why can we use the position of an element in the periodic table to predict its properties? (3.5) K/U
31. Draw an energy-level diagram for a potassium ion and a sulfide ion. Which noble gas atom has the same diagrams as these ions? (3.5) K/U C
32. Explain the difference between ferromagnetism and paramagnetism. (3.5) K/U
33. Give the atomic number, number of electrons, and electron configuration for the atom of each of the elements helium, boron, chlorine, neon, and phosphorus. (3.5) K/U
34. Write a complete ground-state electron configuration for each of the following atoms: (3.5) K/U
    (a) Mg
    (b) Ar
    (c) O
    (d) Rb
    (e) Au
35. Write a complete ground-state electron configuration for each of the following ions: (3.5) K/U
    (a) S^{2-}
    (b) K^+
36. Write a shorthand ground-state electron configuration for each of the following atoms: (3.5) K/U
    (a) silicon
    (b) manganese
    (c) $_{73}Ta$
    (d) bromine
    (e) $_{98}Cf$
37. Write a shorthand ground-state electron configuration for the common ion of each of the following atoms. State the charge on the ion. (3.5) K/U
    (a) phosphorus
    (b) beryllium
    (c) nickel
38. Write the shorthand electron configuration for each of the following atoms or ions: (3.5) K/U
    (a) yttrium
    (b) antimony
    (c) barium ion

39. Draw energy-level diagrams representing the ground-state electron configuration for the atom of each of the following elements: (3.5) K/U C
    (a) Na
    (b) Kr
40. Draw an energy-level diagram for a
    (a) potassium atom in the ground state
    (b) potassium atom in an excited state
    (c) potassium ion in the ground state

    Explain the connection between these three diagrams. (3.5) T/I C
41. Identify the neutral elements that have the following electron configurations: (3.5) K/U T/I
    (a) $1s^22s^22p^1$
    (b) $1s^22s^2$
    (c) $1s^22s^22p^63s^23p^5$
    (d) $1s^22s^22p^63s^23p^4$
    (e) $1s^22s^22p^63s^23p^64s^23d^3$
42. Which subshell is highlighted in the periodic table in **Figure 2**? (3.5) K/U

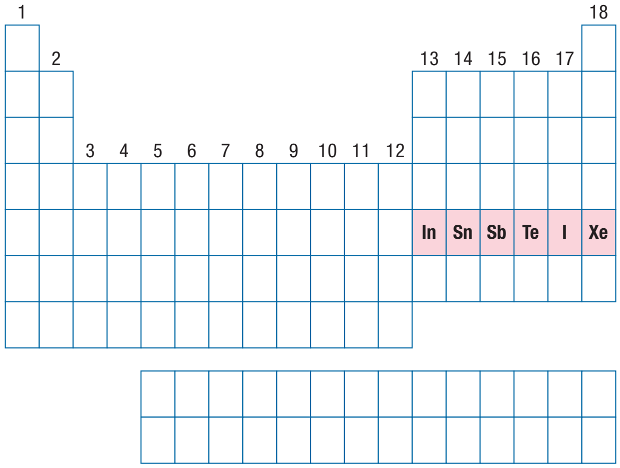


Figure 2

43. Explain the difference between multi-electronic atoms and hydrogen atoms in terms of electron interaction. (3.5) K/U
44. Describe how the aufbau principle explains the structure of the periodic table of elements. (3.5) K/U
45. Identify the following atoms or ions from their electron configurations: (3.5) K/U T/I
    (a) atom A: $1s^22s^22p^63s^23p^64s^23d^{10}4p^3$
    (b) atom Z: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{11}$
    (c) ion X^+: $1s^22s^22p^63s^23p^64s^23d^{10}4p^6$
    (d) ion D^-: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6$
46. In your own words, explain Hund's rule and how it is used in writing electron configurations. (3.5) K/U
47. Use the concepts you learned in this chapter to describe or explain the following observations. Share your explanations with a classmate. Do you agree with each other? (3.5) K/U C A
    (a) Sodium is a very reactive metal. It reacts vigorously with water. Chlorine is a toxic gas. Sodium and chlorine react to produce inert sodium chloride (table salt).
    (b) Lithium produces a red flame when burned, but sodium produces a yellow flame.
    (c) Sodium chloride, $NaCl(s)$, and silver chloride, $AgCl(s)$, have similar empirical formulas.
    (d) The empirically determined formulas for the chlorides of tin are $SnCl_2(s)$ and $SnCl_4(s)$.
48. State the number of valence electrons in each of the following neutral atoms, and state the orbitals in which they are found. (3.5) K/U
    (a) element 20
    (b) O
    (c) element 117
    (d) In
    (e) Ar
    (f) Bi
49. Energy-level diagrams and electron configurations are both ways of showing electron arrangements in the atom. State one advantage and disadvantage of each. (3.5) K/U
50. One of your classmates missed the lesson relating electron configurations to the periodic table. Your classmate has asked you to explain the connection. Clearly describe how you can use the periodic table to predict an electron configuration. Use a list of steps, a series of diagrams, or some other format to illustrate your explanation. (3.5) K/U C
51. One piece of evidence that supports the quantum mechanical model lies in the magnetic properties of matter. Atoms with unpaired electrons are attracted by magnetic fields and thus are said to exhibit paramagnetism. The degree to which this effect is observed is directly related to the number of unpaired electrons present in the atom. Consider the ground-state electron configurations for Li, N, Ni, Te, Ba, and Hg. Which of these atoms would be expected to be paramagnetic, and how many unpaired electrons are present in each paramagnetic atom? (3.5) K/U T/I
52. Describe three applications of quantum technologies in daily life. (3.6) K/U A
53. Use a flow chart or a series of diagrams to explain how a laser works. (3.6) K/U C A

Analysis and Application

54. Rutherford's gold foil experiment consisted of firing positively charged alpha particles at a thin sheet of gold metal. Describe the results that would have been obtained if
    (a) the nucleus were very large and took up most of the space in the atom
    (b) the alpha particles had a *negative* charge
    (c) the nucleus of the atom were negatively charged (3.1) T/I A
55. (a) What is the atomic symbol for an ion with 63 protons, 60 electrons, and 88 neutrons?
    (b) An ion contains 50 protons, 68 neutrons, and 48 electrons. What is its atomic symbol? (3.1) K/U T/I
56. (a) Name 3 ions that are isoelectronic with a neutral krypton atom.
    (b) State the orbitals that lose or gain electrons when these atoms become ions. (3.5) K/U T/I
57. One atom has 20 protons and a mass number of 44. Another atom has 20 protons and a mass number of 40. What is the identity of each of these atoms? How do you account for the difference in mass number? (3.1) K/U A
58. Apply what you know about quantum mechanics to draw an orbital diagram of uranium. (3.2) K/U C A
59. A mining company notices an unidentified puddle of a substance, as seen in **Figure 3** on the ground. What are some experimental techniques the chemists at the company could use to identify the substance? (3.2) T/I A

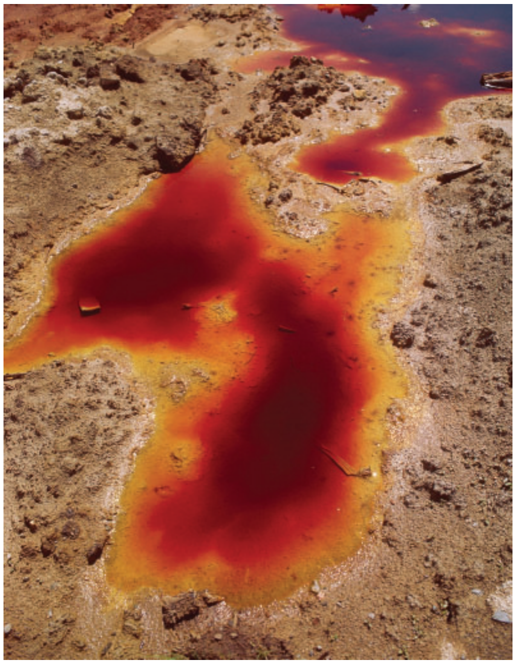


Figure 3

60. **Figure 4** is the line spectrum of the hydrogen atom. (3.2) K/U T/I
    (a) Explain what each line represents.
    (b) Explain why a line spectrum is like a fingerprint.

Figure 4

61. Draw a Bohr–Rutherford diagram of an excited fluorine atom. (3.2) T/I K/U C
62. In Section 3.3, an analogy was made comparing students to electrons to describe the orbital in an atom. Use your understanding of the atom to suggest another analogy for the orbital. (3.3) T/I C
63. (a) Write the electron configuration for aluminum.
    (b) Use different colours to draw the orbitals surrounding the aluminum nucleus. Ensure that they are to scale. Include a colour key. (3.4) T/I C
64. Rutherford's model is often referred to the solar system model of the atom. Use a Venn diagram to compare the solar system to Rutherford's atomic model. (3.1) K/U T/I C
65. Predict which of the following elements are paramagnetic. Justify your answer using electron configurations. (3.5) T/I
    (a) aluminum
    (b) beryllium
    (c) titanium
    (d) mercury
66. Iron can form two common ions, Fe^{2+} and Fe^{3+}. Write the electron configuration of each ion, and explain why it forms. (3.5) T/I
67. Write the electron configuration for a
    (a) calcium atom in the ground state
    (b) calcium atom in the excited state
    (c) calcium ion (3.5) T/I C
68. (a) In your own words, describe how to determine the electron configuration of an atom, using the periodic table as a guide.
    (b) Explain how the various theories introduced in this chapter help us write electron configurations.
    (c) Why are electron configurations important tools for chemists? (3.5) K/U T/I

69. (a) Determine the atomic number for the element molybdenum.
    (b) Write the electron configuration for the molybdenum atom using the rules you learned in this chapter.
    (c) Compare the electron configuration for what you wrote in (b) with the one on the periodic table. Explain any differences. (3.5) T/I

70. (a) Explain why lead can form a 2+ or a 4+ ion.
    (b) Explain why nickel can form a 2+ or a 3+ ion. (3.5) T/I

71. Sodium metal and oxygen gas combine to form solid sodium oxide, $Na_2O(s)$. Use the periodic table to predict the chemical formulas of the oxides of potassium, rubidium, and cesium. What periodic property of elements are you using to make your predictions? (3.5) T/I

72. Four iron(II) ions, Fe^{2+}, are key components of hemoglobin, the protein that transports oxygen in the blood. Assuming that these ions are $^{53}Fe^{2+}$, how many protons and neutrons are present in each nucleus and how many electrons are present in each ion? (3.5) K/U A

73. Use the periodic table to invent a system of street addresses that would locate every element and specify its electron configurations. (3.5) T/I C A

74. Explain why laser light is monochromatic. (3.6) K/U A

75. Describe three applications of laser technology. (3.6) A

76. Many schools have banned laser pointers. Give a possible reason for this decision. (3.6) A

77. A doctor is concerned about a possible growth on the liver of one of your friends. The doctor suggests a diagnostic scan. (3.6) K/U A
    (a) Would you recommend an MRI, X-ray, or CAT scan? Explain your reasoning.
    (b) What are the possible problems associated with each type of scan?

78. What are some of the dangers associated with the accidental release of nanoparticles into the air? (3.7) K/U A

79. What is the purpose of adding nanochemicals to fabric and textiles? (3.7) K/U A

80. Nanoparticles have many potential uses. They are already being added to some materials used to make clothing. Design a flyer to advertise the positive attributes of material containing nanotubes. (3.7) C A

81. Suggest ways in which nanotechnology could be used as a weapon. (3.7) A

82. What could happen if a nano-cancer drug attacked the wrong cells? (3.7) A

Evaluation

83. (a) Describe Thomson's experiment, his observations, and the conclusions he drew.
    (b) Explain how Thomson's model was the first atomic model that allowed for ionization of atoms.
    (c) Some people draw Thomson's model as shown in **Figure 5**. Describe what is wrong with this diagram. (3.1) K/U T/I C

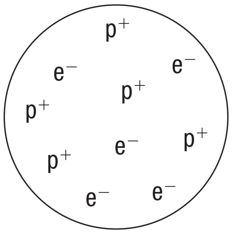


Figure 5

84. Heinrich Hertz inadvertently discovered the photoelectric effect around 1887. Hertz was attempting to generate electromagnetic waves with induction coils. The result made radio, TV, radar, and microwave radiation possible. What impact did the discovery of the photoelectric effect have on the classical theory of light? (3.1) T/I A

85. (a) A website uses the analogy of climbing a staircase to model the transition of electrons to different energy levels in an atom. Is this analogy appropriate? Explain your answer.
    (b) Is a computer simulation useful for testing the validity of the quantum/wave mechanical model of the atom? Give reasons for your answer. (3.2, 3.3) T/I A

86. Form groups with your classmates. Critique the following experimental designs. Suggest better designs to meet each purpose. (3.2, 3.5) T/I A
    (a) A student uses a hand-held spectrometer to observe the visible and infrared spectrum of a gaseous element in a discharge tube.
    (b) A student uses a flame test to identify a mixture.
    (c) To determine whether iron-fortified breakfast cereal contains solid iron, a student holds a magnet near the side of a box of the cereal.
    (d) To determine whether calcium metal is paramagnetic, a student suspends a solution of calcium sulfate in a test tube and holds a strong magnet near the tube.

87. Iron, nickel, and cobalt are strongly magnetic, whereas many elements located near them in the periodic table display only weak magnetic properties. (3.5) K/U T/I
   (a) Explain why some elements display weak magnetic properties. Use diagrams to aid your explanation.
   (b) Explain why iron, nickel, and cobalt are more strongly magnetic than most elements. Use diagrams to aid your explanation.
   (c) What terms are used to describe the elements in (a) and (b)?
88. List three or more examples of how medical diagnosis has benefited from an improved understanding of atomic structure. (3.6) A
89. Give arguments for and against government support of research into atomic structure from at least three perspectives, such as economic, social, and scientific. (3.6) K/U T/I C
90. (a) Use a graphic organizer to summarize the advantages and disadvantages of nanoparticles.
   (b) Do you think the work to develop new technologies associated with nanoparticles should be continued? Explain your reasoning. (3.7) T/I C A

Reflect on Your Learning

91. Consider the different topics you have studied in this chapter. Choose one that you feel has an important impact on your life. Write a one-page report about the topic and why it is important to you. What else would you like to know about this topic? C A
92. How did the information you learned in this chapter affect your thinking about atomic theory? C A
93. In what areas of your daily experience do you now see applications of quantum mechanics? A
94. How does what you have learned in this chapter connect with what you learned in previous chemistry courses? C A

Research

WEB LINK

95. Is it fair to state that everything there is to learn about quantum mechanics has been discovered? Use what you have learned in this chapter and further research to defend your position. T/I A
96. Many Canadian scientists have contributed to the field of atomic and molecular theory. For example, Robert J. LeRoy, of the University of Waterloo, developed the mathematical technique to determine the atomic radius of molecules, called the LeRoy radius. Research the LeRoy radius. T/I A
   (a) What observation led to the LeRoy radius?
   (b) What is the *m*-dependent LeRoy radius?
97. Select one of the physicists mentioned in this chapter, and research further contributions this physicist made to the study of quantum mechanics. Predict what this scientist might believe about the most recent discoveries and theories in this subject. Present your thoughts in a comic book, poster, or slideshow. T/I C A
98. Investigate possible commercial applications of Bose–Einstein condensates. Evaluate the feasibility of companies using the product. Present your findings in an advertisement, oral presentation, or written report. T/I C A
99. Science fiction is often based on real-life technology and theory. Research an example of science-fiction weapons and technology that are based on quantum mechanics. Some examples may include photon torpedoes, laser guns, and transporters. Use your understanding of modern atomic theory to describe any real scientific basis for the technology and to describe any fundamental flaws in the idea behind the technology. Present your findings in a poster or cartoon. T/I C A
100. You are the director of Health Canada and have been charged with developing policies regarding the use of nanotechnology in medicine production. Research the pros and cons of using the technology and develop a plan of acceptable practices for companies to follow regarding the use of nanotechnology. Present your plan in a written executive summary. T/I C A
101. Research infrared spectroscopy. How does infrared spectroscopy help in forensic investigations? Present your findings in the form of a journal article, with an abstract. See Appendix A4. T/I C A
102. Research mass spectrometry and spectrophotometers (**Figure 6**). How has the use of mass spectrometry advanced our understanding of the structure of chemical entities? What social benefits are associated with such advances? T/I C A

Figure 6

CHAPTER 4 Chemical Bonding

KEY CONCEPTS

After completing this chapter you will be able to

- relate the periodic table and atomic theory to bonding theories
- predict the type of bonding in a reaction product and describe the properties of the product that depend on bonding
- predict the shapes of simple molecules and ions using the valence shell electron-pair repulsion (VSEPR) theory
- draw diagrams of simple molecules and ions
- explain the nature of ionic, polar covalent, and non-polar covalent bonds
- predict the type of solid (ionic, molecular, covalent network, metallic) formed by a given substance in a chemical reaction, and describe the properties of that solid
- explain how physical properties of a solid or liquid depend on the particles and the types of intermolecular and intramolecular forces

How Does Chemical Bonding Help to Explain the Properties of Chemical Substances?

Rocks, coal, soil, petroleum, trees, and the human body are all complex mixtures of chemical compounds in different compositions. Chemical compounds are made up of 2 or more elements that are bonded together. Although there are substances in nature that consist of unbonded atoms, they are very rare. Two examples are unbonded argon gas atoms in the atmosphere and unbonded helium gas atoms that may be found mixed with natural gas reserves.

The type of chemical bonds in a substance has a profound effect on the chemical and physical properties of the substance. For example, graphite and diamond both consist of only carbon atoms bonded together. Graphite is the soft, slippery material found in your pencil, whereas diamond is one of the hardest materials in existence. Why do these substances have such different properties? The answer lies in how the atoms are bound together. Graphite exists as sheets of carbon atoms that are bound together in a two-dimensional plane. When you write with a pencil, you are sliding sheets of carbon onto your paper. In diamond, the carbon atoms are arranged in a rigid, three-dimensional network. All the carbon atoms are continuously linked throughout the crystal, which makes diamond hard enough to drill through concrete.

Scientists have recently discovered other carbon compounds with unique properties that make them useful for a variety of applications. For example, the image on the facing page is a model of cubane, a synthetic compound consisting of carbon atoms arranged in a cube-like formation. The bonds are highly strained, which makes cubane highly reactive. Cubane also has a very high density, so it can store large quantities of energy. For this reason, cubane shows promise as a fuel or an explosive that could be used to fuel airplanes and rocket boosters.

How does chemical bonding affect humans? The work of enzymes during digestion, the transfer of genetic material during cell division, and the transport of oxygen throughout the body all depend on subtle differences in the structure of chemical entities to channel a chemical reaction one way as opposed to another.

To understand how pure substances behave in chemical reactions, scientists try to understand how chemical bonds form and the factors that control their structures. In this chapter you will examine various types of pure substances that illustrate the different types of chemical bonds. You will investigate theories that describe the structures and bonding characteristics of pure substances in nature. You will then have a better understanding of how the physical and chemical properties of various pure substances depend on different types of chemical bonds.

STARTING **POINTS**

Answer the following questions using your current knowledge. You will have a chance to revisit these questions later, applying concepts and skills from the chapter.

1. What types of forces hold atoms or ions together?
2. (a) Are all chemical bonds the same?
   (b) How can you tell what type of bond exists between atoms or ions in a pure substance?
3. Why do atoms or ions bond to each other?
4. How do chemical bonds influence a compound's properties?
5. Give an example of how knowledge about chemical bonds can solve a real-world problem.

Mini Investigation

Liquid Glue

Skills: Performing, Observing, Analyzing, Communicating

SKILLS HANDBOOK **A2.3**

In this investigation, you will study interactions between some molecules. You will observe how different liquids interact with glass molecules. Then, you will interpret your observations in terms of the cohesive and adhesive forces of the materials.

Equipment and Materials: 2 small glass Petri dishes; 2 flat glass plates; dishwashing liquid; vegetable oil

1. Place a Petri dish, right side up, on one of the glass plates so that the flat surfaces of each one contact each other.
2. Move the Petri dish in a circle, and lift it off the glass plate.
3. Add dishwashing liquid to the glass plate until it is about 2 mm deep, and repeat Steps 1 and 2.
4. Obtain a new Petri dish and glass plate. Add vegetable oil to the glass plate until it is about 2 mm deep and repeat Steps 1 and 2.
5. Rinse each glass plate under a stream of warm tap water, and observe what happens to the dishwashing liquid and oil.

A. Both the glass plate and the Petri dish are smooth objects. What happened when you moved the Petri dish in a circular motion and lifted it from the glass plate? T/I

B. In Step 3, what effect did the dishwashing liquid have when you tried to lift the Petri dish off the glass plate? T/I

C. In Step 4, what effect did the vegetable oil have when you tried to lift the Petri dish off the glass plate? T/I

D. When you rinsed each of the plates under warm water in Step 5, what did you observe? T/I

4.1 Types of Chemical Bonds

With a few rare exceptions, everything that you can see, taste, or touch is made up of atoms or ions of elements connected to other atoms or ions by chemical bonds. Chemical bonds hold the world as we know it together. What exactly is a chemical bond? In earlier science courses, you learned that a chemical bond is the electrical attraction that holds atoms or ions together in a molecular element or in an ionic or molecular compound (**Figure 1**). When bonds form, the atoms or ions that are joined function as a unit. Atoms combine to form molecular elements or compounds. Molecular elements are molecules that consist of atoms of the same element, such as nitrogen gas, $N_2(g)$. Molecular compounds comprise atoms of 2 or more different elements. Finally, an ionic compound is a pure substance composed of 2 or more ions combined in a fixed ratio.

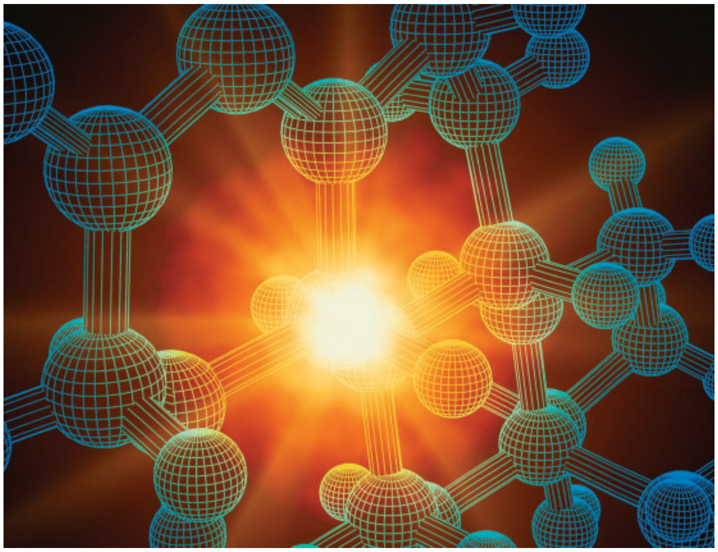


Figure 1 Artist's representation of chemical bonds that hold atoms together

ionic bond the electrostatic attraction between oppositely charged ions

Ionic Compounds and Ionic Bonding

When solid sodium, Na(s), and chlorine gas, $Cl_2(g)$, react to form solid sodium chloride, NaCl(s), a transfer of electrons occurs from the sodium atoms to the chlorine atoms to form sodium ions, Na^+, and chloride ions, Cl^-. The electron transfer occurs because chlorine atoms have a much higher electronegativity than sodium atoms, and hence have a very strong attraction for the sodium atoms' single valence electron. The sodium and chloride ions now have opposite electric charges. As you know, oppositely charged objects attract each other. An **ionic bond** is a chemical bond between oppositely charged ions. Ionic compounds form when an atom that loses electrons relatively easily reacts with an atom that gains electrons relatively easily. Typically, an ionic compound results when a metal element reacts with a non-metal element to form positively charged and negatively charged ions that are held together by electrostatic attraction.

The electrostatic attraction between positively charged sodium ions and negatively charged chloride ions creates a crystal lattice of sodium chloride, NaCl(s) (**Figure 2**). The chemical formula for sodium chloride, NaCl, is an example of a formula unit: It represents the smallest quantity of sodium chloride that has this chemical formula. The formula unit of sodium chloride indicates that sodium and chlorine ions combine in a 1:1 ratio. Note that crystal formation only occurs when a large number of positive and negative ions come together. This configuration is more stable than if the ions were separated into individual formula units. The ions in a crystal lattice are arranged so that attractions between opposite charges are maximized and repulsions between like charges are minimized (Figure 2(b)).

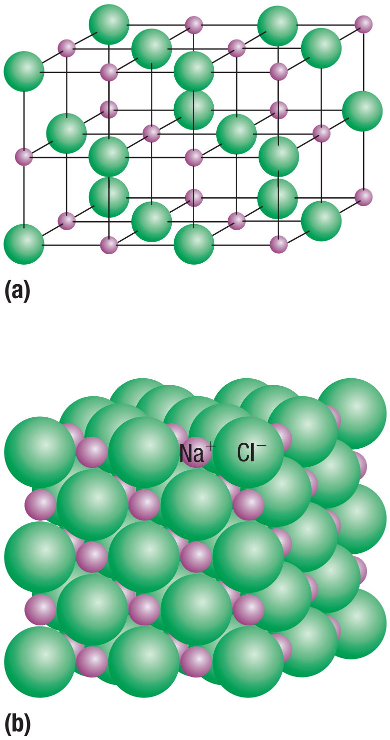


Figure 2 The crystal lattice structure of sodium chloride. (a) Ball-and-stick model. Note that, while not shown here, 6 Cl^- ions surround each Na^+ ion. (b) Representation of the ions as space-filling spheres.

To illustrate the behaviour of electrons in ionic compounds, consider the ionic compound that forms from elemental calcium, Ca(s), and oxygen, O_2(g). You can predict the compound that will form by examining the valence electron configurations of both calcium and oxygen:

Ca: $[\mathrm{Ar}]4s^2$

O: $[\mathrm{He}]2s^2 2p^4$

Recall that the electron configurations of the noble gases are generally the most stable. Atoms and ions are more stable if they have the same number of electrons as the noble gas closest to them in the periodic table; that is, if they are **isoelectronic** with a noble gas. So, calcium would be more stable if it lost some electrons to become isoelectronic with argon ($1s^2 2s^2 2p^6 3s^2 3p^6$). Similarly, oxygen would be more stable if it gained some electrons to become isoelectronic with neon ($1s^2 2s^2 2p^6$). If calcium transfers 2 of its electrons to oxygen, both atoms can achieve a noble gas configuration for the electrons in their valence shells. The new electron configuration for oxygen now becomes the same as that of neon, because its valence orbital now has 8 electrons. By losing 2 electrons, calcium achieves the electron configuration of argon. This configuration results in calcium also having 8 electrons in its valence orbital.

isoelectronic having the same number of electrons per atom, ion, or molecule

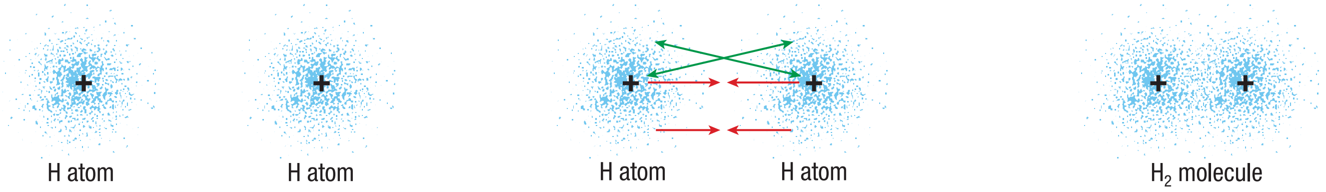
$$\underset{2e^-}{\underbrace{\mathrm{Ca} + \mathrm{O}}} \longrightarrow \mathrm{Ca}^{2+} + \mathrm{O}^{2-}$$

To predict the formula of the ionic compound, remember that chemical compounds are always electrically neutral. The number of positive charges balances the number of negative charges. In this case, both Ca^{2+} and O^{2-} ions have equal but opposite charges. Therefore, the formula unit for calcium oxide is CaO. WEB LINK

Molecular Elements and Compounds, and Covalent Bonding

When a metal and a non-metal react to form oppositely charged ions, an ionic bond develops. What kind of bond develops between 2 atoms that are similar, or even identical? Consider what happens when two hydrogen atoms move close together.

Remember that a hydrogen atom has 1 proton and 1 electron. The attraction of each electron by the proton of the other hydrogen atom creates a force that pulls both atoms toward each other. When the hydrogen atoms are a certain optimum distance from each other, the attractive proton–electron force balances the repulsive proton–proton and electron–electron forces. The resulting hydrogen molecule is more stable and therefore has lower energy than the individual atoms that comprise it (**Figure 3**).



Sufficiently far apart to have no interaction

As they move closer together, the electron cloud of one atom attracts the nucleus of the other atom (green arrows). The two electron clouds and nuclei repel each other (red arrows).

Optimum distance to achieve lowest overall energy of system

(a) **(b)** **(c)**

Figure 3 The interaction of two hydrogen atoms as they move closer together. (a) When the atoms are far apart, they have no interaction. (b) The atoms begin to interact as they move closer to each other. (c) The atoms interact to form the H_2 molecule at the distance that minimizes their energy.

The type of bond that forms when atoms share electrons is called a **covalent bond**. These shared electrons are called **bonding electron pairs**. Covalent bonds typically form between atoms of non-metal elements.

covalent bond a chemical bond in which atoms share the bonding electrons

bonding electron pair an electron pair that is involved in bonding, found in the space between 2 atoms

Lewis Theory of Bonding

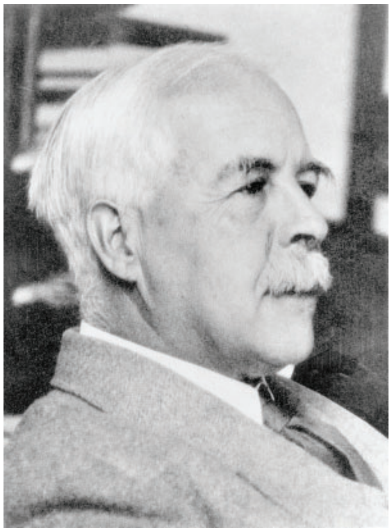


Figure 4 G.N. Lewis (1875–1946)

In 1916, Gilbert Lewis (**Figure 4**) provided the first straightforward view of chemical bonding. He gathered information about chemical formulas, valence electrons, and models of the atom in an attempt to understand chemical bonds. From the data he collected, Lewis made predictions about the nature of bonding in what is now known as the Lewis theory of bonding. Ideas from this theory include the following:

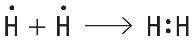
- Atoms and ions are stable if they have a full valence shell of electrons.
- Electrons are most stable when they are paired.
- Atoms form chemical bonds to achieve a full valence shell of electrons.
- A full valence shell of electrons may be achieved by an exchange of electrons between metal and non-metal atoms.
- A full valence shell of electrons may be achieved by the sharing of electrons between non-metal atoms.
- The sharing of electrons results in a covalent bond.

Lewis Structures

Based on his theory, Lewis drew structures to represent pure substances. A **Lewis structure** shows the arrangement of electrons and bonds in a molecule or polyatomic ion. After making observations of thousands of pure substances, chemists have identified rules for drawing Lewis structures. As you have already learned, the most important requirement for the formation of a stable substance is that the participating atoms are isoelectronic with noble gases. Hydrogen, in the first period of the periodic table, follows the **duet rule**: a hydrogen atom forms stable configurations when it shares 2 electrons, represented by dots, to obtain a full valence shell (**Figure 5**).

Lewis structure a diagram that represents the arrangement of covalent electrons and bonds in a molecule or polyatomic ion

duet rule the observation that the complete outer shell of valence electrons when hydrogen and period 2 metals are involved in bonding



$\dot{H} + \dot{H} \longrightarrow H{:}H$

Figure 5 Two hydrogen atoms combine to form the H_2 molecule.

In this manner, hydrogen atoms become isoelectronic with helium atoms (**Figure 6**). A helium atom has 2 valence electrons so its valance shell is already full ($1s^2$). Consequently, helium does not form bonds.

He:

Figure 6 Lewis symbol of a helium atom. A Lewis symbol shows the valence electrons in an atom of each element. Lewis symbols (of atoms) are used to draw Lewis structures (of pure substances).

Atoms of non-metals in period 2 of the periodic table (carbon through fluorine) form stable configurations when they obey the octet rule. The **octet rule** states that many atoms form the most stable substances when they are isoelectronic with neon. Neon, a noble gas, does not form bonds because each neon atom already has an octet of valence electrons (**Figure 7**).

octet rule the observation that many atoms tend to form the most stable substances when they are surrounded by 8 electrons in their valence shells

$:\ddot{\underset{\cdot\cdot}{Ne}}:$

Figure 7 Lewis symbol of a neon atom

In atoms of period 2 non-metals, the valence shell consists of the single 2*s* and three 2*p* orbitals. Each orbital can hold at most 2 electrons, so 8 electrons fill the valence shell. For example, the F_2 molecule has a total of 8 valence electrons surrounding each atom (**Figure 8**). Each fluorine atom is now isoelectronic with neon.

$:\ddot{\underset{\cdot\cdot}{F}}\cdot \longrightarrow :\ddot{\underset{\cdot\cdot}{F}}:\ddot{\underset{\cdot\cdot}{F}}: \longleftarrow \cdot\ddot{\underset{\cdot\cdot}{F}}:$

Figure 8 An atom of fluorine has 7 electrons in its valence shell. If it shares one electron with another fluorine atom in a fluorine molecule, each atom will have a total of 8 valence electrons, and become isoelectronic with neon.

Even though each fluorine atom shares 1 of its electrons with the other fluorine atom in F_2, it also has 3 pairs of electrons that are not involved in bonding. Pairs of electrons that do not participate in chemical bonds are called **lone electron pairs**.

lone electron pair a pair of valence electrons that is localized to a given atom but not involved in bonding

Follow the steps below to draw Lewis structures.

Steps for Drawing Lewis Structures

1. Identify the central atom, which is usually the element with the highest bonding capacity. Write the symbol for the central atom, then arrange the symbols of the atoms for the rest of the elements in the pure substance around it.
2. Add up the number of valence electrons available in an atom of each of the elements. This number represents the total number of electrons (dots) you will draw in your Lewis structure. If the structure is a polyatomic ion, add 1 electron for each unit of negative charge, or subtract 1 for each unit of positive charge.
3. Place 1 pair of electrons between each adjacent pair of atoms. Every 2 of these dots represent a bonding electron pair that forms a single covalent bond.
4. Place pairs of the remaining valence electrons as lone pairs on the surrounding atoms (not the central atom). Follow the duet rule for hydrogen atoms and the octet rule for all other atoms.
5. Determine how many electrons are still available by subtracting the number of electrons you have used so far from the total number of valence electrons.
6. Place the remaining electrons on the central atom in pairs.
7. If the central atom(s) does not have a full octet, move lone pairs from the surrounding atoms into a bonding position between those atoms and the central atom until all octets are complete.
8. If the surrounding atoms have complete octets and there are electrons remaining, add these electrons as lone pairs onto the central atom(s). Check the finished structure. All atoms (except hydrogen) should have a complete octet, counting shared and lone pairs to complete the Lewis structure. If you are representing a polyatomic ion, place square brackets around the entire structure and write the charge outside the brackets.

You can write the structural formula of a molecule or polyatomic ion based on a Lewis structure. Remove the dots representing the lone electron pairs, and replace the dots representing bonding electron pairs with solid lines to represent covalent bonds. Use double or triple lines for double or triple bonds.

Tutorial 1 Drawing Lewis Structures

In this Tutorial, you will practise drawing Lewis structures for various substances containing elements from the first two periods of the periodic table. You will also write structural formulas for substances based on their Lewis structures.

Sample Problem 1: Drawing a Lewis Structure for a Molecule

Methanal, or formaldehyde, is a gas with a distinct odour. Formaldehyde is used in the production of cosmetics, pharmaceuticals, and textiles (**Figure 9**). The chemical formula of this molecule is H_2CO. Draw the Lewis structure and then write the structural formula for this molecule.

Figure 9 Formaldehyde may be used to make fibres wrinkle-resistant, such as this permanent-press acetate cloth.

Solution

Step 1. Identify the central atom, which is the element with the highest bonding capacity. Write the symbol for the central atom, then arrange the symbols of the atoms for the rest of elements in the substance around it.

The central atom for methanal is carbon.

H
  C O
H

Step 2. Add up the number of valence electrons available in an atom of each of the elements. This number represents the total number of electrons (dots) you will draw in your Lewis structure. Since methanal is not a polyatomic ion, you do not need to make changes to this number to compensate for charge.

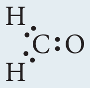
1 C atoms: $1(4e^-) = 4e^-$

2 H atoms: $2(1e^-) = 2e^-$

1 O atoms: $1(6e^-) = 6e^-$

Total: $12e^-$

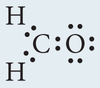
Step 3. Place 1 pair of electrons between each adjacent pair of atoms to represent the bonding electron pairs. Record the total number of electrons available and the number of electrons used so far.



Start: $12e^-$

Used: $6e^-$

Step 4. Place pairs of the remaining valence electrons as lone pairs on the surrounding atoms (not the central atom). Follow the duet rule for any hydrogen atoms and the octet rule for all other atoms.



Step 5. Determine how many electrons are still available by subtracting the number of electrons you have used so far from the total number of valence electrons.

Start: $12e^-$

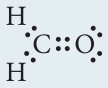
Used: $12e^-$

Remaining: $12e^- - 12e^- = 0e^-$

Step 6. Place the remaining electrons on the central atom(s) in pairs.

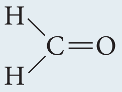
There are no remaining electrons in this case.

Step 7. If the central atom(s) does not have a full octet, move lone pairs from the surrounding atoms into a bonding position between those atoms and the central atom until all octets are complete.



Step 8. If the surrounding atoms have complete octets and there are electrons remaining, add these electrons as lone pairs onto the central atom(s). Check the finished structure. All atoms (except hydrogen) should have a complete octet, counting shared and lone pairs. This is not a polyatomic ion, so no square brackets are needed. Your Lewis structure is therefore complete.

Step 9. To draw the structural formula, remove the dots representing the lone pairs. Replace the dots representing bonding electron pairs with solid lines to represent covalent bonds. Use double or triple lines for double or triple bonds.



Methanal is a neutral molecule. You therefore do not need to represent a charge, so your structural formula for methanal is complete.

Sample Problem 2: Drawing a Lewis Structure for a Polyatomic Ion

Sodium nitrate, $NaNO_3$, is a versatile compound used in many products, such as fireworks, pottery enamel, and even as a preservative in smoked meats (**Figure 10**). It contains the polyatomic ion called nitrate, NO_3^-. Draw the Lewis structure and the structural formula for nitrate.

Solution

Step 1. Identify the central atom and write its symbol. Then, arrange the symbols of the atoms for the rest of elements around it.

Nitrogen is the central atom.

Step 2. Add up the number of valence electrons available in each of the atoms. This number represents the total number of electrons (dots) you will draw in your Lewis structure. If the structure is a polyatomic ion, add 1 electron for each unit of negative charge, or subtract 1 for each unit of positive charge.

1 N atom: $1(5e^-) = 5e^-$

3 O atoms: $3(6e^-) = 18e^-$

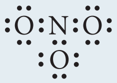
charge $= 1e^-$

Total: $24e^-$

Step 3. Place 1 pair of electrons between each adjacent pair of atoms to represent the bonding electrons.

Start: $24e^-$
Used: $6e^-$

Step 4. Place pairs of the remaining valence electrons, or lone pairs, on the surrounding atoms, following the duet rule or octet rule appropriately.



Step 5. Determine how many electrons are still available.

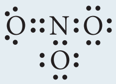
Start: $24e^-$

Used: $24e^-$

$24e^- - 24e^- = 0e^-$ left

Step 6. There are no remaining electrons to place on the central atom.

Step 7. The central N atom has an incomplete octet. Move a lone pair on one oxygen atom to between nitrogen and oxygen.



Step 8. There are no electrons remaining. Since you are representing a polyatomic ion, place brackets around the entire structure and write the charge outside the brackets. Your Lewis structure is now complete.

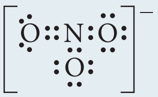
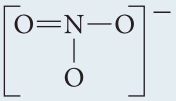


Figure 10 Sodium nitrate is used in the curing of smoked meat. This compound slows the growth of bacteria, extending the shelf life of the product. Sodium nitrate also occurs naturally in some vegetables. For example, 1 kg of celery contains about 1 g of sodium nitrate.

Step 9. Remove the dots representing lone electron pairs, and replace the dots representing bonding electron pairs with solid lines.



Your structural formula for the nitrate ion is now complete.

Practice

1. Draw the Lewis structure and the structural formula for each of the following molecules: T/I C
   (a) NBr_3
   (b) CF_4
   (c) N_2
   (d) C_2H_4
2. Draw the Lewis structure and the structural formula for each of the following polyatomic ions: T/I C
   (a) PO_3^{3-}
   (b) CN^-
   (c) NO_2^-
   (d) ClO^-

Exceptions to the Octet Rule

When drawing Lewis structures for molecules, hydrogen atoms always obey the duet rule, and carbon, nitrogen, oxygen, and fluorine atoms (and other halogens) obey the octet rule in all circumstances. However, there are exceptions to the octet rule. The first exception applies to molecules with central atoms that are surrounded by fewer than 8 electrons. These central atoms are said to have underfilled octets. The second exception applies to molecules with central atoms that are surrounded by more than 8 electrons. These central atoms are said to have overfilled octets.

Boron forms compounds in which the boron atom has fewer than 8 electrons around it. The boron atom therefore has an underfilled octet. Boron trifluoride, BF_3, is a gas at normal temperatures and pressures (**Figure 11**). It reacts very energetically with molecules such as water and ammonia, which have lone pairs of electrons that do not participate in a chemical bond. The boron atom has 3 valence electrons, and each fluorine atom has 7 valence electrons. Therefore, boron trifluoride has a total of 24 valence electrons (**Figure 12**).

Figure 11 Boron trifluoride gas is used to improve the quality of aluminum casts, such as those used to make automobile parts.

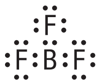


Figure 12 The Lewis structure for boron trifluoride

In this structure, each fluorine atom has 3 lone pairs of electrons, which total to 18 electrons. The remaining 6 electrons surround the boron atom, causing it to be electron deficient. The reactivity of boron trifluoride with electron-rich molecules such as water and ammonia, NH_3, occurs because the boron atom is electron deficient.

The molecule that forms from the reaction of boron trifluoride with ammonia has the chemical formula H_3NBF_3. **Figure 13** shows the reactants and products of this reaction using simplified Lewis structures. In a **simplified Lewis structure**, dots representing bonding electron pairs are replaced by solid lines and any dots representing lone electron pairs are kept. In the H_3NBF_3 molecule, the boron atom obtains an octet of electrons.

simplified Lewis structure a Lewis structure in which bonding electron pairs are represented by solid lines and lone electron pairs by dots

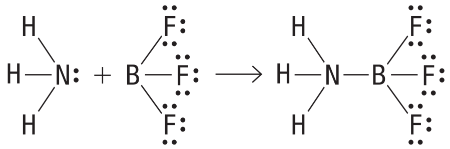


Figure 13 Simplified Lewis structures showing the formation of H_3NBF_3

Some atoms can exceed the octet rule (have an overfilled octet). These atoms use nearby vacant *d* orbitals to exceed their octet. Therefore, you do not observe this behaviour for elements in periods 1 or 2 of the periodic table. An example of an atom exceeding the octet rule is the sulfur atom in sulfur hexafluoride, SF_6. A **space-filling model** shows the relative sizes of the atoms and their relative orientations in three-dimensional space. **Figure 14** shows a space-filling model of sulfur hexafluoride. Sulfur hexafluoride is a very stable molecule. The sum of the valence electrons in this unusual molecule is as follows:

space-filling model a model of a molecule showing the relative sizes of the atoms and their relative orientations

1 S atom: $1(6e^-) = 6e^-$

6 F atoms: $6(7e^-) = 42e^-$

Total valence electrons: $6e^- + 42e^- = 48e^-$

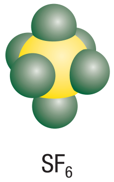


Figure 14 A space-filling model of a molecule of SF_6

Figure 15 shows the arrangement of electrons around the sulfur atom in sulfur hexafluoride.

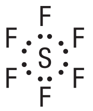


Figure 15 The sulfur atom in a sulfur hexafluoride molecule has an overfilled octet.

Notice in Figure 15 that 12 electrons form the S–F bonds. The total number of valence electrons is 48, so there are 36 electrons unaccounted for. Since fluorine atoms always follow the octet rule, you can complete the octet for each of the 6 fluorine atoms to give the Lewis structure shown in **Figure 16**.

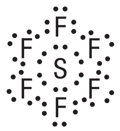
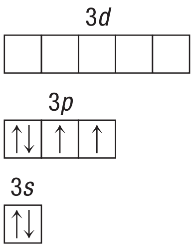


Figure 16 Lewis structure of a sulfur hexafluoride molecule

This structure uses all 48 valence electrons for sulfur hexafluoride, but the sulfur atom has 12 electrons around it, which exceeds the octet rule. How is this possible?

To answer this question, consider the types of valence orbitals that are available for second- and third-period elements. The second-period elements have 2*s* and 2*p* valence orbitals. The third-period elements have 3*s*, 3*p*, and 3*d* orbitals. As you examine the electron distribution of the atoms in the third period, notice that as you move across the periodic table from sodium to argon, the 3*s* and 3*p* orbitals fill with electrons but the 3*d* orbitals remain empty. The valence orbital diagram for a sulfur atom is



The sulfur atom in a sulfur hexafluoride molecule can have 12 electrons in its valence shell by using the 3*s*, 3*p*, and 3*d* orbitals.

Tutorial 2 Drawing Simplified Lewis Structures of Molecules That Are Exceptions to the Octet Rule

In this Tutorial, you will draw simplified Lewis structures for molecules that contain atoms that have underfilled or overfilled octets.

Sample Problem 1: Molecules with Underfilled Octets

Beryllium forms compounds in which the beryllium atom has fewer than 8 electrons around it. Draw the simplified Lewis structure for a molecule of beryllium chloride, $BeCl_2$.

Solution

Step 1. Identify the central atom, and write its symbol. Then, arrange the symbols of the atoms for the rest of the elements in the molecule around it.

$$\mathrm{Cl}\ \ \mathrm{Be}\ \ \mathrm{Cl}$$

Step 2. Count all the valence electrons for all the atoms in the molecule. The total represents the total number of electrons (dots) you will draw in your Lewis structure.

1 Be atom: $1(2e^-) = 2e^-$

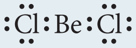
2 Cl atoms: $2(7e^-) = 14e^-$

Total: $16e^-$

Step 3. Place 1 pair of electrons between each adjacent pair of atoms, forming single covalent bonds.

$$\mathrm{Cl}:\mathrm{Be}:\mathrm{Cl}$$

Step 4. Place pairs of the remaining valence electrons as lone pairs on the surrounding atoms, following the duet rule or octet rule as appropriate.



$$:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:\mathrm{Be}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$$

Step 5. Determine the number of electrons still available.

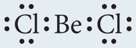
Start: $16e^-$

Used: $16e^-$

$16e^- - 16e^- = 0\ e^-$ left

Step 6. Place the remaining electrons on the central atom(s) in pairs.
There are no remaining electrons.

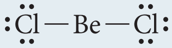
Step 7. The central Be atom has an incomplete octet. You could move 1 lone pair of electrons from each chlorine atom to complete the octet for the beryllium atom. However, since you know that the beryllium atom will be underfilled when it forms a compound, the Lewis structure of beryllium chloride is best represented as the following:



$$:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:\mathrm{Be}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$$

Step 8. There are no electrons remaining, so the Lewis structure for beryllium chloride is complete.

Step 9. Replace the dots between atoms with lines to represent bonds to simplify the Lewis structure.



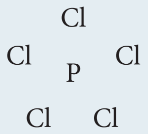
$$:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}-\mathrm{Be}-\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$$

Sample Problem 2: Molecules with Overfilled Octets

Phosphorus forms molecular compounds in which the phosphorus atom shares more than 8 electrons. Draw the simplified Lewis structure for a molecule of phosphorus pentachloride, PCl_5.

Solution

Step 1. Identify the central atom and write its symbol. Then, arrange the symbols of the atoms for the rest of the elements in the molecule around it.



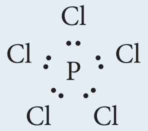
Step 2. Count all the valence electrons for all the atoms in the molecule. The total represents the total number of electrons (dots) to draw in your Lewis structure.

1 P atom: $1(5e^-) = 5e^-$

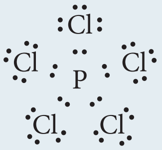
5 Cl atoms: $5(7e^-) = 35e^-$

Total: $40e^-$

Step 3. Place 1 pair of electrons between each adjacent pair of atoms, forming single covalent bonds. Draw 1 pair of electrons between each chlorine atom and phosphorus atom. You will have a total of 10 electrons around the phosphorus atom. Since you know that the phosphorus atom is overfilled, you can accept this arrangement.



Step 4. Place pairs of the remaining valence electrons as lone pairs on the surrounding atoms, following the duet rule or octet rule as appropriate.



Step 5. Determine the number of electrons still available.

Start: $40e^-$

Used: $40e^-$

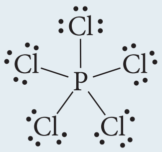
$40e^- - 40e^- = 0e^-$ left

Step 6. Place the remaining electrons on the central atom(s) in pairs. There are no remaining electrons.

Step 7. Each chlorine atom has a full octet and the phosphorus atom is overfilled, so you do not need to move any electrons.

Step 8. There are no electrons remaining, so the Lewis structure for phosphorus pentachloride is complete.

Step 9. Replace the dots between atoms with lines to represent bonds to simplify the Lewis structure.



Practice

1. Draw the simplified Lewis structure for each of the following molecules. T/I C
   - (a) ICl_5
   - (b) $RnCl_2$
2. Draw the simplified Lewis structure for each of the following: T/I C
   - (a) ClF_3
   - (b) NO^+
   - (c) ICl_4^-

Coordinate Covalent Bonding

coordinate covalent bond a covalent bond in which the electrons involved in bonding are from one atom

When 2 hydrogen atoms form a covalent bond, each hydrogen atom donates 1 electron to form the bond. However, sometimes the covalent bond that forms between 2 atoms involves 2 electrons donated by a single atom. This type of bond is called a **coordinate covalent bond**. One example of this type of bond occurs in the ammonium ion, NH_4^+. In this ion, the nitrogen atom contributes 5 electrons, and the 3 hydrogen atoms each contribute 1 electron to the structure. A single covalent bond forms between the nitrogen atom and each of the 3 hydrogen atoms to form a molecule of ammonia, NH_3. Thus, 2 valence electrons of the nitrogen atom do not participate in bond formation. When a hydrogen ion, H^+, interacts with a molecule of ammonia, it forms a covalent bond with this remaining electron pair (**Figure 17**). Both of the electrons that make up this covalent bond come from the nitrogen atom.

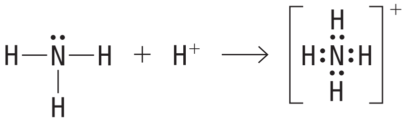


Figure 17 Lewis structures of the reaction between ammonia and a hydrogen ion to form the ammonium ion

Aluminum chloride can exist in two forms, given by the formulas $AlCl_3$ and Al_2Cl_6. The molecule Al_2Cl_6 has a coordinate covalent bond. A molecule of Al_2Cl_6 forms from 2 molecules of $AlCl_3$. A Lewis structure of $AlCl_3$ reveals that the aluminum atom does not have an octet of valence electrons. Both sets of the electrons involved in the coordinate covalent bonds come from chlorine atoms (**Figure 18**).

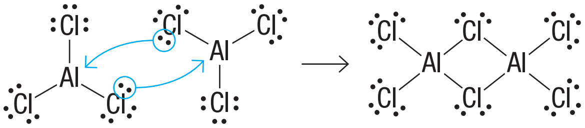


Figure 18 Simplified Lewis structures of the reaction between two molecules of $AlCl_3$ to form Al_2Cl_6

4.1 Review

Summary

- Chemical bonds hold atoms together to form molecules and ionic compounds.
- Chemical bonds form when a group of atoms has a lower total energy.
- Noble gas configurations of atoms are generally the most stable.
- The two main types of chemical bonds are ionic and covalent bonds.
- Lewis structures can be used to represent molecules and polyatomic ions.
- Most Lewis structures contain atoms that obey the octet rule or the duet rule (for the hydrogen atom).
- There are exceptions to the octet rule in which the central atom has an underfilled or an overfilled octet.
- A coordinate covalent bond is a covalent bond in which the electrons involved in bonding are from one atom.

Questions

1. Carbon tetrafluoride gas, $CF_4(g)$, is used as a refrigerant. It is very stable when released into the atmosphere and is a known potent greenhouse gas. Calcium fluoride, $CaF_2(s)$, is the main source of the world's supply of fluorine. It is used in the production of specialized lenses and window materials. K/U
   (a) Describe the bonding in a molecule of carbon tetrafluoride.
   (b) Compare and contrast the bonding of carbon tetrafluoride and calcium fluoride.
2. Some plant fertilizers contain the following compounds: ammonium sulfate, $(NH_4)_2SO_4$; calcium phosphate, $Ca_3(PO_4)_2$; potassium oxide, K_2O; diphosphorus pentoxide, P_2O_5; and potassium chloride, KCl. K/U
   (a) Which compounds contain ionic bonds?
   (b) Which compounds contain covalent bonds?
   (c) Do any compounds contain both ionic and covalent bonds? Explain how this is possible.
3. Aluminum metal is produced by heating aluminum oxide, $Al_2O_3(s)$, and other substances to almost 1000 °C until the mixture melts. Molten aluminum oxide is an excellent conductor. An electric current passed through liquid aluminum oxide can provide the electrons needed to convert the aluminum ions to neutral metal atoms. Explain the following properties of aluminum oxide in terms of ionic bonding: K/U
   (a) its high electrical conductivity when molten
   (b) its high melting point
4. Draw Lewis structures for each of the following molecules or polyatomic ions. State whether they obey the octet rule and if any coordinate covalent bonds form. In each case, the first atom listed is the central atom. K/U C
   (a) $POCl_3$
   (b) SO_4^{2-}
   (c) PO_4^{3-}
   (d) ClO_4^-
5. An exception to the octet rule is a central atom with fewer than 8 valence electrons. Beryllium hydride, BeH_2, and borane, BH_3, are both examples. Draw the Lewis structures of these 2 molecules. K/U C
6. Common exceptions to the octet rule are compounds and polyatomic ions with central atoms having more than 8 electrons around them. Phosphorus pentafluoride, PF_5; sulfur tetrafluoride, SF_4; xenon tetrafluoride, XeF_4; and tri-iodide ion, I_3^-, are all examples of exceptions to the octet rule. K/U C
   (a) Draw the Lewis structures of these substances.
   (b) For which elements in these substances can the atoms have more than 8 electrons around them?
   (c) How can the atoms of the elements you identified in Part (b) be surrounded by more than 8 electrons?
7. A classmate does not understand the concept of coordinate covalent bonding. Make up and write an analogy to help him or her understand. T/I C

4.2

Three-Dimensional Structure

three-dimensional structure the three-dimensional arrangement of ions or atoms making up a pure substance

Chemical bonds play an important role in determining the nature of various substances. So does the three-dimensional structure. The **three-dimensional structure** of a substance refers to the arrangement in three dimensions of atoms that the substance comprises. Three-dimensional structure often helps determine how the pure substance will behave in chemical reactions. It also influences interactions with other substances, especially in biological systems, where reactions have to be efficient and highly specific.

For example, enzymes, an important group of molecules in living organisms, interact with other molecules primarily based on molecular shape (molecular geometry). Enzymes and the molecules they act on interact in a manner similar to locks and keys. You cannot use just any key to open a lock. The ridges and shape of the key must be complementary to the shape of the inside of the lock. Receptor proteins on the surfaces of cells function very much like a lock. A specific molecule, such as a hormone or a neurotransmitter, must fit perfectly in the receptor pocket before it will signal the cell interior. At the cellular level, communication, growth, defence, and differentiation all ultimately depend on molecular shape. Beyond the cellular level, entire organisms can communicate through a process called semiochemical communication, where chemicals act as messengers to relay information from one organism to another. For example, queen bees secrete a unique chemical, or pheromone, to prevent worker bees from rebelling (**Figure 1**). WEB LINK

Figure 1 A queen bee secretes a chemical that the worker bees immediately recognize. This chemical prevents the worker bees from competing against the queen bee.

The VSEPR Theory

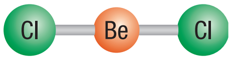
valence shell electron-pair repulsion (VSEPR) theory a method to determine the geometry of a molecule based on the idea that electron pairs are as far apart as possible

electron-pair repulsion the repulsive force that occurs between electron pairs, causing them to be positioned as far apart as possible in a molecule

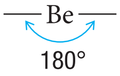
Many sophisticated and highly accurate methods, such as X-ray crystallography and nuclear magnetic resonance (NMR) spectroscopy, exist for determining three-dimensional structure. We must use these methods when we need precise information about a molecule's structure, but they require lengthy experiments and expensive equipment. However, you can predict the approximate structure of a molecule or ionic compound using the **valence shell electron-pair repulsion (VSEPR) theory**. The main idea behind the VSEPR theory is that you can determine the structure around an atom by minimizing the repulsive force between electron pairs. Remember that electrons are all negatively charged and, thus, repel each other. Atoms can share electron pairs in a covalent bond (bonding electron pairs), and can also have lone electron pairs that do not participate in chemical bonds. You saw examples of this in the previous section when you drew Lewis structures. According to VSEPR theory, bonded and lone pair electrons position themselves as far apart as possible in a molecule to minimize the repulsive forces between them, a concept called **electron-pair repulsion**.

To illustrate VSEPR theory, consider beryllium chloride, $BeCl_2$. Beryllium chloride is a rather unusual substance. It is a molecule, not an ionic compound. Although covalent bonds typically occur between atoms of non-metals, in beryllium chloride covalent bonds occur between a metal atom and a non-metal atom. You will learn more about how this happens in Section 4.6. Beryllium chloride can be represented by the following structural formula and ball-and-stick model:

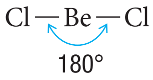
$$Cl-Be-Cl$$



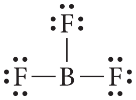
Note that there are 2 bonding electron pairs around the beryllium atom. What geometric arrangement of these electron pairs allows them to be as far apart as possible to minimize the repulsive forces between them? The best arrangement is to place the electron pairs on opposite sides of the atom, or 180° apart.



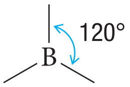
Now that you have determined the optimal arrangement of the electron pairs around the central atom, you can specify the three-dimensional structure of beryllium chloride. Since the beryllium atom shares each bonding electron pair with a chlorine atom, the molecule has a linear structure with a 180° bond angle.



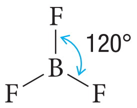
Next, consider boron trifluoride, BF_3, which can be represented by the following simplified Lewis structure.

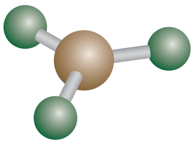


In this Lewis structure, 3 bonding electron pairs surround the boron atom. What arrangement will minimize electron-pair repulsion? The bonding electron pairs are the farthest apart at angles of 120° in a two-dimensional plane.



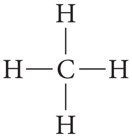
Since the boron atom shares an electron pair with each fluorine atom, the three-dimensional structure can be represented as



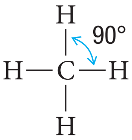


The shape of this molecule is planar (flat) and triangular, and it is described as a trigonal planar structure.

Next, consider the methane molecule, CH_4, which can be represented by this structural formula.

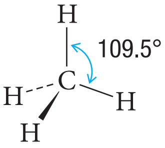


There are 4 bonded electron pairs surrounding the central carbon atom. What arrangement of these electron pairs minimizes the electron-pair repulsions? First, try to arrange the molecule into a square planar arrangement, where all 4 bonds lie in the same plane:



In this arrangement, the carbon atom and the electron pairs are centred in the plane of the paper, and the angles between the electron pairs are all 90°.

There is another arrangement that would put the electron pairs even farther away from each other. The tetrahedral structure has angles of 109.5°, and the atoms are equally positioned in four locations around the central atom. This arrangement can be represented by the following structural formula and ball-and-stick model:



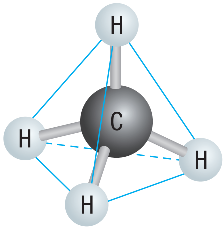


Table 1 Conventions for Depicting Bonds in Three Dimensions

Symbol	Description
—	bond lies in the plane of the paper
- - -	bond extends backwards, away from the viewer, "into" the paper or electronic screen
◀	bond protrudes forwards, toward the viewer, "out of" the paper or electronic screen

This three-dimensional arrangement allows the maximum possible separation of 4 pairs of electrons around a central atom. In the structural formula for the methane molecule, some bonds are represented as dashes or wedges to better communicate the arrangement of the atoms. **Table 1** summarizes the conventions for representing the three-dimensional arrangement of atoms in structural formulas. Blue lines were added to the ball-and-stick model of methane on the previous page to emphasize the tetrahedron. Whenever 4 pairs of electrons are present around a central atom, always place them at the vertices of a regular tetrahedron.

Recall from Section 4.1 that the central atom of phosphorus pentachloride, PCl_5, is overfilled. There are 5 covalent bonds between the phosphorus atom and the 5 chlorine atoms. In this case, the geometric structure that minimizes electron repulsion is a trigonal bipyramidal structure. In a phosphorus pentachloride molecule, 3 P–Cl bonds are in the same plane and 120° apart from each other, and the remaining 2 P–Cl bonds are 90° from these bonds and 180° from each other (**Figure 2(a)**). Similarly, sulfur hexafluoride, SF_6, forms 6 covalent bonds. The predicted VSEPR theory structure for this molecule is an octahedral structure. In this structure, 4 S–F bonds are in the same plane separated by 90° angles. The other 2 S–F bonds are perpendicular to this plane, 1 above it and 1 below it (**Figure 2(b)**).

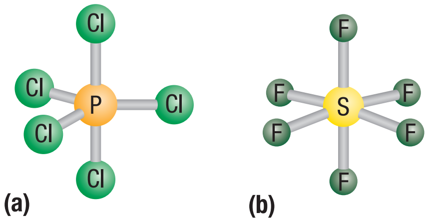
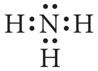


Figure 2 (a) The trigonal bipyramidal structure of PCl_5 and (b) the octahedral structure of SF_6

VSEPR theory helps you to determine the arrangement of electron pairs around a central atom that minimizes electron-pair repulsions. The lone electron pairs surrounding non-central atoms do not play a role in determining molecular shape. However, when the central atom has 1 or more lone pairs of electrons, the geometric structure of the molecule and the positions of the surrounding atoms are affected. Consider ammonia, NH_3, which has a single lone electron pair on the central atom:



$$\begin{array}{c}\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{H}\\ \mathrm{H}\end{array}$$

You might predict that this molecule has a tetrahedral structure because there are 4 pairs of electrons around the central nitrogen atom. However, the lone electron pair repels a little more than the bonding pairs, and thus pushes the bonding pairs closer together. As a result, the bond angles decrease from 109.5° to 107°. This forms a trigonal pyramidal structure, because the central atom is at the vertex of a pyramid with a triangular base (**Figure 3**).

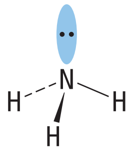


Figure 3 The structure of ammonia is trigonal pyramidal due to the repulsion of the lone pair against the 3 N–H bonds.

Note that the three-dimensional structure classification depends only on the spatial arrangement of the atoms bonded to the central atom. Although the lone pairs strongly influence the angles between the bonds and thus the structure of the molecule, the lone pairs are disregarded when describing the overall shape of the molecule. Consider water, H_2O. Its Lewis structure is

$$\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$$

Ignoring the lone pairs around oxygen, you would predict a linear structure, like beryllium chloride. However, the lone pairs of electrons on the central atom repel the bonding pairs, thereby decreasing the angle between them. If you place the bonding and non-bonding electron pairs around the oxygen atom as far apart as possible, the structure will be tetrahedral, as in methane. However, in the water molecule, the 2 lone pairs of electrons repel the bonding pairs with more force, making the H–O–H bond angle 104.5° instead of 109.5°. The result is a V-shaped or bent structure (**Figure 4**).

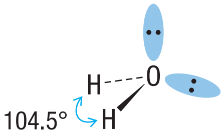


Figure 4 The structure of water is bent due to the repulsion of the 2 lone pairs (blue ellipses) against the 2 O–H bonds.

Common three-dimensional structures predicted by the VSPER theory are summarized in **Table 2** (on the next two pages). CAREER LINK

Table 2 VSEPR Theory Common Three-Dimensional Structures

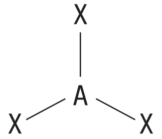
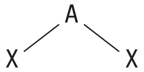
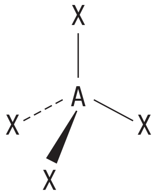
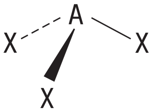
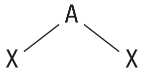
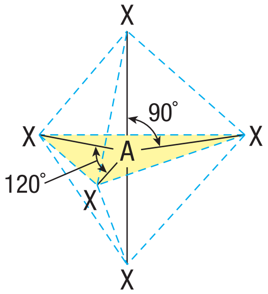
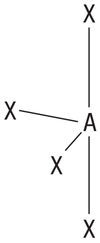
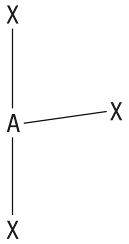
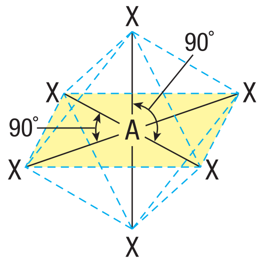
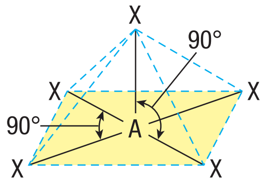
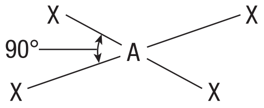
Total number of electron pairs	Number of lone pairs	Name of structure	Angle (most common)	Example	Three-dimensional shape
2	0	linear	180°	$BeCl_2$	X—A—X
3	0	trigonal planar	120°	BH_3	
	1	bent	120°	SO_2	
4	0	tetrahedral	109.5°	CH_4	
	1	trigonal pyramidal	107°	NH_3	
	2	bent	104.5°	H_2O	
5	0	trigonal bipyramidal	90°, 120°	PCl_5	
	1	seesaw	90°, 180°	SF_4	
	2	T-shaped	90°, 180°	ClF_3	
	3	linear	180°	I_3^-	X—A—X

Table 2 VSEPR Theory Common Three-Dimensional Structures (*continued*)

Total number of electron pairs	Number of lone pairs	Name of structure	Angle (most common)	Example	Three-dimensional shape
6	0	octahedral	90°	SF_6	
	1	square pyramidal	90°	BrF_5	
	2	square planar	90°	XeF_4	

Mini Investigation

Balloon Model of Electron Repulsion

Skills: Performing, Observing, Analyzing, Communicating

SKILLS HANDBOOK A2.3

In this investigation you will use balloons as models for the electron repulsion of electrons in atoms.

Equipment and Materials: chemical safety goggles; 9 balloons; string

1. Put on your safety goggles.
2. Inflate all the balloons.
3. Tie 2 of the balloons close together, and place them on a table.
4. Repeat Step 3 with 3 balloons.
5. Repeat Step 3 with 4 balloons.

A. How do the 2 balloons tied together orient themselves? T/I

B. How do the 3 balloons tied together orient themselves? T/I

C. How do the 4 balloons tied together orient themselves? T/I

D. Are balloons good models of valence shell electron-pair repulsion? Why or why not? T/I

E. What would happen in any of the models if you pushed the balloons together and then let go? T/I

F. With 4 balloons tied together, imagine 1 of them being a lone pair. What would the three-dimensional structure be? What if 2 balloons were lone pairs? T/I

Investigation 4.2.1

Three-Dimensional Shape (page 255)

Now that you have learned how to determine molecular structures, perform Investigation 4.2.1 to compare your three-dimensional structure predictions to actual molecular models.

Steps for Applying the VSEPR Theory

The steps below summarize how to predict the structure of a pure substance using the VSEPR theory.

1. Draw the simplified Lewis structure.
2. Count the electron pairs surrounding the central atom, including both bonded and lone electron pairs, and arrange them in a way that minimizes electron-pair repulsion. Do this by putting the electron pairs as far apart as possible in a three-dimensional space.
3. Place the atoms bonded to the central atom at the ends of their bonded electron pairs.
4. Determine the name of the structure from the positions of the atoms and lone pairs of electrons.

Tutorial 1 Using the VSEPR Theory to Predict Molecular Shapes

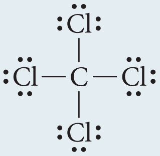
In this Tutorial, you will use the step-by-step approach described on the previous page to use the VSEPR theory to predict the shape of molecules and polyatomic ions.

Sample Problem 1: The Shape of a Molecule without Lone Electron Pairs

Predict the structure of carbon tetrachloride, CCl_4, using the step-by-step VSEPR approach.

Solution

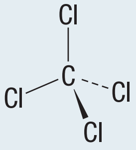
Step 1. Draw the simplified Lewis structure.



Step 2. Count the electron pairs surrounding the central atom, and arrange them to minimize electron-pair repulsion.

The carbon tetrachloride molecule has 4 pairs of bonding electrons around the central atom. There are no lone electron pairs on the carbon atom. The best arrangement of the 4 bonding electron pairs around the central atom is a tetrahedral structure.

Step 3. Place the atoms bonded to the central atom at the ends of their bonded electron pairs.



Step 4. Name the three-dimensional structure.

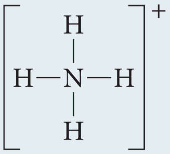
Carbon tetrachloride has a tetrahedral structure.

Sample Problem 2: The Shape of a Polyatomic Ion

Predict the structure of the ammonium ion, NH_4^+, using the step-by-step VSEPR approach.

Solution

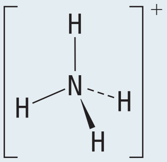
Step 1. Draw the simplified Lewis structure for the polyatomic ion.



Step 2. Count the electron pairs surrounding the central atom and arrange them to minimize repulsions.

The ammonium ion has 4 pairs of bonding electrons around the central atom. There are no lone electron pairs in the ion. The best arrangement of the 4 bonding electron pairs around the central atom is tetrahedral.

Step 3. Place the atoms bonded to the central atom at the ends of their bonded electron pairs.



Step 4. Name the three-dimensional structure.

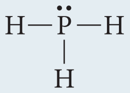
The ammonium ion has a tetrahedral structure.

Sample Problem 3: The Shape of a Molecule with Lone Electron Pairs

Predict the structure of phosphine, PH_3, using the step-by-step VSEPR approach.

Solution

Step 1. Draw the simplified Lewis structure for the molecule.

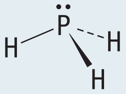


$$\begin{array}{ccccc} H & - & \ddot{P} & - & H \\ & & | & & \\ & & H & & \end{array}$$

Step 2. Count the electron pairs surrounding the central atom and arrange them to minimize repulsions.

The phosphine molecule has 3 pairs of bonding electrons around the central atom. There is 1 lone electron pair on the phosphorus atom. The best arrangement of the 4 electron pairs (3 bonding and 1 lone pair) around the central atom is tetrahedral.

Step 3. Place the atoms bonded to the central atom at the ends of their bonded electron pairs.



Step 4. Name the three-dimensional structure.

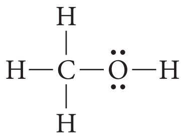
The phosphine molecule has a tetrahedral arrangement of electron pairs. However, because it has a lone electron pair, its structure is trigonal pyramidal.

Practice

1. Use VSEPR theory to predict the geometry of each of the following molecules: T/I
   (a) HBr [ans: linear]
   (b) $SiCl_4$ [ans: tetrahedral]
   (c) BF_3 [ans: trigonal planar]
   (d) NCl_3 [ans: trigonal pyramidal]
2. Use VSEPR theory to predict the geometry of each of the following substances. Draw the structures. T/I C
   (a) BCl_3 [ans: trigonal planar]
   (b) BH_4^- [ans: tetrahedral]
   (c) CF_4 [ans: tetrahedral]
   (d) H_2S [ans: bent]

The VSEPR Theory and Molecules with More Than One Central Atom

So far, you have investigated pure substances that contain just 1 central atom surrounded by other atoms. Many others have more than 1 central atom. You can still use the VSEPR theory to predict the three-dimensional structure of these more complex molecules. Consider methanol, CH_3OH, which has 2 central atoms, carbon and oxygen. Methanol can be represented by the following simplified Lewis structure:



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & \underset{\cdot\cdot}{\ddot{O}} & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

You can predict the three-dimensional structure from the arrangement of electron pairs around both the carbon and oxygen atoms. In a molecule or ionic compound with more than 1 central atom, you first need to predict the arrangement of electrons around each atom individually. Then, combine these arrangements to predict the overall structure. There are 4 pairs of electrons around the carbon atom, so it has a tetrahedral arrangement (**Figure 5(a)**). The oxygen atom also has 4 electron pairs (2 bonding pairs and 2 lone pairs), so it too has a tetrahedral arrangement. The oxygen atom has a slight distortion of the tetrahedron because of the space requirements of the lone electron pairs, so the three-dimensional structure around the oxygen atom is bent (**Figure 5(b)**). The overall geometric arrangement for the methanol molecule is shown in **Figure 5(c)**.

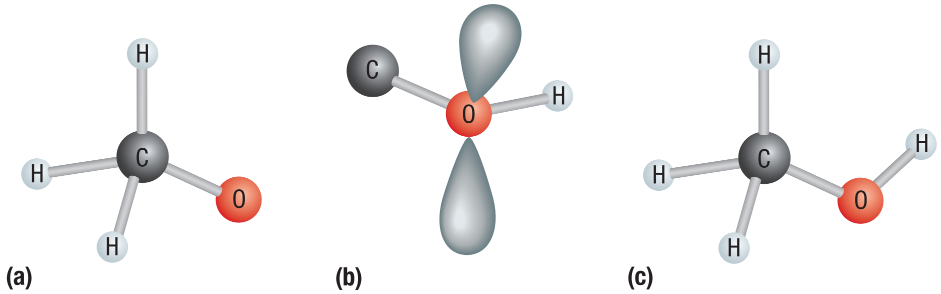


Figure 5 (a) The arrangement of atoms around the carbon atom is tetrahedral. (b) The arrangement of atoms and lone electron pairs around the oxygen atom is bent. (c) The three-dimensional structure of methanol.

Tutorial 2 Structures of Molecules with Two Central Atoms

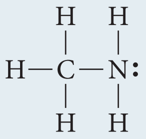
In this Tutorial, you will use the VSEPR theory to predict the shape of molecules that contain more than 1 atom as the central atom.

Sample Problem 1: Molecular Shape with No Single Central Atom

Predict the structure of methylamine, CH_3NH_2, using the step-by-step VSEPR approach.

Solution

Step 1. Draw the simplified Lewis structure. There are 2 central atoms in this structure, carbon and nitrogen.

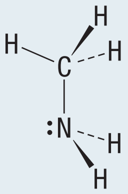


$$\begin{array}{ccccc} & & H & & H \\ & & | & & | \\ H & - & C & - & N\!: \\ & & | & & | \\ & & H & & H \end{array}$$

Step 2. Count the electron pairs surrounding the central atom, and arrange them to minimize electron-pair repulsion.

The methylamine molecule has 4 pairs of bonding electrons around the central carbon atom and 3 pairs of bonding electrons around the nitrogen atom. There is also 1 lone pair of electrons around the nitrogen atom. Both central atoms therefore have a tetrahedral arrangement.

Step 3. Place the atoms bonded to the central atom at the ends of their bonded electron pairs.



Step 4. Name the three-dimensional structure.

The carbon atom in methylamine has a tetrahedral arrangement of atoms, and the nitrogen atom has a trigonal pyramidal arrangement of atoms because it has 1 lone pair of electrons.

Practice

1. For each of the following molecules, use the step-by-step VSEPR approach to predict the shape of the molecule. Draw a three-dimensional structural formula to illustrate your answer, and state the shape around each central atom. T/I C
   (a) CH_3BH_2
   (b) CH_3OCH_3
   (c) CH_3CH_2OH

VSEPR Theory and Multiple Bonds

Molecules or ionic compounds with double and triple bonds have different chemical properties than those with single bonds. For example, hydrocarbons with double or triple bonds react quickly with bromine or potassium permanganate, whereas hydrocarbons with single bonds react much more slowly. Double and triple bonds are shorter and stronger than single bonds between the same types of atoms. However, pure substances with double and triple bonds behave very similarly to pure substances with single bonds when it comes to three-dimensional structure. In a double or triple bond, there is more than 1 bonding pair of electrons. When using the VSEPR theory to determine structure, you must place all of the multiple bonding electrons together, as you will see in the following tutorial.

Tutorial 3 Structures of Molecules with Multiple Bonds

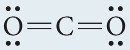
This Tutorial explains how to use the VSEPR theory to determine the shape of a molecule that contains multiple bonds.

Sample Problem 1: Predicting the Shape of a Molecule with Multiple Bonds

Predict the structure of carbon dioxide, CO_2, using the step-by-step VSEPR approach.

Solution

Step 1. Draw the simplified Lewis structure for the molecule. In the carbon dioxide molecule, carbon is the central atom and is bonded by double bonds to each oxygen atom.



$$\ddot{\underset{\cdot\cdot}{O}}=C=\ddot{\underset{\cdot\cdot}{O}}$$

Step 2. Count the electron pairs surrounding the central atom, and arrange them to minimize electron-pair repulsion.

The carbon dioxide molecule has 4 pairs of bonding electrons around the central atom. Each C—O bond is a double bond that consists of 2 pairs of electrons (4 electrons) each. For the purposes of VSEPR, treat a multiple bond as a single group of electrons. In effect, you are counting the number of bonded atoms. There are 2 atoms bonded to the central carbon. Therefore the shape is linear. The generalizations outlined in Table 2 on pages 209–210 still apply to multiple bonding if you count atoms bonded to the central atom rather than electron pairs.

Step 3. Determine the positions of the atoms.

Place the atoms bonded to the central atom at the ends of their bonded electron pairs.

$$\mathrm{O{=}C{=}O}$$

Step 4. Name the three-dimensional structure.

The carbon dioxide molecule has a linear structure. Since each oxygen atom forms a double bond with the carbon atom, the configuration that maximizes the separation of electrons is a linear shape. The electrons are 180° from each other.

Practice

1. Use a simplified Lewis structure and VSEPR theory to predict the shape of a nitrite ion, NO_2^-. T/I C
2. Use VSEPR theory to predict the shapes of the following molecules. Draw structures to illustrate your answers. T/I C
   (a) SiO_2
   (b) HCN
   (c) $XeOF_4$

The VSEPR Theory: How Well Does It Work?

The VSEPR theory works well for most molecules and ionic substances that contain non-metallic elements. However, the theory fails in a few instances. For example, phosphine, PH_3, has the same Lewis structure as ammonia, NH_3: trigonal pyramidal. From the VSEPR theory, you would expect phosphine to have the same bond angles as NH_3: 107°. However, the bond angles of phosphine are actually 94° (**Figure 6**). There are ways to explain this difference, but you have to add more rules to the theory. This example illustrates that simple theories are likely to have exceptions. The amazing thing about the VSEPR theory is that it correctly predicts the structures of so many pure substances.

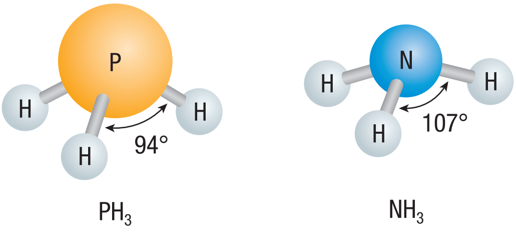


Figure 6 Even though phosphine has the same three-dimensional structure as ammonia, the angles between bonding atoms in the molecules are different: 94° in phosphine and 107° in ammonia.

4.2 Review

Summary

- The valence shell electron-pair repulsion (VSEPR) theory predicts the distribution of atoms covalently bonded to a central atom based on the repulsion between bonding and lone electron pairs associated with the central atom.
- You can use the VSEPR theory to predict the geometry of simple and complex pure substances with covalent bonds by minimizing electron-pair repulsion.
- The VSEPR theory predicts several common arrangements of atoms that minimize electron-pair repulsion.
- There are some exceptions in which the VSEPR theory does not accurately describe the structure of a pure substance.

Questions

1. How do the words that make up the initialism "VSEPR" describe the ideas of the theory? K/U
2. Predict the three-dimensional structure and bond angles for each of the following molecules: T/I
   - (a) CCl_4
   - (b) NF_3
   - (c) $SeCl_2$
   - (d) ICl
   - (e) PCl_3
   - (f) SCl_2
   - (g) SiF_4
3. Predict the three-dimensional structure and bond angles for each of the following ions: T/I
   - (a) NO_2^-
   - (b) NO_3^-
   - (c) OCN^- (carbon is the central atom)
   - (d) N_3^-
4. What is the shape of molecules such as iodine chloride, ICl, and hydrogen bromide, HBr? How can you tell? What is the name of this shape? T/I
5. Identify which of the following substances contain atoms in a trigonal planar arrangement. T/I
   - (a) $AlCl_3$
   - (b) B_2H_4
   - (c) CH_3COH, where O is double-bonded to C
   - (d) CH_3CH_2COOH, where one O is double-bonded to C
6. State whether any of the following molecules or polyatomic ions have a tetrahedral arrangement of either atoms or electrons: T/I
   - (a) CH_3OH
   - (b) SO_4^{2-}
   - (c) CH_3NH_2
7. Use VSEPR theory to predict the geometry of the following molecules, then draw their structures: T/I C
   - (a) BeI_2
   - (b) $SiBr_4$
   - (c) BBr_3
   - (d) CH_3COCH_3 (C is double-bonded to O)
   - (e) CH_2F_4
8. Use the VSEPR theory to predict the geometry of the following polyatomic ions, then draw their structures: T/I C
   - (a) PO_3^{3-}
   - (b) CO_3^{2-}
   - (c) CN^-
9. The molecule $CH_3CH{=}CHCH_2CH_3$ is a 5-carbon chain with 1 double bond between the second and third carbon atoms. Use the VSEPR theory to describe the geometry around each of the carbon atoms. T/I
10. Create a table with the headings shown in **Table 3**. Then, complete the table by filling in the appropriate information for each of the following compounds: NBr_3; CS_2; SeH_4; SeF_6; ICl_4^-; ICl; CH_3Cl; $BrCl_5$; BrF_3; XeI_3^-; SBr_4; BrO_2^-; OF_2; CF_2Cl_2; H_2Se; and PBr_6^-. T/I C

Table 3

Compound	Number of pairs of electrons on central atom	Number of lone pairs	Name of shape	Diagram of shape

Electronegativity and Bond Polarity

4.3

In Section 4.1, you learned about two types of chemical bonding: ionic and covalent. During ionic bonding, 1 or more electrons transfer from a metal atom to a non-metal atom to form negative and positive ions. These ions attract each other. In covalent bonding, neutral atoms share pairs of electrons. In some cases, 2 covalently bonded atoms share electrons equally while, in other cases, 1 of the atoms attracts the shared electron pair more strongly than the other atom. A **non-polar covalent bond** forms when the 2 atoms in a covalent bond share electrons equally. Non-polar covalent bonds usually form between 2 identical atoms, such as in molecular elements like hydrogen, nitrogen, and chlorine. **Polar covalent bonds** form between atoms that attract shared pairs of electrons with different abilities to attract electrons. When you place a sample of hydrogen fluoride gas, HF(g), in an electric field, the molecules orient themselves such that the fluorine end faces the positive pole and the hydrogen end faces the negative pole (**Figure 1**).

non-polar covalent bond a covalent bond in which the electrons are shared equally between atoms

polar covalent bond a covalent bond in which the electrons are not shared equally because 1 atom attracts them more strongly than the other atom

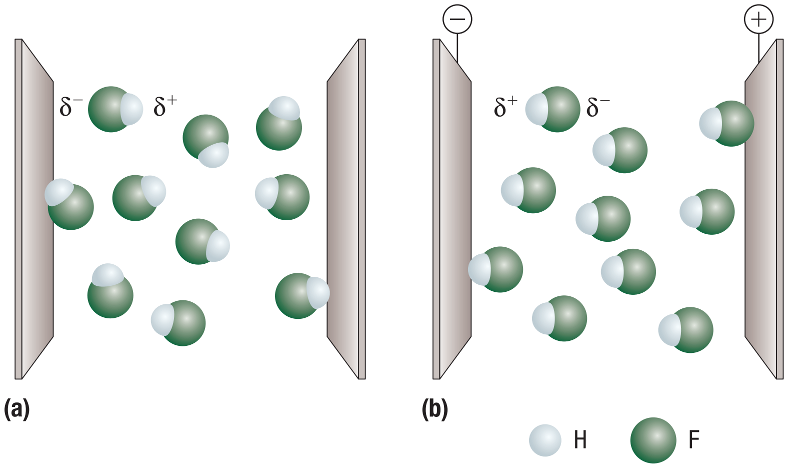


Figure 1 The effect of an electric field on hydrogen fluoride molecules. (a) When no electric field is present, the molecules are randomly oriented. (b) When the field is turned on, the molecules tend to line up with the negative end (fluorine) oriented toward the positive pole and the positive end (hydrogen) oriented toward the negative pole.

This result suggests that in the hydrogen fluoride molecule, the hydrogen and the fluorine atoms share electrons unequally. The symbol δ (lowercase Greek letter delta) represents a partial charge. The hydrogen atom in hydrogen fluoride has a partial positive charge, and the fluorine atom has a partial negative charge:

$$\underset{\delta^+}{\mathrm{H}}-\underset{\delta^-}{\mathrm{F}}$$

You can account for the polarity of the hydrogen fluoride molecule by stating that the fluorine atom has a stronger attraction for the shared electrons than the hydrogen atom does. Similarly, in a water molecule, H_2O, the oxygen atom attracts the shared electrons more strongly than do the hydrogen atoms (**Figure 2**). Bond polarity affects the chemical properties of molecules, so it is useful to quantify the ability of an atom to attract shared electrons.

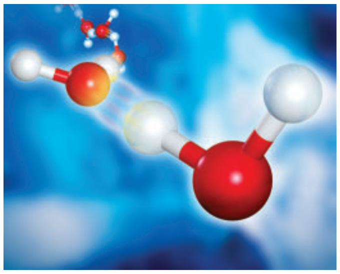


Figure 2 The polarity of the chemical bonds is responsible for some of the unique properties of water.

Electronegativity

electronegativity the ability of an atom in a molecule to attract shared electrons to itself

The **electronegativity** of an atom defines how strongly an atom attracts a pair of electrons it shares with another atom in a covalent bond. Atoms of different elements have different electronegativities.

Consider a hypothetical molecule, HY. If atoms H and Y have identical electronegativities, such as in a hydrogen molecule, H_2, then they share their bonding electrons equally. In general, when the electronegativity difference, ΔEN, between 2 atoms is very small or zero, the covalent bond between them is non-polar. When the electronegativity difference between 2 atoms is relatively large, such as in that of hydrogen fluoride, the covalent bond between them is polar, with a charge distribution as follows:

$$\begin{array}{cc} \mathrm{H} - & \mathrm{Y} \\ \delta^{+} & \delta^{-} \end{array}$$

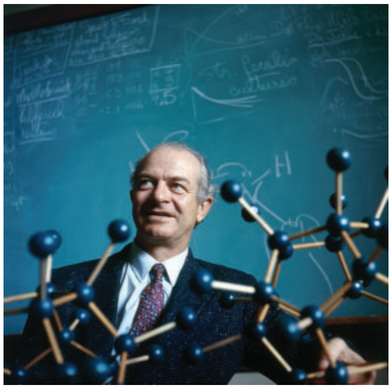


Figure 3 Linus Pauling (1901–1994) won the Nobel Prize in Chemistry for his work on the nature of chemical bonds.

Linus Pauling (**Figure 3**) created a method for determining the electronegativity values of atoms. His table of electronegativity values for all atoms is shown in **Figure 4**. Note that electronegativity generally increases from left to right across a period and decreases going down a group. Electronegativity values range from a high of 4.0 for fluorine (the most electronegative element) to a low of 0.7 for cesium (the least electronegative element). The scale is somewhat arbitrary, and other scientists have proposed slightly different values, based on various assumptions. You may notice that francium also has an electronegativity of 0.7. Due to its high radioactivity, francium is so rare in nature (as little as 20–30 g exists at any given time in Earth's crust) that, for all practical purposes, it is impossible to synthesize and test compounds containing francium. It is possible that francium's electronegativity is even lower than that of cesium.

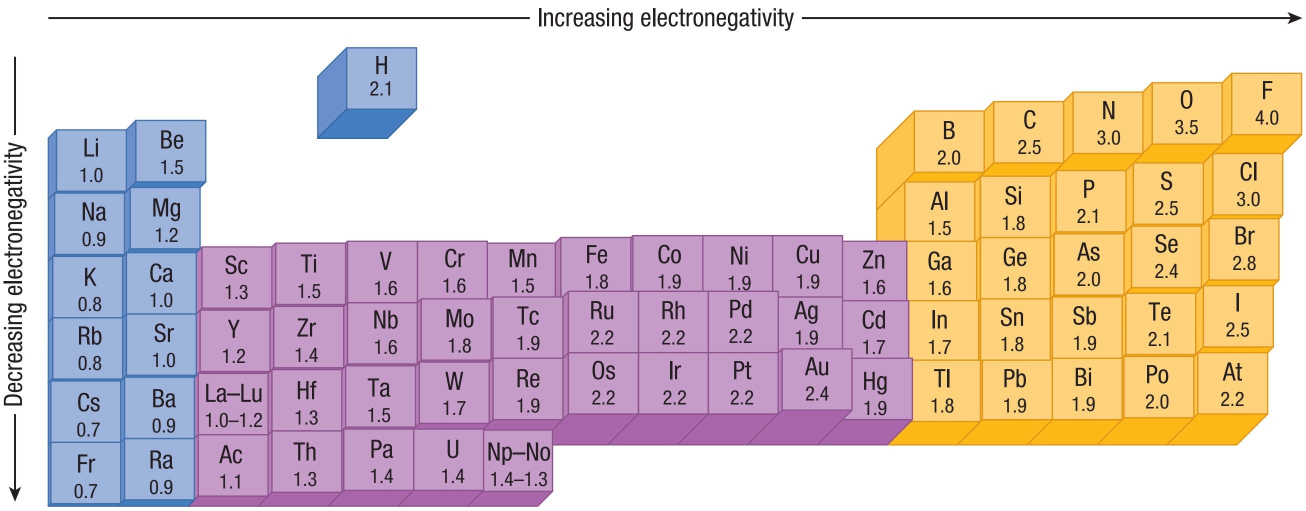


Figure 4 Electronegativity values as determined by Pauling. Electronegativity generally increases across a period and decreases down a group.

You can determine the relative electronegativities of 2 atoms by calculating the difference between their electronegativities. If 2 atoms have an electronegativity difference of less than 0.5, the bond between them is considered non-polar. If the electronegativity difference is 0.5 or greater, the bond is polar. Using Figure 4, you can determine the electronegativity difference for the polar covalent bond in hydrogen chloride, HCl, as follows:

$$\begin{aligned} \Delta \mathrm{EN} &= \mathrm{EN}_{\mathrm{Cl}} - \mathrm{EN}_{\mathrm{H}} \\ &= 3.0 - 2.1 \\ \Delta \mathrm{EN} &= 0.9 \end{aligned}$$

As a general rule, as the electronegativity difference increases, the ionic character of the bond increases. When the difference in electronegativity is greater than 1.7, the chemical bond is considered ionic. A chemical bond that has an electronegativity difference from 0.5 to 1.7 is considered polar covalent (see **Table 1** and **Figure 5**). Labelling bonds as non-polar covalent, polar covalent, or ionic according to these electronegativity difference boundaries is somewhat arbitrary. In reality, with the exception of molecular elements, all bonds are a mixture of covalent and ionic character, which results in the spectrum of values depicted graphically in Figure 5.

UNIT TASK BOOKMARK

As you work on the Unit Task on page 268, think about electronegativity. Does the trend change?

Table 1 Relationship between Electronegativity Difference and Bond Type

ΔEN	Bond type	Character
<0.5	non-polar covalent	covalent
0.5–1.7	polar covalent	covalent and ionic
>1.7	ionic	ionic

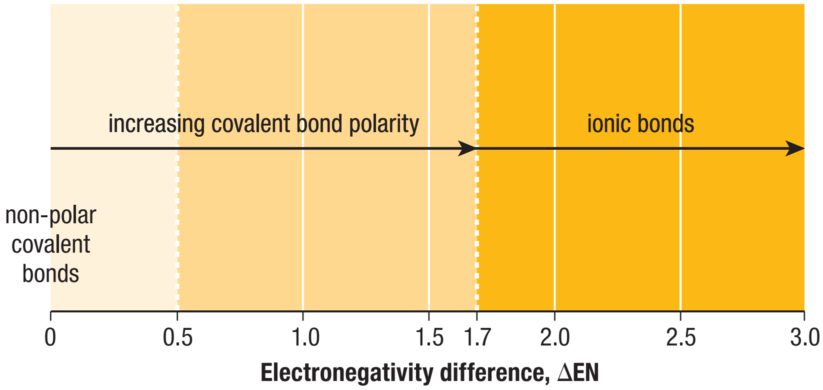


Figure 5 The difference in electronegativity between the atoms involved in bonding determines the character of the chemical bond. A small difference (≤ 1.7) indicates a covalent or polar covalent bond, and a large difference (>1.7) indicates an ionic bond.

Bond Polarities and Dipoles in Diatomic Molecules

When you place hydrogen fluoride gas in an electric field, the molecules orient themselves in a particular way (Figure 1, page 217)). This occurs because of the charge distribution in the hydrogen fluoride molecule, which has a positive end and a negative end. This separation of charges in a covalent bond is called a **dipole**. **Figure 6** shows the convention for representing a dipole in a diatomic molecule. Notice how an arrow points to the negatively charged end, while the tail of the arrow is in the region of the positively charged end. WEB LINK

dipole a separation of positive and negative charges in a region in space

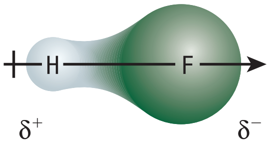


Figure 6 Space-filling view of hydrogen fluoride. The dipole of the hydrogen fluoride molecule is indicated by an arrow. This arrow is drawn so that its head points toward the negative region and its tail to the positive region.

Tutorial 1 Using Electronegativity Values to Predict Bond Polarity

In this Tutorial, you will predict relative bond polarities and the types of bonds based on the electronegativity difference of atoms.

Sample Problem 1: Predicting Relative Bond Polarity

List the following molecules in order of increasing predicted bond polarity: H–H, O–H, Cl–H, S–H, F–H

Solution

Step 1. Using the values in Figure 4, page 218, predict the difference in electronegativity between atoms.

$$\begin{aligned}\Delta EN_{H-H} &= EN_H - EN_H \\ &= 2.1 - 2.1 \\ \Delta EN_{H-H} &= 0\end{aligned}$$

$$\begin{aligned}\Delta EN_{O-H} &= EN_O - EN_H \\ &= 3.5 - 2.1 \\ \Delta EN_{O-H} &= 1.4\end{aligned}$$

$$\begin{aligned}\Delta EN_{O-H} &= EN_{Cl} - EN_H \\ &= 3.0 - 2.1 \\ \Delta EN_{Cl-H} &= 0.9\end{aligned}$$

$$\begin{aligned}\Delta EN_{S-H} &= EN_S - EN_H \\ &= 2.5 - 2.1 \\ \Delta EN_{S-H} &= 0.4\end{aligned}$$

$$\begin{aligned}\Delta EN_{F-H} &= EN_F - EN_H \\ &= 4.0 - 2.1 \\ \Delta EN_{F-H} &= 1.9\end{aligned}$$

Step 2. List the bonds in order of smallest ΔEN to greatest ΔEN.

$\Delta EN_{H-H} = 0$; $\Delta EN_{S-H} = 0.4$; $\Delta EN_{Cl-H} = 0.9$;

$\Delta EN_{O-H} = 1.4$; $\Delta EN_{F-H} = 1.9$

Step 3. According to accepted theory, the polarity of a bond increases as the difference in electronegativity increases. Therefore, the order of these molecules according to their predicted bond polarity, from least to greatest, is

H–H < S–H < Cl–H < O–H < F–H

Sample Problem 2: Predicting the Polarity of a Chemical Bond

Determine the electronegativity difference, and classify the type of bond in the following pairs of atoms:
(a) N–H; (b) P–H; (c) K–Br

Solution

Step 1. Using Figure 4, page 218, predict the difference in electronegativity between atoms.

(a) $$\begin{aligned}\Delta EN_{N-H} &= EN_N - EN_H \\ &= 3.0 - 2.1 \\ \Delta EN_{N-H} &= 0.9\end{aligned}$$

(b) $$\begin{aligned}\Delta EN_{P-H} &= EN_P - EN_H \\ &= 2.1 - 2.1 \\ \Delta EN_{P-H} &= 0\end{aligned}$$

(c) $$\begin{aligned}\Delta EN_{K-Br} &= EN_{Br} - EN_K \\ &= 2.8 - 0.8 \\ \Delta EN_{K-Br} &= 2.0\end{aligned}$$

Step 2. Use Table 1, page 219, to classify the type of bond in each compound.

(a) $\Delta EN_{N-H} = 0.9$

Since $0.5 < \Delta EN < 1.7$, this bond is a polar covalent bond.

(b) $\Delta EN_{P-H} = 0$

Since $\Delta EN < 0.5$, this bond is a non-polar covalent bond.

(c) $\Delta EN_{K-Br} = 2.0$

Since $\Delta EN > 1.7$, this bond is an ionic bond.

Practice

1. Use the electronegativity differences between atoms to classify each of the following bonds as polar covalent, non-polar covalent, or ionic: T/I
   - (a) C–F
   - (b) P–Cl
   - (c) Li–Cl
2. Arrange the bonds in the following sets of atom pairs in order of increasing bond polarity: T/I A
   - (a) B–H, H–H, C–H, H–F, O–H, Na–H, Mg–H
   - (b) Al–Cl, P–Cl, Li–Cl, Cl–Cl, I–Cl, Rb–Cl
   - (c) C–H, C–F, C–Cl, C–O, C–S, C–C

4.3 Review

Summary

- The electronegativity of an atom is the relative ability of the atom to attract shared electrons.
- The polarity of a bond increases as the electronegativity difference increases.
- A diatomic molecule with a polar bond has a region of positive and negative charge, called a dipole.
- The charges in a dipole will orient themselves in an electric field.
- The electronegativity difference, ΔEN, of bonded atoms can be used to predict bond type. The bond will likely be ionic when $\Delta EN > 1.7$, polar covalent when $0.5 \leq \Delta EN \leq 1.7$, and non-polar covalent when $0 < \Delta EN < 0.5$.

Questions

1. Arrange each of the following in order of increasing electronegativity: K/U
   (a) C, N, O
   (b) S, Se, Cl
   (c) Si, Ge, Sn
   (d) Tl, S, Ge
2. If you did not have access to a set of values of the electronegativities of atoms similar to Figure 4, how could you use the periodic table to determine the polarity of a chemical bond? K/U
3. Without using Figure 4 (you can use a periodic table), determine the bond type between each of the following atoms: K/U
   (a) C–O
   (b) F–I
   (c) Li–F
   (d) Ge–Sn
   (e) Al–Cl
4. Without using Figure 4, predict which bond in each of the following groups will be the most polar. Explain your answer. K/U T/I
   (a) C–F, Si–F, Ge–F
   (b) P–Cl or S–Cl
   (c) S–F, S–Cl, S–Br
   (d) Be–Cl, Mg–Cl, Ca–Cl
5. Referring to the electronegativities of the atoms in the bond, describe how the bonds K–Br, C–Br, and Br–Br are different. K/U
6. By indicating the partial positive and partial negative atoms, show the bond polarity for each of the following molecules: K/U C
   (a) O–F
   (b) Br–Br
   (c) C–Br
   (d) C–O
7. For each of the following, state whether the bond polarity is shown correctly. If not, show the bond polarity correctly. K/U T/I C
   (a) $\delta^{+}\text{H}-\text{Br}\delta^{-}$
   (b) $\delta^{+}\text{Cl}-\text{I}\delta^{-}$
   (c) $\delta^{+}\text{Si}-\text{S}\delta^{-}$
   (d) $\delta^{+}\text{F}-\text{F}\delta^{-}$
   (e) $\delta^{+}\text{O}-\text{P}\delta^{-}$
8. (a) Determine the electronegativity difference between C and F.
   (b) What type of bond is the C–F bond?
   (c) When you place molecules of CF_4 in an electric field, the molecules do not display any particular orientation. Explain why. K/U T/I
9. An atom, when bonded to nitrogen, results in a polar covalent bond, with nitrogen having a partial positive charge. K/U T/I
   (a) List all possible atoms that this atom could be.
   (b) Which of the atoms listed in (a) would result in the most polar bond?
   (c) Which atoms, when bonded to nitrogen, would result in a non-polar covalent bond?
10. Predict the type of bond (ionic, non-polar covalent, or polar covalent) that would be expected to form between each pair of atoms: K/U T/I
    (a) Rb and Cl
    (b) S and S
    (c) C and F
    (d) Ba and C
    (e) B and Se
    (f) Cs and Br

Gillespie and the VSEPR Model

SKILLS HANDBOOK A4

ABSTRACT

Professor Emeritus Ronald J. Gillespie of McMaster University in Hamilton, Ontario, has made many important contributions to chemistry. As a young inorganic chemist, Gillespie was interested in superacids, which are acids that are more acidic than 100 % sulfuric acid. He became curious about the structure and behaviour of different polyatomic ions. He used X-ray crystallography and spectroscopy to investigate these structures. However, Gillespie's greatest contribution to chemistry was his development of the VSEPR theory to predict three-dimensional structure, which he developed with another chemist, Ronald Nyholm. Gillespie and Nyholm built the VSEPR theory beginning with models developed by other chemists before them. Thanks to Gillespie's understanding of inorganic and structural chemistry, we now have a simple method for predicting three-dimensional structure based on the electrical repulsion of valence electrons.

Gillespie's Early Training

Dr. Ronald Gillespie was one of the contributing scientists who developed the VSEPR theory to predict three-dimensional structure (**Figure 1**). However, his career started with the study of acids. Gillespie was born in London, England, in 1924 and received a bachelor of science degree in 1944 from University College London. As a graduate student, he showed that when nitric acid was placed in a sulfuric acid solution, a nitronium ion, NO_2^+, was formed. This work provided the first evidence of a superacid, which formed in a highly viscous medium. Although Gillespie's most celebrated work was in the field of three-dimensional structure, his work on superacids initiated and laid the foundation for other studies on strong acids.

Figure 1 Dr. Ronald Gillespie

From Superacids to VSEPR

Gillespie's work on superacids led him to investigate other polyatomic ions that form in superacidic solutions. He then became interested in the three-dimensional structure of these ions. In the early to mid-1950s, there were few physical and spectroscopic techniques available for studying chemical structures. As technology developed, Gillespie used new techniques, including X-ray crystallography and nuclear magnetic resonance (NMR), to characterize the new polyatomic ions that he discovered. From this work, Gillespie noticed that the angles between chemical bonds followed patterns, which led him to study chemical bonding and three-dimensional structure.

Shortly after completing his Ph.D., Gillespie travelled to the United States for a one-year fellowship at Brown University in Rhode Island. During this time, he met Australian chemist Dr. Ronald Nyholm. Gillespie and Nyholm collaborated on a review that eventually developed into the model for which they are famous: the VSEPR theory of chemical bonding.

Predicting Three-Dimensional Structure

The goal of Gillespie and Nyholm was to summarize the main principles determining the three-dimensional structure of inorganic molecules. While reading a paper on molecular geometry, Gillespie realized that if he arranged a molecule so that the valence electrons surrounding the central atom were as far apart as possible, he could predict the three-dimensional structure (**Figure 2**). Gillespie recognized that this approach was an easier way to describe the geometry of molecules containing the main group elements, and he showed that it worked for a large number of molecules. In his initial paper in 1957, Gillespie described how the repulsion of valence electrons was a result of the Pauli exclusion principle: no 2 electrons can have the same 4 quantum numbers.

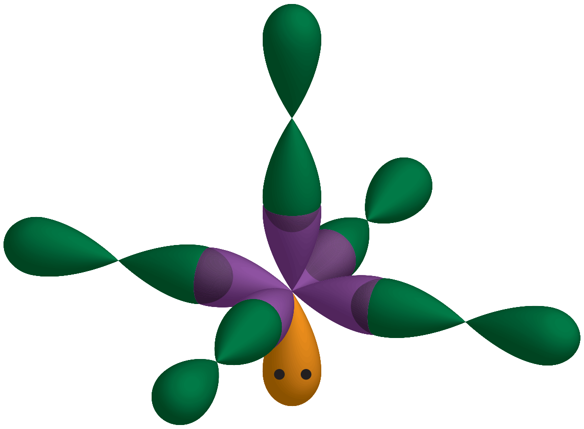


Figure 2 The three-dimensional structure of iodine pentafluoride as predicted by the VSEPR theory

Gillespie has continued to develop the VSEPR theory since his initial paper. As other chemists discovered exceptions to or inconsistencies in the model, he refined the theory to include or explain the exceptions, thereby improving both the theory and our understanding of three-dimensional structure. His current area of research is studying the transition metals—the largest class of exceptions to the VSEPR theory.

Dedication to Teaching

As Gillespie was completing his Ph.D. in Chemistry, he was invited to teach a course in molecular properties. He then began teaching as an Assistant Lecturer at University College London. Afterwards, as a professor at McMaster University, Hamilton, Ontario, Gillespie continued to spend much of his time teaching. He first introduced the VSEPR theory to help his students understand how bonding affects three-dimensional structure. His passion for communicating his knowledge and enthusiasm for chemistry led to the authoring and coauthoring of several undergraduate chemistry textbooks. According to Gillespie,

> *One problem is that students have difficulty making the connection between the macroscopic world of observations and the microscopic world of atoms and molecules. Yet it is this aspect of chemistry that sets it apart from the other sciences. . . . An understanding of this connection is probably the most important thing that a student can get out of an introductory [chemistry] course.* (Reforming the General Chemistry Textbook, 1997)

Gillespie's success in research, teaching, and the development of the VSEPR theory demonstrate what having a dedication to one's passion can achieve. During his tenure at McMaster University, Gillespie has received many coveted honours. Some of these honours include election as Fellow of the Royal Society of Canada in 1965, and of the Royal Society of London in 1977, and receipt of an Honorary Fellowship of the Chemical Institute of Canada in 1993.

Further Reading

Cardellini, L. (2010). Modeling chemistry for effective chemical education: An interview with Ronald J. Gillespie. *Journal of Chemical Education*, 87 (5): 482–486.

Gillespie, R.J. (2008). Fifty years of the VSEPR model. *Coordination Chemistry Reviews*, 252 (12–14): 1315–1327.

Gillespie, R.J. (1997). Reforming the general chemistry textbook. *Journal of Chemical Education*, Vol. 74 No. 5: 484–485.

Gillespie, R.J., & Hargittai, I. (1991). *The VSEPR model of molecular geometry*. Boston: Allyn & Bacon.

WEB LINK

4.4 Questions

1. The article states that Gillespie has spent much time doing both science research and science education. Explain how teaching might have helped Gillespie continue developing the VSEPR theory. A
2. According to Gillespie, what is the greatest challenge for students learning chemistry? Do you agree or disagree? Explain. K/U A
3. A central goal of science is to find a few key principles that help to explain the overwhelming complexity of the real world. How do you think the VSEPR theory helped to make chemistry more comprehensible? A
4. Scientists continually refine and even replace theories when newer theories do a better job of explaining observations. How do you think the VSEPR model has changed over the past 50 years? K/U A
5. What connection did Gillespie make between VSEPR theory and quantum theory? K/U

4.5 Molecular Polarity

You have learned that different atoms can have different tendencies to attract bonding pairs of electrons. When 2 atoms with sufficiently different electronegativities combine, a dipole forms: one end of the bond is negative, and the other end is positive.

Figure 1 shows what happens when a balloon charged with static electricity is placed near a stream of running tap water. As gravity pulls the water vertically down, the water bends. What causes this effect?

Figure 1 When you place an electrostatically charged balloon near a stream of water, the water stream bends toward the balloon.

Polar and Non-polar Polyatomic Molecules

You have learned that diatomic molecules, such as hydrogen fluoride, are polar when their atoms have sufficiently different electronegativities. Polyatomic molecules (molecules with more than 2 atoms) can also exhibit polar behaviour. Water molecules are an example of this. Each water molecule is composed of 1 oxygen atom and 2 hydrogen atoms. Since an oxygen atom has a greater electronegativity than a hydrogen atom, each H–O bond is polar (has a bond dipole). **Figure 2** shows the charge distribution in a water molecule.

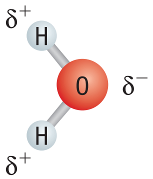


Figure 2 Representation of the charge distribution in a water molecule, using a ball-and-stick model

The polarity of the individual water molecules causes the bending of the stream of running tap water in Figure 1. The static charge on the balloon is a negatively charged electric field. As shown in **Figure 3**, the dipoles in the water molecules become oriented toward this electric field, causing the entire stream of water to be pulled toward the charged balloon.

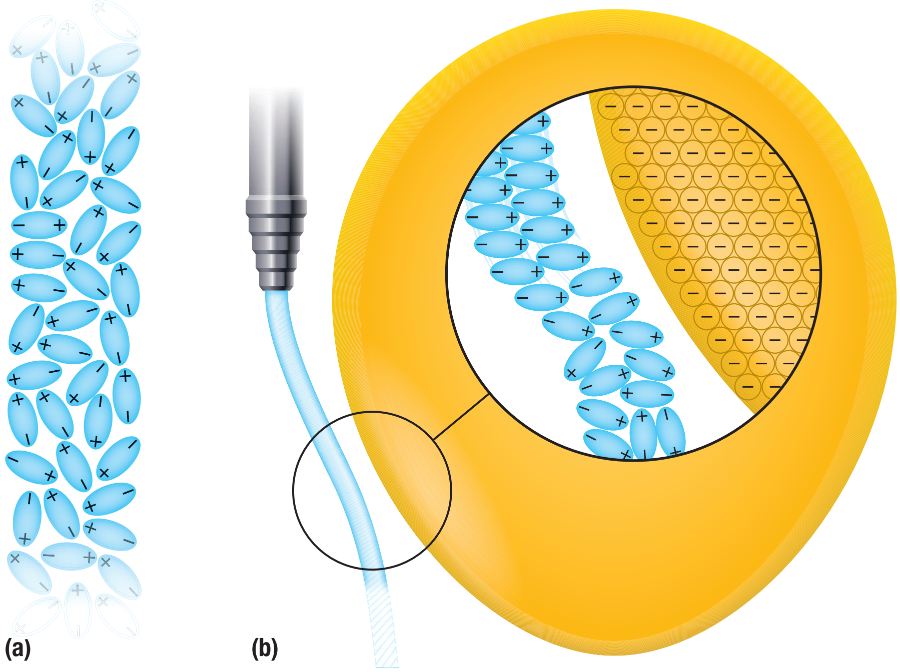


Figure 3 (a) In the absence of an electric field, the dipoles in water molecules are randomly oriented. (b) When a negatively charged balloon is placed next to the stream of water molecules, the dipoles cause the water molecules to move so that their positive poles align closer to the balloon.

Since an oxygen atom is more electronegative than a hydrogen atom, the negative ends of both bond dipoles in a water molecule point in the direction of the oxygen atom (**Figure 4**). Water has two lone pairs of electrons on the oxygen atom that give it a bent or V-shaped three-dimensional structure. As a result, the bond dipoles add together to give the water molecule a net dipole, represented by the red arrow in Figure 4. Therefore, water molecules are strongly polar. Molecules that have net dipoles are **polar molecules**.

polar molecule a molecule that has a net dipole

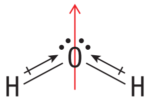


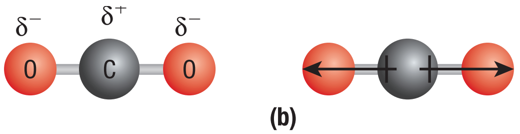
Figure 4 Water has a net negative dipole in the direction of the oxygen atom.

However, not every molecule that has polar covalent bonds is a polar molecule. A **non-polar molecule** is a molecule with no net dipole. Some non-polar molecules have polar bonds but do not have a net dipole, due to the arrangement of atoms in a molecule. This happens when the sum of the individual bond dipoles is zero. For example, a carbon dioxide molecule is linear, with the negative charge distribution on the oxygen atoms and the positive charge distribution on the central carbon atom (**Figure 5**). However, since the polarities of these bonds are equal and opposite, they cancel each other out.

non-polar molecule a molecule that has only non-polar bonds, or a bond dipole sum of zero

Investigation 4.5.1

Testing for Polar Molecules (page 256)
Now that you know the polarity of a molecule affects its behaviour when it is near differently charged objects, perform Investigation 4.5.1 to examine the effect of charge on different substances.

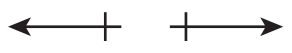
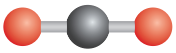
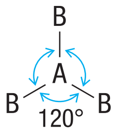
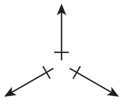
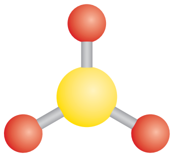
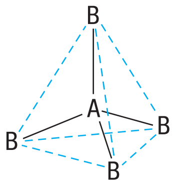
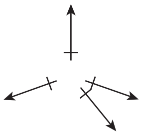
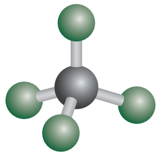


(a) **(b)**

Figure 5 (a) The structure of and charge distribution in carbon dioxide. Oxygen is more electronegative than carbon. (b) The opposing bond polarities of carbon dioxide cancel each other out, and the carbon dioxide molecule has no net dipole.

To predict whether a specific molecule is polar or non-polar, you must consider two characteristics: the types of bonds in the molecule (polar or non-polar) and the geometric shape of the molecule. **Table 1** lists some common molecular structures that give rise to non-polar molecules. WEB LINK

Table 1 Types of Molecular Structures with Polar Bonds but No Net Dipole

Type	General example	Cancellation of polar bonds	Specific example	Ball-and-stick model
linear molecules with 2 identical bonds	B—A—B		CO_2	
planar molecules with 3 identical bonds			SO_3	
tetrahedral molecules with 4 identical bonds (109.5° apart)			CCl_4	

Tutorial 1 Predicting the Polarity of Molecules

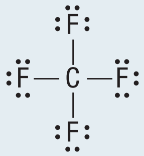
In this Tutorial, you will determine the net dipole of a molecule. If the sum of the dipoles in the molecule is zero, the molecule is non-polar. If the sum is non-zero, the molecule is polar. Since you only want to know whether the molecular dipole is zero, you can use symmetry arguments.

Sample Problem 1: Predicting the Polarity of Tetrafluoromethane

Predict whether tetrafluoromethane, CF_4, is a polar or a non-polar molecule.

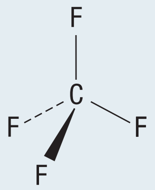
Solution

Step 1. Draw the simplified Lewis structure of tetrafluoromethane.



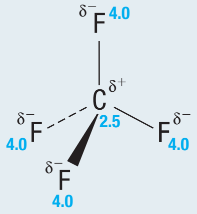
Step 2. Use the VSEPR theory to predict the three-dimensional structure, then draw a diagram.

Since carbon is the central atom and it is bonded to 4 fluorine atoms, you would expect a molecule of tetrafluoromethane to have a tetrahedral shape.



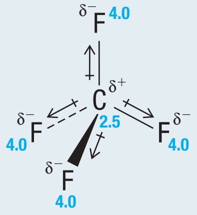
Step 3. Identify the electronegativity of each atom, and determine the partial charges in the molecule.

The carbon atom is less electronegative than the surrounding fluorine atoms, so it accumulates a partial positive charge from each bond with fluorine. Each fluorine atom acquires a partial negative charge.



Step 4. Draw the bond dipoles, and determine whether the molecule has a net dipole.

In this tetrahedral shape, all of the atoms bonded to the central carbon atom are identical and all the directions are equivalent. Therefore, the four bond dipoles cancel each other. The overall net dipole is zero, so tetrafluoromethane is a non-polar molecule.

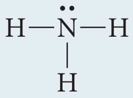


Sample Problem 2: Predicting the Polarity of Ammonia

Predict whether ammonia, NH_3, is a polar or a non-polar molecule.

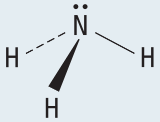
Solution

Step 1. Draw the simplified Lewis structure of ammonia.



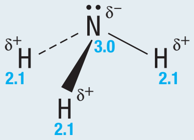
Step 2. Use VSEPR theory to predict the three-dimensional structure, then draw a diagram.

Nitrogen is the central atom that is bonded to 3 hydrogen atoms. There is 1 lone pair of electrons on the nitrogen atom. The three-dimensional structure of ammonia is therefore trigonal pyramidal.



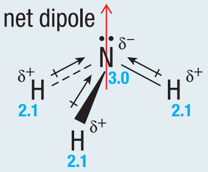
Step 3. Identify the electronegativity of each atom, and determine the partial charges in the molecule.

The nitrogen atom is more electronegative than the hydrogen atoms, so it has a partial negative charge from each bond. Each hydrogen atom acquires a partial positive charge.



Step 4. Draw the bond dipoles, and determine whether the molecule has a net dipole.

In a trigonal pyramidal shape, all of the atoms bonded to nitrogen are identical, but the bond dipoles do not cancel each other out. Therefore, the ammonia molecule has a net dipole. Ammonia is a polar molecule with a net dipole pointing in the direction of the lone pair of electrons on the nitrogen atom.



Practice

1. Predict the polarity of each of the following molecules. Include a three-dimensional structure for each molecule. If the molecule is polar, indicate the direction of the net dipole. T/I C
   (a) NF_3 [ans: polar]
   (b) CBr_4 [ans: non-polar]
   (c) SF_2 [ans: polar]
2. Predict the polarity of each the following molecules or ions: T/I C
   (a) PO_3^{3-} [ans: polar]
   (b) NH_4^+ [ans: non-polar]
   (c) B_2H_6 [ans: non-polar]
   (d) CH_3CH_2OH [ans: polar]

3. Some substances have bonds that we predict to be polar, but the molecule turns out to be non-polar. K/U T/I C
   (a) Write the formula of one such substance.
   (b) Draw the Lewis structure of the molecule, and show calculations to support the polarity of the bond.
   (c) Draw a diagram illustrating the structure of the molecule, and show why the molecule is non-polar.

You have seen that bond polarity, molecular shape, and the distribution of atoms all influence the polarity of a molecule. **Figure 6** is a flow chart that you can use to help you predict whether a molecule is polar or non-polar.

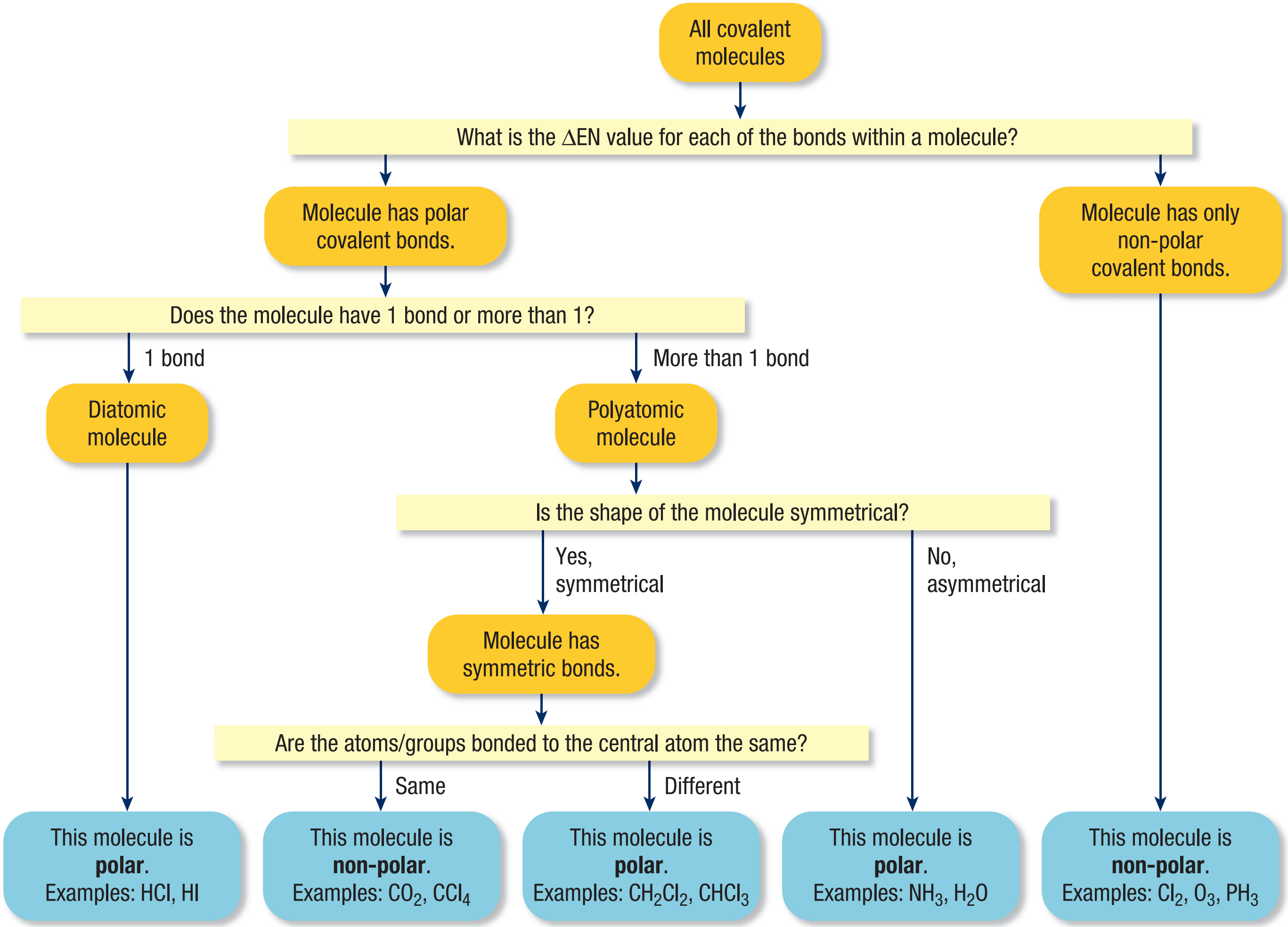


Figure 6 Flow chart to determine whether a molecule is polar or non-polar

4.5 Review

Summary

- The polarity of a molecule depends on both the direction and polarity of its bonds.
- When the sum of the bond dipoles is non-zero, the molecule is polar.
- The bond dipoles for molecules with symmetrically arranged atoms add up to zero and the molecules are non-polar.
- The polarity of a molecule can be predicted based on bond polarity, molecular shape, and the distribution of atoms.

Questions

1. Use the VSEPR theory to explain why a molecule of diboron tetrafluoride, B_2F_4, is non-polar. K/U
2. Use the VSEPR theory to explain why a molecule of methanol, CH_3OH, is polar. K/U
3. Explain why phosphorus trihydride, PH_3, is a non-polar molecule, while phosphorus trifluoride, PF_3, is a polar molecule. K/U
4. Use partial charges to represent the dipole in the bonds of the following molecules: K/U C
   (a) F–B in BF_3
   (b) N–Cl in NCl_3
   (c) H–C in C_4H_{10}
   (d) C–C in C_4H_{10}
5. Predict whether each of the following molecules is polar or non-polar: T/I C
   (a) OCl_2
   (b) BeH_2
   (c) SiF_4
   (d) SO_2
   (e) SO_3
   (f) CHF_3
   (g) CCl_2F_2
6. For each of the following molecules, draw the simplified Lewis structures and predict whether each molecule is polar or non-polar: T/I C
   (a) HOCN
   (b) CF_3Cl
   (c) H_2CO
7. Draw a three-dimensional diagram for each of the following molecules, and determine whether each molecule is polar or non-polar. Indicate any polarity on your diagram. T/I C
   (a) PCl_3
   (b) ClF_3
   (c) $XeCl_4$
   (d) H_2S
   (e) FCN
8. (a) The molecule dichlorofluoromethane, $CHFCl_2$, is used as a refrigerant. Tetrafluoromethane, CF_4, was also considered as a possible refrigerant. Draw the three-dimensional structures of $CHFCl_2$ and CF_4. Predict the polarities of both molecules.
   (b) Explain the difference between the two molecules. What causes the difference?
   (c) What physical properties would be different due to the different polarities of these molecules? Which of these properties could be important to the use of each gas as a refrigerant? K/U T/I C A
9. When a crystal of sodium chloride dissolves in water, the positive ends of the water dipole align with the negative chloride ions, and the negative ends of the water dipole align with the positive sodium ions. Draw a series of diagrams that illustrate this process. T/I C
10. Both water and carbon dioxide are important greenhouse gases because they can absorb infrared energy from sunlight, convert it into thermal energy, and release energy into the atmosphere. To absorb infrared energy, a molecule must have a vibrating dipole whose vibrational frequency matches the frequency of the infrared energy. Water has a strong dipole, so infrared energy vibrations cause its dipole to vibrate. Research the role of water and carbon dioxide as greenhouse gases to find answers to the following questions: K/U T/I A
    (a) While water absorbs infrared light some 80 times more efficiently than carbon dioxide, carbon dioxide absorbs enough to be a legitimate source of concern for climate change. However, given that carbon dioxide has no net dipole, how can it absorb infrared light at all?
    (b) When scientists discuss the greenhouse effect, carbon dioxide is the gas that is held responsible, even though there are other greenhouse gases such as water vapour. Why do you think this is?

WEB LINK

4.6 Quantum Mechanics and Bonding: Hybridization

Benzene is a common non-polar liquid, known and used by pharmacists and perfumers in various forms since the fifteenth century. English scientist Michael Faraday (1791–1867) was the first to isolate benzene and determine its molecular formula: C_6H_6. For decades, the unusual formula of benzene stumped chemists because they were unable to determine the structure of a molecule that has an equal number of carbon and hydrogen atoms. Finally, in 1865—40 years after Faraday's discovery—the German chemist Friedrich Kekulé (1829–1896) proposed a three-dimensional structure for benzene (**Figure 1(a)**).

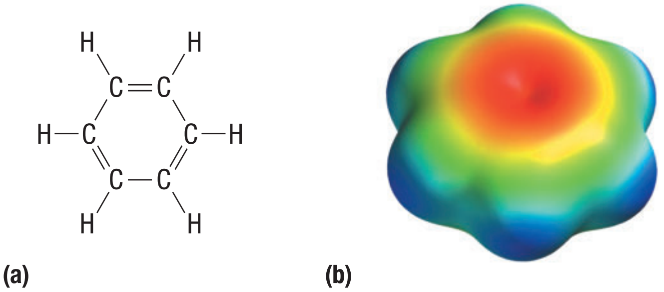


Figure 1 (a) The simplified Lewis structure of benzene (b) A computer-generated model showing the three-dimensional charge distribution in a benzene molecule. Red represents the region of highest electron density, and blue represents the region of lowest electron density.

Notice how, in this structure, each carbon atom bonds to 1 hydrogen atom. It took another 65 years before this ring structure was confirmed by X-ray crystallography. This technology also revealed that all of the carbon–carbon bonds are equal in length: shorter than single bonds but longer than double bonds. The understanding of benzene's structure was so important at the time that, 25 years after Kekulé's first paper, the German Chemical Society honoured him with an elaborate celebration. There, Kekulé explained how he recognized the cyclic structure of benzene from a daydream in which he imagined a snake seizing its own tail.

Look at the two different structures for benzene in Figure 1. What differences do you notice between them? The simplified Lewis structure in Figure 1(a) suggests that there are two types of carbon–carbon bonds: 3 single bonds and 3 double bonds. In such a structure, electrons making up the double bonds are always localized between the same 2 carbon atoms. A model of the three-dimensional charge distribution in benzene would be expected to show the carbon–carbon double bonds having a higher electron density than the carbon–carbon single bonds. Yet, the computer-generated model in Figure 1(b) shows only that electron density decreases uniformly as you move away from the centre of the molecule. This model suggests that there are no differences in the lengths of any of the carbon–carbon bonds and that the electrons are concentrated in the centre of the benzene ring.

How have scientists explained these observations of the structure of benzene? One explanation is that the electrons in the carbon–carbon double bonds are not always localized between the same 2 carbon atoms. This idea is based on the concepts of quantum mechanics. You learned in Chapter 3 that the location of electrons is defined by probability distributions—regions in space where there is the greatest likelihood of finding an electron.

The Lewis structure of a molecule provides a simplified view of bond formation, and allows you to determine the number of bonding and lone electron pairs. You can then predict molecular geometry using the VSEPR theory. But neither Lewis structures nor VSEPR theory describes how bonds are actually formed, and how orbitals interact. In this section, you will learn more about molecular orbitals and how they are involved in bond formation.

Valence Bond Theory

In Chapter 3, you learned how quantum numbers are used to describe the locations of electrons in an atom. Electron clouds can be constructed for a particular atom to represent areas that have a high probability of containing an electron. The complex Schrödinger wave functions and probability densities can be used to describe bonding and electrons.

However, calculating the electron clouds surrounding a single atom, much less in a bond, is difficult. Even though modern computers have expanded the scope of quantum mechanics calculations to include relatively large molecules, the computer power and time needed to calculate electron clouds increase dramatically as the complexity of the molecule increases. So, it is very difficult to calculate quantitatively the distribution of electrons in the bonds of unusual molecules.

A simpler approach to describing the location of electrons in bonds is to start with an atom and its valence orbitals and to form covalent bonds in these atoms through the valence orbitals. This method is called the valence bond theory. According to **valence bond theory**, a covalent bond forms when 2 atomic orbitals, each with an unpaired electron, overlap. When the covalent bond forms, the lowest energy state is obtained when participating electrons are of opposite spin.

valence bond theory a theory stating that atomic orbitals overlap to form a new orbital with a pair of opposite-spin electrons

The simplest example of the valence bond theory is the bonding of 2 hydrogen atoms. The electrons in each of the hydrogen atoms reside in the 1*s* orbital (**Figure 2**). When the 2*s* orbitals overlap, a covalent bond forms. In this bond, the electrons in the bonded 1*s* orbital have opposite spins (**Figure 3**), similar to a filled atomic orbital.

Figure 2 The valence orbital diagram of a hydrogen atom. One electron is in the 1*s* orbital.

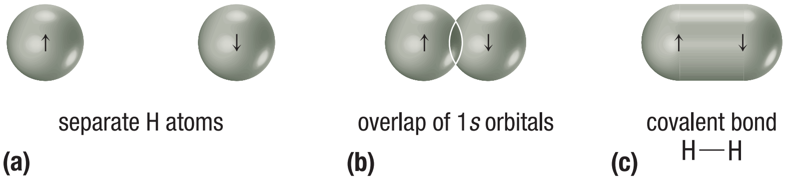
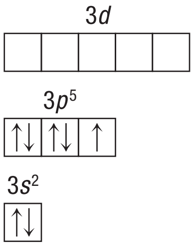


Figure 3 The formation of a covalent bond in elemental hydrogen, H_2, according to valence bond theory. When the hydrogen molecule forms, each 1*s* orbital (a) overlaps to form a covalent bond (b). In the hydrogen molecule, the electrons have opposite spins, with a lower energy state than the separate hydrogen atoms (c).

The example of 2 hydrogen atoms forming a covalent bond involves electrons from the 1*s* orbital. Yet any unfilled orbital can overlap with another unfilled orbital. The diatomic molecule hydrogen chloride, HCl, also forms covalent bonds. The hydrogen atom contributes 1 electron from its 1*s* orbital to form the bond. The valence orbital diagram of a chlorine atom is



In the chlorine atom, the 3*s* orbital and two of the 3*p* orbitals are full with 2 electrons of opposite spin. However, one of the 3*p* orbitals contains 1 unpaired electron. The 1*s* orbital from the hydrogen atom can overlap with this 3*p* orbital in the chlorine atom to form a covalent bond (**Figure 4**). The *p* orbital in the chlorine atom has 2 lobes. When the bond forms, 1 lobe of the chlorine atom overlaps with the 1*s* orbital from the hydrogen atom.

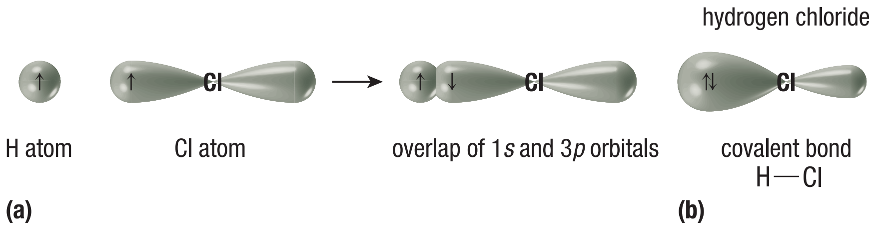


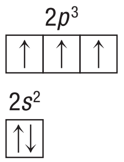
Figure 4 (a) When the hydrogen chloride molecule forms, the 1*s* orbital in the hydrogen atom overlaps with the 3*p* orbital of the chlorine atom to form a covalent bond. (b) In the hydrogen chloride molecule, the electrons have opposite spins, with a lower energy state than the separate atoms.

UNIT TASK BOOKMARK

As you work on the Unit Task on page 268, think about how chemical bonding would be affected in the new periodic table.

The valence bond theory involves taking existing atomic orbitals and overlapping them to produce new molecular orbitals for the bonding electrons. These new molecular orbitals concentrate electron density between the bonded atoms, as the VSEPR theory postulates. The VSEPR theory assumes that the majority of the electron density for bonded pairs of electrons is in the vicinity of the bond. The valence bond theory helps explain why this assumption is justified.

So far, you have considered only bonding in diatomic molecules. The valence bond theory can also describe bonding in polyatomic molecules. Consider a molecule of ammonia, which consists of 1 nitrogen atom and 3 hydrogen atoms arranged in a trigonal pyramidal structure. The valence electron diagram of the nitrogen atom has 3 unpaired electrons in the *p* orbital:



Each of the 3 hydrogen atoms contributes 1 electron from its 1*s* orbital. From the previous examples, you would expect the 3 unpaired electrons from the 2*p* orbitals of the nitrogen atom to overlap with the 1*s* orbital of each hydrogen atom, forming 3 covalent bonds that have a lower energy state than the individual atoms (**Figure 5**).

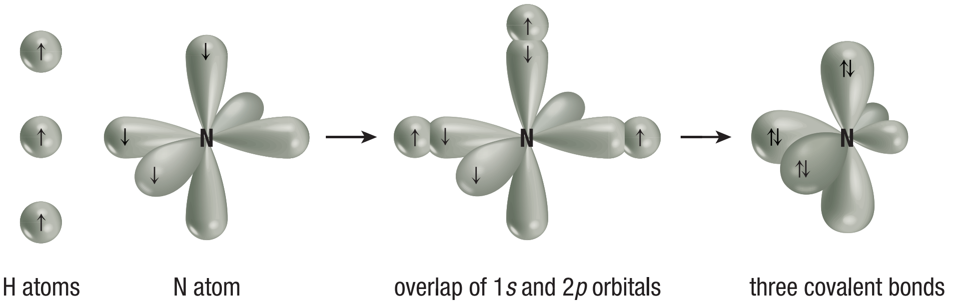
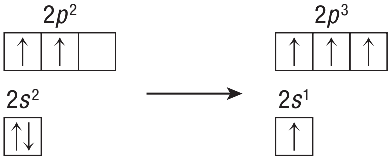


Figure 5 When the ammonia molecule forms, each 1*s* orbital in the hydrogen atom overlaps with the 2*p* orbital with an unpaired electron from the nitrogen atom, forming three covalent bonds. In the ammonia molecule, the bonding electrons have opposite spins, with a lower energy state than the individual atoms.

The final structure in Figure 5 suggests that the bond angles in ammonia are 90°. Yet, you know from the VSEPR theory that the geometry of ammonia is a trigonal pyramidal structure with bond angles of 107°. To account for this observed bond angle, valence bond theory must be expanded to include the concept of orbital hybridization.

Hybrid Orbitals

Suppose you were to use valence bond theory to describe the bonding in a molecule of methane, CH_4. Each hydrogen atom contributes one 1*s* electron. When you place the 4 valence electrons for carbon, 1 of the 2 electrons in the 2*s* orbital must go into the empty 2*p* orbital.



Since the *s* and *p* orbitals have different shapes, they should form two different types of chemical bonds with the 4 hydrogen atoms. One bond type would result from 2 overlapping *s* orbitals, and the other would result from overlapping an *s* and a *p* orbital. However, the C−H bonds in methane are all of equal length and are arranged symmetrically in a tetrahedral geometry. This is one of the problems with the valence bond theory. How does it account for the 4 equivalent chemical bonds in methane?

The chemical bonds in molecules such as methane can be explained by the concept of hybrid orbitals. **Hybrid orbitals** form by combining orbitals with different shapes. For the carbon atom, you start with 1 *s* orbital and 3 *p* orbitals, and finish with four hybrid sp^3 orbitals. The process of forming hybrid orbitals is called **hybridization**. **Figure 6** illustrates how sp^3 hybrid orbitals form.

hybrid orbital an orbital that forms from the combination of at least 2 different orbitals

hybridization the process of forming hybrid orbitals from the combination of at least 2 different orbitals

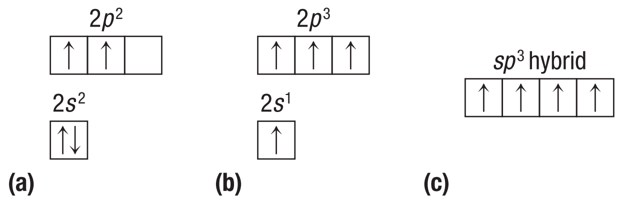


Figure 6 The electrons in a hybrid orbital. (a) A carbon atom with 4 valence electrons has two paired 2*s* electrons and two unpaired 2*p* electrons. (b) To create equal orbitals, a paired electron from the *s* orbital is promoted to the unfilled 2*p* orbital. (c) The *s* and *p* orbitals then merge to form a set of equivalent hybrid sp^3 orbitals, each with 1 unpaired electron. Since four orbitals are combined, four orbitals are produced.

Each of the hybrid sp^3 orbitals is identical to the other. Since each hybrid orbital contains an unpaired electron, these sp^3 orbitals can overlap with the 1*s* orbital of a hydrogen atom to form the 4 equal covalent bonds in a methane molecule. The sp^3 hybrid orbitals have a large lobe and a small lobe pointing in opposite directions (**Figure 7**). The large lobes of the four sp^3 orbitals have the tetrahedral arrangement predicted for the bonding electron pairs in the VSEPR description of the methane molecule.

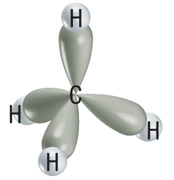
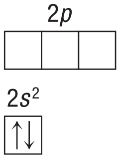


Figure 7 Each bond in a methane molecule arises from the formation of a hybrid sp^3 orbital in the carbon atom. This creates 4 hybrid orbitals with similar properties and results in equivalent chemical bonds with each hydrogen atom.

There are many other examples where hybridization is needed to account for the observed properties of chemical bonds. One example is the beryllium hydride molecule, BeH_2. Each hydrogen atom contributes a single 1*s* electron to each chemical bond. The valence electron diagram for a beryllium atom is



Notice that there are no half-empty orbitals available for bonding. For a chemical bond to form, the *s* orbital and one of the *p* orbitals hybridize after a 2*s* electron is promoted to a 2*p* orbital, leaving 2 empty 2*p* orbitals.

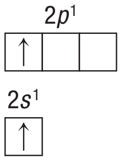
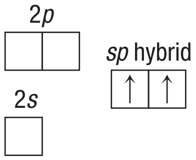
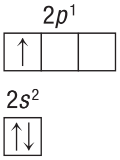


Figure 8 Beryllium hydride is a linear molecule.

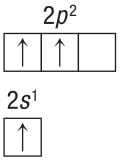
The result is the formation of 2 equivalent hybrid *sp* orbitals. The *sp* orbitals have a linear arrangement, so a beryllium molecule has a linear structure (**Figure 8**).



Now consider the borane molecule, BH_3. Using the VSEPR theory, you can predict that this molecule has a trigonal planar structure and that each hydrogen atom contributes one 1*s* electron to each chemical bond. The valence electron diagram for the boron atom is



An electron is promoted from the 2*s* orbital to a vacant 2*p* orbital. There are now three unpaired electrons, one in the *s* orbital and two in two different *p* orbitals.



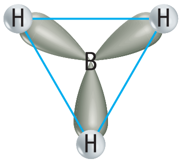


Figure 9 Borane, BH_3, is a trigonal planar molecule. The hybridized sp^2 orbital results in three equivalent chemical bonds to the hydrogen atoms.

These orbitals combine to form the hybrid sp^2 orbitals. The sp^2 orbitals have a trigonal planar arrangement (**Figure 9**).

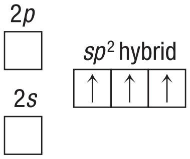
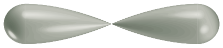
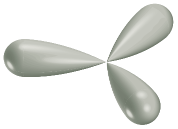
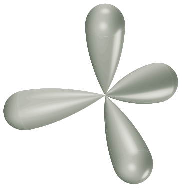


Table 1 shows common hybrid orbitals and the resulting molecular structures that form from these orbitals.

Table 1 Types of Hybrid Orbitals

Number of valence electrons	Initial orbital	Hybrid orbital	Geometry	Example	Orbital diagram
2	*s*	*sp*	linear	BeH_2	
3	2*s*, 2*p*	sp^2	trigonal planar	BH_3	
4	2*s*, 2*p*	sp^3	tetrahedral	CH_4	

Double and Triple Covalent Bonds

The valence bond theory creates a second dilemma. How do you describe the chemical bonding in molecules with multiple bonds? In the molecules you have examined so far, bonding occurs between unpaired electrons from *s* orbitals (H–H), *p* orbitals (H–Cl), and the *sp*, sp^2, and sp^3 hybrid orbitals (beryllium hydride, borane, and methane, respectively). These orbitals directly overlap with each other when one end of an orbital meets the other orbital. The lobes of each orbital point toward each other. This direct overlap results in the formation of a **sigma (σ) bond**, which is a bond that is formed when *s* orbitals, *p* orbitals, or hybrid orbitals overlap (**Figure 10**).

sigma (σ) bond a bond that is formed when the lobes of 2 orbitals directly overlap end to end

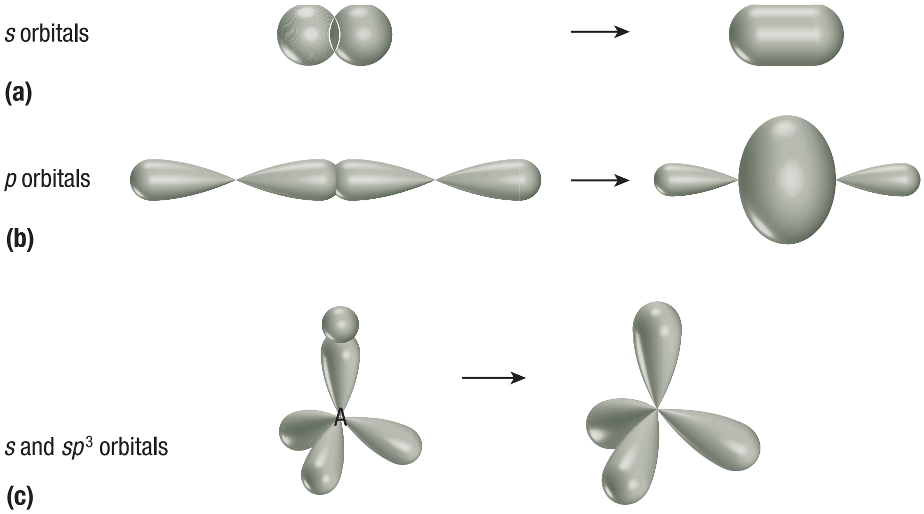


Figure 10 The formation of sigma bonds. (a) A sigma bond forms from the overlap of two *s* orbitals. (b) A sigma bond can also form when two *p* orbitals overlap, or (c) when *sp*, sp^2, or sp^3 orbitals overlap with other orbitals.

However, sigma bonds do not explain how multiple bonds form. Therefore, a different type of bond must exist in molecules with double and triple bonds. In a multiple bond, orbitals that are parallel to each other overlap, which results in the formation of **pi (π) bonds**. The formation of pi bonds between two *p* orbitals is illustrated in **Figure 11**.

pi (π) bond a bond that is formed when the sides of the lobes of 2 orbitals overlap

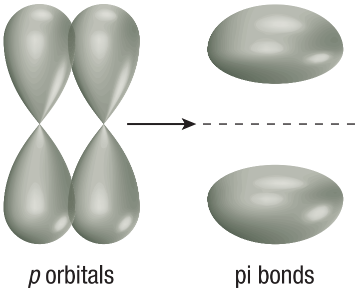


Figure 11 The formation of pi bonds. Two *p* orbitals form bonds when the sides of the orbitals overlap. The result is that the electron density is above and below the bond axis.

To investigate the formation of pi bonds, consider the double bonds of ethene, C_2H_4. From the Lewis structure of ethene (**Figure 12(a)**, page 236), you can see that each carbon atom forms bonds with 3 other atoms. These bonds are sigma bonds that directly overlap with each other. The carbon atom undergoes partial hybridization to form three sp^2 orbitals. The remaining *p* orbital is left with 1 electron in it (**Figure 12(b)**).

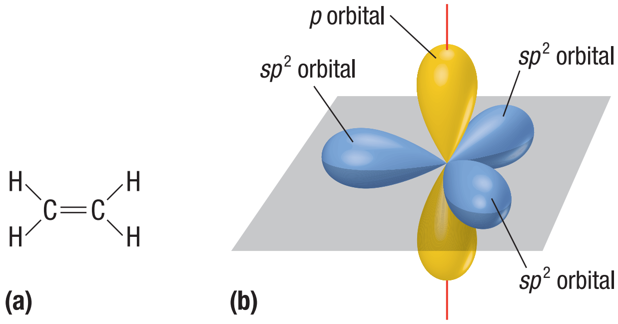


Figure 12 (a) Structural formula of ethene, C_2H_4. (b) In the ethene molecule, an *s* and a *p* orbital hybridize to form three sp^2 orbitals. A single *p* orbital remains perpendicular to the plane of the hybrid orbitals.

In ethene, both carbon atoms are partially hybridized in this way. The carbon atoms can each form 3 sigma bonds using the sp^2 orbitals: 1 sigma bond forms with the second carbon atom and 2 sigma bonds form with hydrogen atoms (**Figure 13(a)**). This arrangement leaves each carbon atom with 1 additional unpaired electron in a *p* orbital. These unpaired electrons form the pi bond. The pi bond forms in the region above and below the sigma bonds (**Figure 13(b)**). WEB LINK

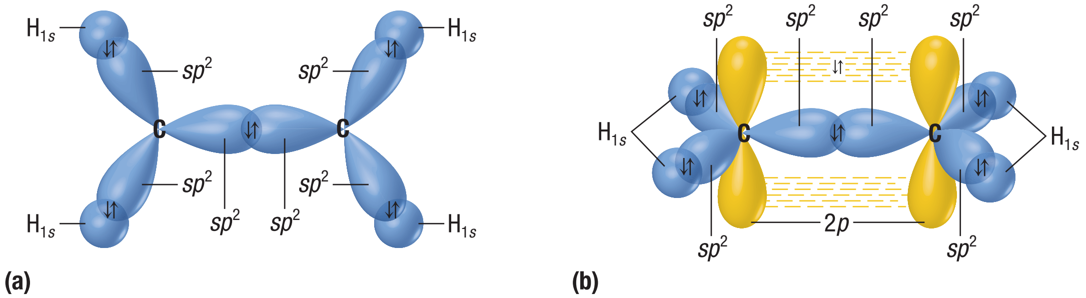


Figure 13 The carbon atoms in a molecule of C_2H_4 form hybrid sp^2 orbitals. (a) These orbitals result in sigma bonds between C–C and C–H. (b) The remaining electron from each carbon atom forms a pi bond, shown as dashed lines. The sides of the *p* orbitals of each carbon atom overlap.

A double bond always consists of 1 sigma bond and 1 pi bond. In the sigma bond between carbon atoms in ethene, the electron pair resides in the space *between* the atoms. In the pi bond between the carbon atoms, the electron pair occupies the space *above* and *below* the sigma bond. The electrons in a pi bond have opposite spins, just as in sigma bonds. Since there is an additional pair of electrons between atoms in the pi bond, a double bond is shorter in length than a single bond. In addition, a double bond is stronger and requires more energy to break than a single bond.

Pi bonds are also present in triple bonds. To illustrate triple bonds, consider the molecule ethyne, C_2H_2, commonly known as acetylene. The Lewis structure for this molecule is

$$H-C\equiv C-H$$

Since ethyne is a linear molecule, neither the sp^3 nor the sp^2 hybrid orbitals will describe the bonding in this molecule. As for double bonds, you have seen that all of the orbitals in a carbon atom do not necessarily form sp^3 hybrid orbitals. A partial hybridization is possible, in which 2 *sp* hybrid orbitals form and 2 remaining *p* orbitals each hold a single electron. In ethyne, both carbon atoms are partially hybridized in this manner (**Figure 14**).

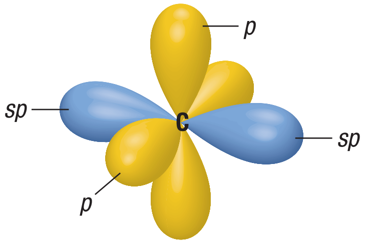


Figure 14 In an ethyne molecule, an *s* and a *p* orbital hybridize to form two *sp* hybrid orbitals (blue); two *p* orbitals remain (gold). The two *p* orbitals are 90° from each other.

The carbon atoms can each form 2 sigma bonds using these *sp* orbitals: 1 sigma bond forms with the second carbon atom, and 1 sigma bond forms with a hydrogen atom (**Figure 15(a)**). Each carbon atom is left with 2 additional unpaired electrons, each in a *p* orbital (**Figure 15(b)**). These unpaired electrons form pi bonds with the second carbon atom. One pi bond forms in the region above and below the sigma bonds. The second pi bond forms at a 90° angle from the first pi bond. Thus, a triple bond consists of 1 sigma bond and 2 pi bonds (**Figure 15(c)**).

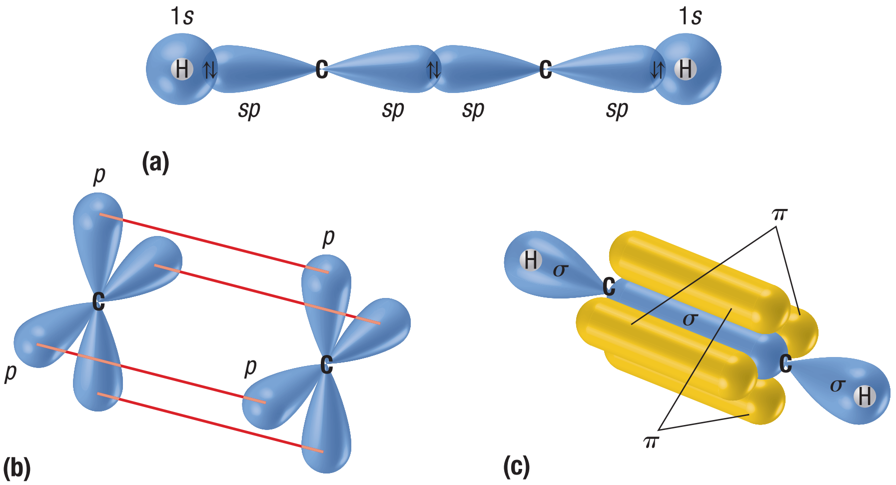


Figure 15 (a) The *sp* orbitals of the carbon atom in an ethyne molecule form sigma bonds with a hydrogen atom and the opposite carbon atom. (b) The *p* orbitals of a carbon atom form 2 pi bonds. These pi bonds reside 90° from each other. (c) The complete sigma and pi bonds in ethyne

Recall from Figure 1, page 230, that the benzene molecule has 3 double bonds. Based on what you have learned in this section, you now know that sigma and pi bonds create the double bonds. Sigma bonds form between the carbon and hydrogen atoms, and between the carbon atoms. Pi bonds form between the carbon atoms. As in ethene, the pi bonds occupy the space above and below the sigma bonds. However, in benzene there are 6 electrons in the pi bonds because there are 3 double bonds in the molecule. These electrons are distributed in a ring shape above or below the sigma bonds, anywhere within the ring. A computer-generated model of the molecule demonstrates the bonding and electron density in benzene (**Figure 16**).

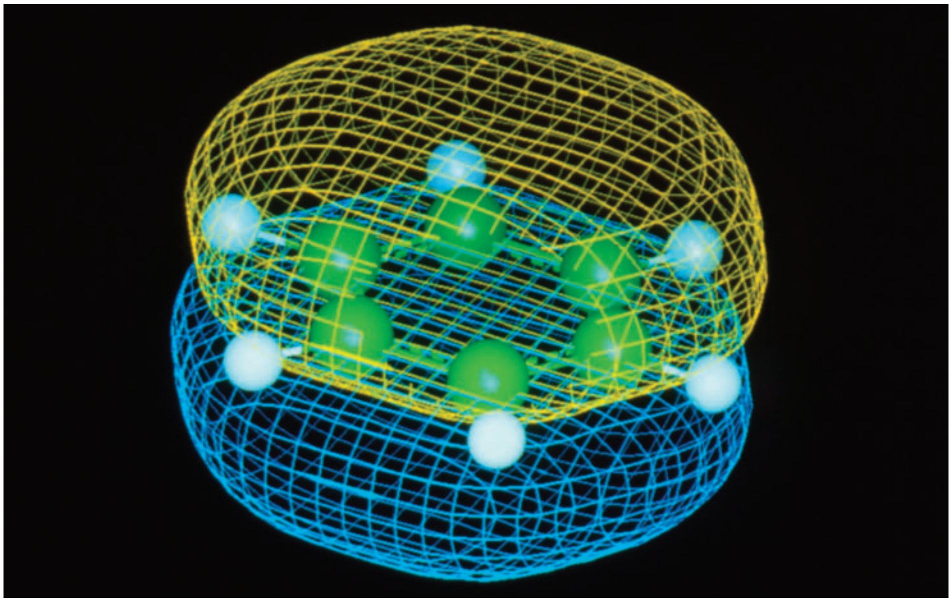


Figure 16 Representation of pi bonding in benzene. The pi bonds are shown as yellow and blue cages above and below the plane of the molecule. The cages represent delocalized bonding in the benzene molecule.

4.6 Review

Summary

- The valence bond theory predicts that a covalent bond forms when two atomic orbitals overlap and share electrons.
- Partially filled *s* and *p* orbitals can overlap to share electrons.
- Sometimes *s* and *p* orbitals hybridize, resulting in the creation of *sp*, sp^2, and sp^3 hybrid orbitals that bond with other atoms.
- When hybridization occurs, four sp^3, three sp^2, or two *sp* orbitals form. The sp^3 orbitals are tetrahedral, the sp^2 orbitals are trigonal planar, and the *sp* orbitals are linear.
- Single covalent bonds consist of sigma bonds, in which the end of one orbital lobe overlaps with another orbital lobe.
- A pi bond is the result of parallel orbital lobes overlapping with each other. Double and triple bonds consist of both sigma and pi bonds.
- A double bond has one sigma bond and one pi bond. A triple bond has one sigma bond and two pi bonds.

Questions

1. Determine the hybrid atomic orbitals that describe the bonding in a molecule of phosphine, PH_3. K/U
2. What is the difference between a pi bond and a sigma bond? K/U
3. Describe the bonding in the elemental oxygen molecule, O_2. Be sure to include terms such as "orbitals," "sigma bonds," and "pi bonds" in your description. K/U
4. (a) State the three-dimensional structure that results from *sp*, sp^2, and sp^3 hybrid orbitals.
   (b) Which of these hybrid orbitals can form multiple bonds? K/U
5. The atoms in a single bond can rotate about the central axis without breaking the sigma bond, yet the bonds in a double or triple bond break when the central axis is rotated. Why? K/U
6. Predict the hybridization of each atom, and describe the three-dimensional structure of the following molecules: K/U T/I
   (a) CO
   (b) H_2CO
   (c) SiF_4
7. Assume that each of the following atoms reacts with hydrogen: (i) boron; (ii) silicon; (iii) nitrogen; and (iv) chlorine. K/U T/I C
   (a) Write the electron configuration for each atom.
   (b) Draw the orbital diagrams, showing the valence electrons.
   (c) Determine whether any electron needs to be promoted. If so, draw a new orbital diagram showing the excited-state atom.
   (d) Hybridize the orbitals as needed. Draw the orbital diagrams, showing the hybrid orbitals.
   (e) How many half-empty orbitals does each atom have? How many orbitals are available for bonding?
   (f) State the orbital each molecule uses to form sigma bonds with hydrogen.
8. What is the hybridization of the central atom in each of the following molecules? K/U T/I
   (a) H_2S
   (b) CCl_4
   (c) NCl_3
   (d) CO_2
   (e) N_2
   (f) B_2F_4
9. In the benzene molecule, each carbon atom bonds to 2 carbon atoms and 1 hydrogen atom. K/U T/I
   (a) What types of hybrid orbitals are involved in these bonds?
   (b) What is the bond angle that you would expect in this molecule?
10. Do you agree with the following statement? If so, explain why. If not, revise the statement so that it is correct. "A triple bond forms from a pi bond and two sigma bonds. In the molecule HCN, the sp^3 hybrid orbital of carbon results in a tetrahedral shape." K/U T/I
11. Propadiene, C_3H_4, is a highly unstable molecule consisting of a linear backbone of linear carbon atoms. K/U T/I C
    (a) Draw the Lewis structure of propadiene.
    (b) What type of hybrid orbitals are involved on the end carbon atoms? Justify your answer.
    (c) Predict the shape about the end carbon atoms.

Intermolecular Forces

4.7

Some of the largest trees in the world are giant sequoias (**Figure 1**). Individuals of this species can grow as tall as a 30-storey building. Imagine how difficult it would be to carry a bucket of water to the top of a 30-storey building. Yet, these large trees regularly transport water from their roots up through their large trunks to their branches and leaves. The enormous sequoias require large amounts of water to flow up to an extraordinary height. How do they accomplish this task? They take advantage of the bonds between molecules. WEB LINK

Figure 1 This sequoia is officially the largest giant sequoia. It is 82.9 m tall.

You have learned that atoms can form stable units (molecules) by sharing electrons with other atoms. The bonds connecting the atoms in a molecule are called **intramolecular bonds**. The prefix *intra*- means "within." Covalent bonds are intramolecular bonds. In addition, molecules can be attracted to one another by forces of attraction called intermolecular forces. The prefix *inter*- means "between." **Intermolecular forces** are forces between molecules, not within molecules. These forces can cause large numbers of molecules to aggregate or interact.

In 1873, Johannes van der Waals suggested that observed deviations from the ideal gas law arose because molecules of a gas that has a small but definite volume exert forces on each other. We now know that the forces described by van der Waals are a combination of many types of intermolecular forces, including dipole–dipole forces and London dispersion forces. (You will learn about London dispersion forces later in this section.) These types of intermolecular forces are simply referred to as **van der Waals forces**. Later, the concept of hydrogen bonding was created to explain anomalous (unexpected) properties of certain liquids and solids. In general, intermolecular forces are considerably weaker than the covalent bonds between the atoms in a molecule.

intramolecular bond the chemical bond within a molecule

intermolecular force a force that causes one molecule to interact with another molecule; occurs between molecules

van der Waals forces many types of intermolecular forces, including dipole–dipole forces, London dispersion forces, and hydrogen bonding

To understand the effects of intermolecular forces, think about what happens when a volume of water changes from solid to liquid to gas. The water molecules do not change. The intramolecular bonds between the hydrogen atoms and the oxygen atom do not break or rearrange. Regardless of whether a volume of water is in the solid, liquid, or gas state, each of its molecules always has 1 oxygen atom covalently bonded to 2 hydrogen atoms. Changes in state are due to changes in the forces of attraction *between* the molecules, not changes in the forces that hold atoms together within the molecules.

In ice, water molecules do not have much ability to move, although they can vibrate. If you supply energy to ice through heating, the motions of the molecules increase. The water molecules eventually absorb enough energy to break away from the adjacent molecules and the ice melts. As you supply more thermal energy to the liquid water, the molecules eventually pass into the gaseous state. The added energy allows some water molecules to overcome their attraction to other water molecules, so these water molecules escape into the gas phase. The water has boiled.

This section focuses primarily on the structural and bonding characteristics of substances in the liquid phase. Section 4.8 will focus on the characteristics of substances in the solid phase.

Dipole–Dipole Forces and Hydrogen Bonding

As you learned in Section 4.3, in an electric field molecules with polar bonds often behave as if they have a centre of positive charge and a centre of negative charge, or dipole. Polar molecules attract each other electrostatically by lining up so that the positive and negative ends are close to each other, causing intermolecular forces called **dipole–dipole forces**. In a liquid, where many molecules are close to each other, dipoles attract each other when opposite charges are aligned and repel one another when similar charges face each other. At any point in time, the dipoles find the best compromise between the attractive and repulsive forces.

dipole–dipole force the intermolecular force that is caused when the dipoles of polar molecules position their positive and negative ends near each other

Figure 2(a) illustrates the alignment of polar molecules due to dipole–dipole forces, and **Figure 2(b)** illustrates the attractive and repulsive action of dipole–dipole forces in a liquid. Dipole–dipole forces are only about 1 % as strong as covalent or ionic bonds. They weaken rapidly as the distance between the dipoles increases. In substances at low pressures in the gas phase, where molecules are far apart from each other, these forces are relatively unimportant.

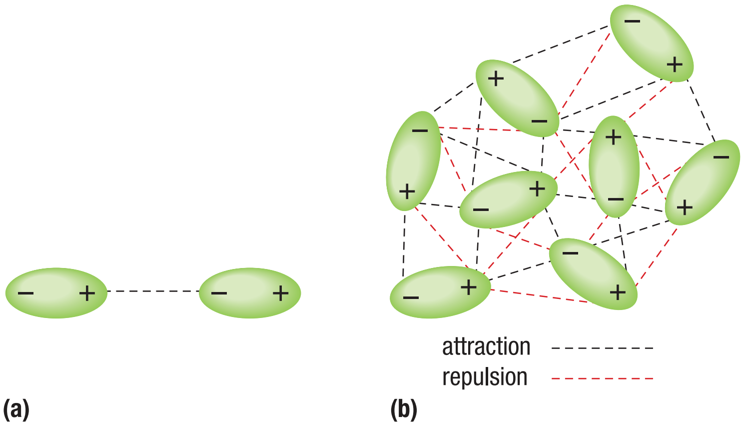


Figure 2 (a) The electrostatic interaction of two polar molecules (b) The interaction of many dipoles in a liquid

hydrogen bond the strong dipole–dipole force that occurs when a hydrogen atom bonded to a highly electronegative atom (oxygen, nitrogen, or fluorine) is attracted to a partially negative atom on a nearby molecule

There are unusually strong dipole–dipole forces among molecules in which a hydrogen atom is bonded to form a covalent bond with a highly electronegative atom—nitrogen, oxygen, or fluorine. Two factors account for the strengths of these dipole–dipole forces: the great polarity of the covalent bond and the unusual closeness with which the dipoles on these molecules can approach each other. Since dipole–dipole attractions of this type are so strong, they have a special name: **hydrogen bonds**. **Figure 3** shows hydrogen bonding among water molecules. The hydrogen bonding occurs between the partially positive hydrogen atoms and the partially negative oxygen atoms.

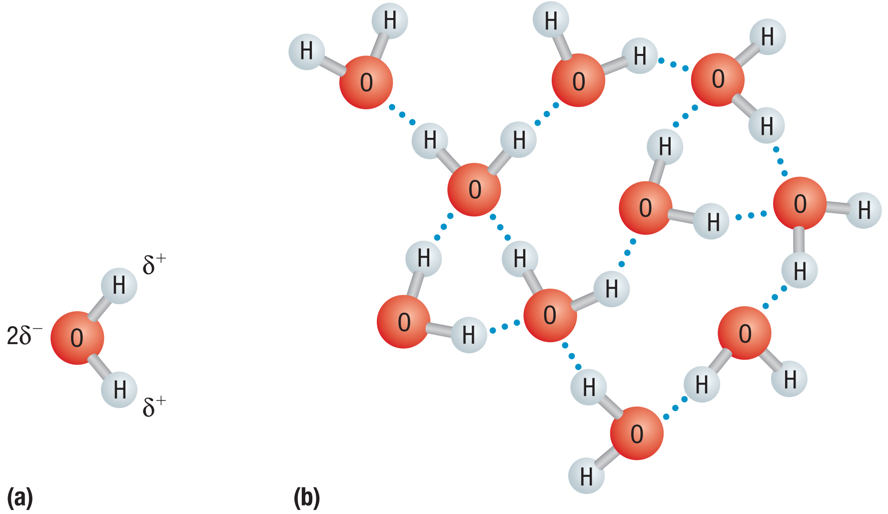


Figure 3 (a) The partial positive and negative dipoles in a water molecule (b) Hydrogen bonding (shown as blue dotted lines) among water molecules. The hydrogen atoms in the water molecules have lost most of their electrons to the more electronegative oxygen atom, so they can be approached more closely by the electron-rich oxygen atoms of adjacent water molecules. Even small changes in distances at the atomic level can result in dramatically larger electrostatic forces.

Investigation **4.7.1**

Hydrogen Bonding (page 257)
Now that you have learned how hydrogen bonds form, perform Investigation 4.7.1 to determine the effect of hydrogen bonds on chemical reactions.

Hydrogen bonding has a very important effect on a substance's physical properties. For example, **Figure 4** shows the boiling points of covalent hydrides of elements in Groups 14, 15, 16, and 17 of the periodic table as a function of the period in which the non-hydrogen atom is found. The tetrahedral hydrides of Group 14 (blue line) show a steady increase in boiling point as the molar mass increases. This result is expected. None of these hydrides have molecular dipoles because each has 4 hydrogen atoms distributed symmetrically about the central atom: they are all non-polar molecules. Every molecule with a central atom from Groups 15, 16, or 17 possesses a molecular dipole, but the lightest members in each group, NH_3, HF, and H_2O, have unexpectedly high boiling points. High boiling points mean that these molecules attract other molecules of the same type with forces that are greater than expected. So, it takes more energy than expected to convert these molecules from a liquid state to a gaseous state. Why do these 3 molecules have such highly attractive forces?

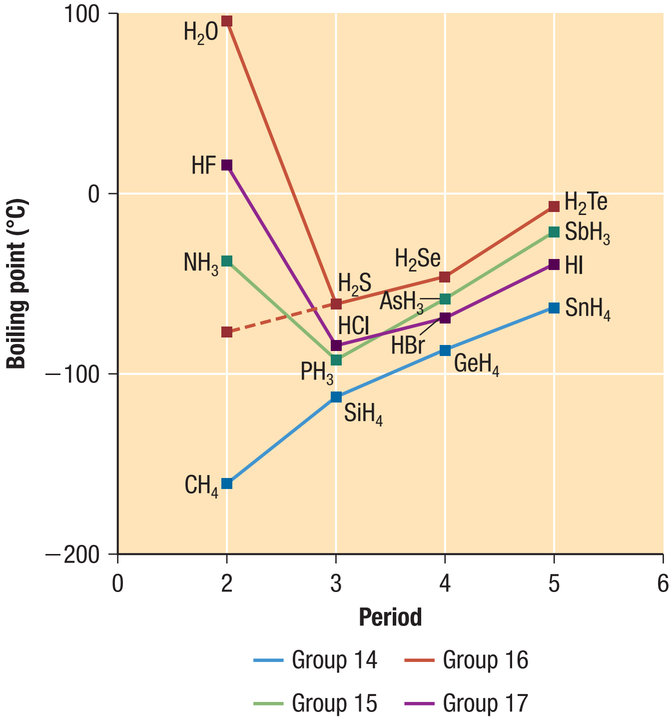


Figure 4 The boiling points of the covalent hydrides of the elements in Groups 14, 15, 16, and 17. The point connected by the dashed line shows the expected boiling point of water if it had no hydrogen bonds.

The especially large dipole–dipole interactions generated by these 3 molecules can be attributed to the large electronegativities of the nitrogen, oxygen, and fluorine atoms they contain. The electronegativities are so large that the hydrogen atom practically loses its electron altogether. Consequently, the negative ends of neighbouring molecules can get very close to the positive hydrogen nucleus (a proton). This results in an unusually large dipole–dipole force of attraction, a hydrogen bond.

Nitrogen, oxygen, and fluorine are the only 3 elements in the periodic table whose atoms have this effect. Atoms of other elements either have a smaller electronegativity or are too large to move inside hydrogen's atomic radius. For example, a chlorine atom has the same electronegativity as a nitrogen atom, but it is too large to get close enough to a hydrogen nucleus on a neighbouring molecule. The unusually strong dipole–dipole forces associated with hydrogen atoms bonded to atoms of nitrogen, oxygen, or fluorine are therefore given the special name of hydrogen bonds. Molecules capable of hydrogen bonding remain in the liquid state even at high temperatures—hence their very high boiling points.

Hydrogen bonds must not be confused with covalent or other intramolecular bonds. As strong and important as hydrogen bonds are, they are still 10 to 20 times weaker than typical covalent bonds. They are, however, central to many important biological systems, such as organic molecules (molecules with a carbon chain backbone). For example, the alcohols methanol, CH_3OH, and ethanol, CH_3CH_2OH, have much higher boiling points than you would expect from their molar masses. The polar O−H bonds in these molecules form hydrogen bonds that result in high boiling points.

UNIT TASK **BOOKMARK**

As you work on the Unit Task on page 268, consider how the groups in your new periodic table will change. How will the physical properties of the elements change?

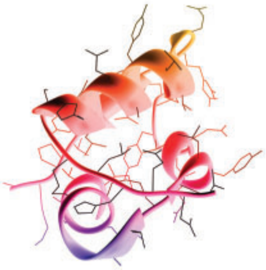


Figure 5 The three-dimensional structure of the insulin protein molecule is in part due to hydrogen bonding between parts of the molecule.

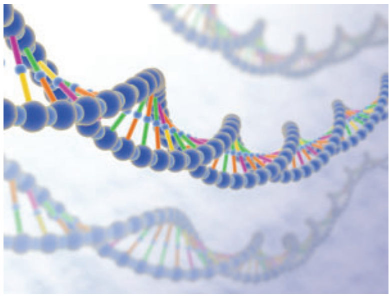


Figure 6 The 2 strands of DNA resemble a twisted ladder. The rungs of the ladder contain hydrogen bonds that form between the bases in each DNA strand.

London dispersion forces the intermolecular forces that exist in non-polar molecules; they increase as the molecular mass increases

Life as we know it would be impossible without hydrogen bonds. Hydrogen bonding is necessary for the proper structure and function of many biological molecules. Proteins are made of chains of different amino acids joined through a covalent amide bond. An amide bond joins the nitrogen atom of an N−H group of one amino acid to the carbon atom of a C=O group of an adjacent amino acid. Both of these functional groups can participate in hydrogen bonding with neighbouring amino acids in other parts of the chain and are partially responsible for the three-dimensional shapes of protein molecules, such as the insulin molecule represented in **Figure 5**. Hydrogen bonds are important to the function of DNA, deoxyribonucleic acid. The three-dimensional structure of DNA is a double helix made of 2 complementary strands held together by hydrogen bonds (**Figure 6**).

London Dispersion Forces

Even molecules without dipoles can exert forces on each other. All substances—even the noble gases—exist in liquid and solid states under certain conditions because of intermolecular forces called **London dispersion forces**. These forces are named after Fritz London, the chemist who first suggested the idea of these forces in non-polar molecules. While studying the boiling points of polar substances, London was not able to identify a specific pattern based on molecular mass and dipole–dipole forces. He hypothesized that there must be an additional force of attraction. He proposed that forces of attraction and/or repulsion exist between any 2 molecules.

To understand the origin of these forces, consider a pair of noble gas atoms. Although you usually assume that the electrons of an atom are uniformly distributed around the nucleus, this is not true at every instant. As the electrons move around the nucleus, a momentary non-symmetrical electron distribution can develop. This effect produces a temporary dipole-like arrangement of charge. The formation of this temporary dipole can affect the electron distribution of a neighbouring atom. An instantaneous dipole that occurs spontaneously in one atom can induce a similar, and opposite, dipole in a neighbouring atom (**Figure 7**).

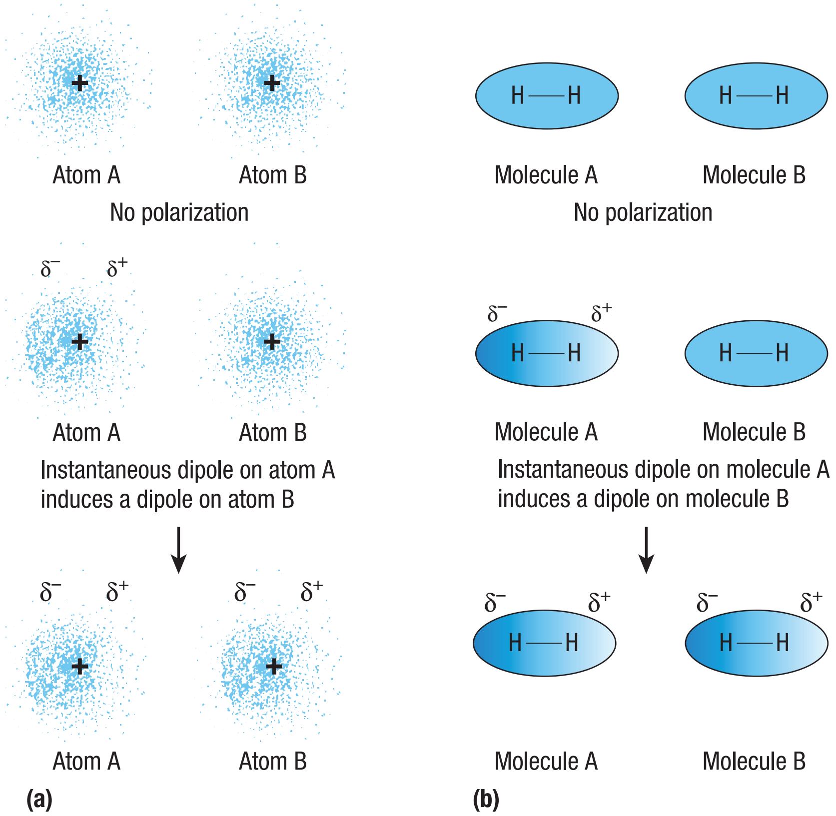


Figure 7 (a) An instantaneous dipole can occur in atom A. This dipole creates an induced dipole on neighbouring atom B. (b) Non-polar molecules such as elemental hydrogen can also develop instantaneous and induced dipoles.

The induced dipole results in an attractive force that is relatively weak and does not last long, but can be very significant for large atoms, for molecules with many atoms, or at low temperatures. For example, when atomic motion slows down sufficiently (in cold temperatures), the attractions due to London dispersion forces can become strong enough to form a solid. These attractions explain why the noble gas elements freeze (**Table 1**).

Table 1 The Freezing Points of the Group 8A Elements

Element	Freezing point (°C)
helium	−269.7
neon	−248.6
argon	−189.4
krypton	−157.3
xenon	−111.9

Note from Table 1 that the freezing point rises as you go down the group. This is because the number of electrons increases as the atomic number increases. Since outer electrons are less tightly held by the nucleus, atoms with more electrons are more easily deformed. This phenomenon is called **polarizability**. The greater an atom's polarizability, the easier it is to deform its charge distribution. Thus, large atoms with many electrons exhibit a higher polarizability than small atoms. The significance of London dispersion forces also increases greatly as the size of the atom increases or as the number of atoms in a molecule increases.

polarizability the ability of a substance to form a dipolar charge distribution

Non-polar molecules such as hydrogen, carbon dioxide, methane, carbon tetrachloride, and alkanes also follow this trend (see Figure 7(b)). Even though none of these molecules has a permanent dipole, they can still attract other molecules through London dispersion forces. All substances experience London dispersion forces. However, these forces are not always apparent because dipole–dipole interactions and hydrogen bonds are much stronger.

Connecting Intermolecular Forces and Physical Properties

Consider some of the physical properties of the hydrogen compounds that form from the Group 14 atoms (C, Si, Ge, and Sn). Based on what you have learned about three-dimensional structure and molecular polarity, you know that these molecules are non-polar tetrahedral molecules. Thus, London dispersion forces are the dominant intermolecular forces present in these molecules. As you go down a group in the periodic table, you would expect the London dispersion forces to increase, so larger molecules should have a greater tendency to stay together. Larger molecules should also have higher melting points and boiling points. The boiling point data in **Table 2** shows that this is exactly what happens.

Table 2 Boiling Points of Group 4A Hydrogen Compounds

Compound	Boiling point (°C)
CH_4	−164
SiH_4	−112
GeH_4	−89
SnH_4	−52

Numerous physical and chemical properties depend on the nature of intermolecular forces. Hydrogen bonds are the strongest intermolecular forces, and dipole–dipole forces are stronger than London dispersion forces. Therefore, molecules with hydrogen bonds have a greater tendency to stick together than molecules with weaker dipole–dipole forces. Similarly, molecules with dipole–dipole forces have a greater attraction to each other than molecules attracted by London dispersion forces only. So, molecules with dipole–dipole forces and/or hydrogen bonds have higher melting points, boiling points, surface tension, and viscosity than similar-sized molecules with only London dispersion forces.

Regardless of the strength of the dipole, a positive dipole always attracts a negative dipole. Thus, 2 different but polar molecules will tend to attract each other. For example, many ionic compounds interact favourably with water and readily dissolve in it. Since water forms hydrogen bonds, other substances that can also form hydrogen bonds are even more soluble in water than molecules with just dipoles. Some important physical properties that strongly depend on intermolecular forces include melting point, boiling point, viscosity, solubility, binding affinity, miscibility, surface tension, adhesion, hydrophobicity, heat of vaporization, heat of fusion, elasticity, tensile strength, and capacitance.

Investigation **4.7.2**

Boiling Points and Intermolecular Forces (page 258)

Now that you have learned how to predict the properties of a substance based on its intermolecular forces, perform Investigation 4.7.2 to compare your predictions to known properties of substances.

Tutorial 1 Intermolecular Forces and Physical Properties

In this Tutorial, you will predict physical properties of different substances from the types of intermolecular forces among the molecules.

Sample Problem 1: Predicting Boiling Points

Predict which of the following molecules has the highest boiling point: H_2, I_2, F_2, Br_2, or Cl_2.

Solution

Step 1. Determine the intermolecular force(s) for the set of molecules.

Since these molecules are all molecular elements, each molecule is non-polar. The dominant intermolecular force is therefore the London dispersion force.

Step 2. Determine the molecular mass of each molecule.

See **Table 3.**

Table 3 Molecules and Their Molecular Masses

Molecule	Molecular mass (u)
H_2	2.0
F_2	38.0
Cl_2	70.9
Br_2	159.8
I_2	253.8

Step 3. Identify the molecule with the largest molecular mass.

From Table 3, this molecule is I_2. Since larger molecules have greater London dispersion forces, you can predict that the I_2 molecule has the highest boiling point.

Statement: The I_2 molecule is predicted to have the highest boiling point.

Table 4 lists the boiling points for the molecules in this Sample Problem. I_2 has the highest boiling point; therefore, the Statement is correct.

Table 4 Boiling Points of Several Molecules

Molecule	Boiling point (°C)
H_2	−253
F_2	−188
Cl_2	−34
Br_2	59
I_2	184

Practice

1. Predict which of the following molecules has the highest boiling point: CH_3OH, CH_3CH_2OH, or $CH_3CH_2CH_2OH$. Explain your reasoning. T/I C [ans: $CH_3CH_2CH_2OH$]
2. Of the 2 molecules $CH_3CH_2CH_2CH_2NH_2$ and Cl_2, which should have a lower boiling point? Why? T/I C [ans: Cl_2]

Physical Properties of Liquids

Liquids and liquid solutions are vital to our lives. Water is our most important liquid. Besides being essential to life, water provides a medium for food preparation, transportation, cooling machines, recreation, cleaning, and countless other uses.

Liquids demonstrate many characteristics that help us understand their nature. A liquid is not as compressible as a gas, but liquids have higher densities than gases. Many of the properties of liquids give us direct information about the forces that exist between their entities (molecules, atoms, or ions). For example, when you pour a liquid onto a solid surface, it tends to bead as droplets. This effect is due to the intermolecular forces in the liquid. Although entities in the centre of a drop of liquid are completely surrounded by other entities, those at the surface experience attractions only from the side and below (**Figure 8**). This uneven pull on the surface entities draws them into the body of the liquid. The energy of the system is lowest only if the number of entities at the surface is as low as it can be; that is, if the surface area is minimized. The result is a droplet of liquid with a shape that has the minimum surface area—a sphere.

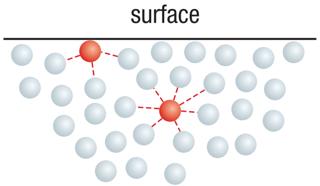


Figure 8 The outer entities of liquid attract entities in the interior. The entities at the surface only interact with entities below and beside them. Remember that the entities in a liquid are in constant motion.

To increase a liquid's surface area, entities must move from the interior of the liquid, where there are many attractions, to the surface, where there are fewer attractions. This movement raises the energy, and the liquid resists. The resistance of a liquid to increase its surface area is the **surface tension** of the liquid. As you would expect, liquids with relatively large intermolecular forces, such as those with polar molecules, have relatively high surface tensions.

surface tension the resistance of a liquid to increase its surface area

Polar liquids also exhibit **capillary action**—the rising of a liquid in a narrow tube. Two types of forces are responsible for capillary action: cohesive forces and adhesive forces. Cohesive forces are intermolecular forces among the entities of the liquid; adhesive forces are the forces between the liquid entities and their container. You have seen examples of cohesion in polar molecules. Adhesive forces come into play when a polar liquid is placed in a container also made from a polar substance. For example, glass contains many oxygen atoms with partial negative charges that attract the positive end of a polar molecule such as water. This force makes the water creep up the walls of a glass tube. Adhesive forces tend to increase the surface area of the water, while cohesive forces try to minimize the surface area. Water has strong cohesive (intermolecular) forces as well as strong adhesive forces toward the glass. The result is that water "pulls itself" up a glass capillary tube (a tube with a small diameter). The height to which the water travels is where the force of gravity on the mass of the water balances the water's attraction to the glass surface. CAREER LINK

capillary action the spontaneous rising of a liquid in a narrow tube

The meniscus that water forms in a narrow tube has a concave shape (**Figure 9(a)**). This shape arises because the adhesive forces among water molecules and glass molecules are stronger than the cohesive forces among the water molecules. On the other hand, a non-polar liquid such as mercury shows a convex meniscus (**Figure 9(b)**). This behaviour is characteristic of a liquid in which the cohesive forces among entities of the liquid are stronger than the adhesive forces among the liquid and glass molecules.

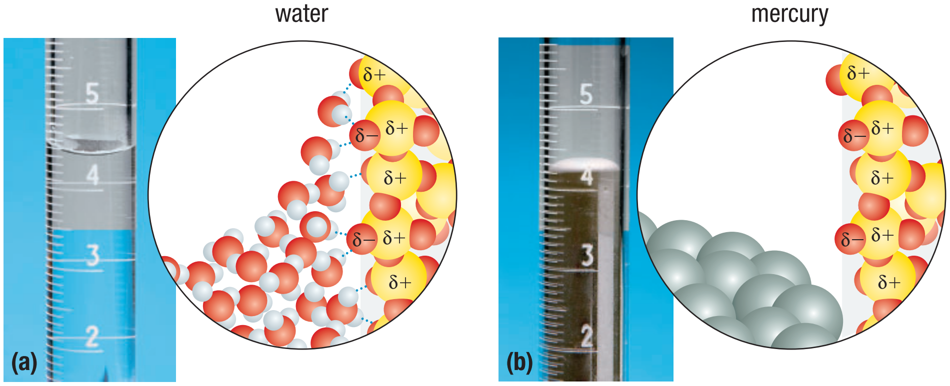
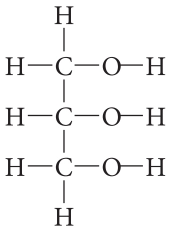


Figure 9 (a) Water molecules have strong adhesive forces toward glass molecules, and form a concave meniscus. (b) Mercury atoms have stronger cohesive than adhesive forces, resulting in a convex meniscus.

viscosity the measure of a liquid's resistance to flow

Another property of liquids that is strongly dependent on intermolecular forces is **viscosity**, the measure of a liquid's resistance to flow. Liquids with large intermolecular forces are highly viscous. For example, glycerol, $C_3H_8O_3$, has the structure



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H-C-O-H} \\ | \\ \mathrm{H-C-O-H} \\ | \\ \mathrm{H-C-O-H} \\ | \\ \mathrm{H} \end{array}$$

Glycerol has an unexpectedly high viscosity—over 1000 times that of water—due to its ability to form multiple hydrogen bonds with its O–H groups (**Figure 10**).

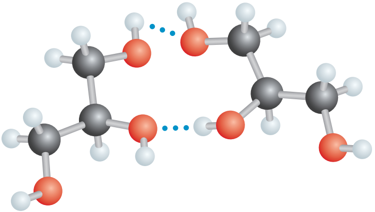


Figure 10 The hydrogen bonding in glycerol gives it a high viscosity.

Longer molecules are usually more viscous than smaller, shorter molecules because long molecules can become tangled with each other. For example, gasoline, with an average length of 8 carbons, is a non-viscous liquid. Yet the hydrocarbon chains in grease, a viscous group of substances, are 20 to 25 carbons long.

How do intermolecular forces explain the transport of water in giant sequoia trees? All plants use very thin tubes called xylem tubes to transport water from the ground to their leaves. In this process, the plant exploits both the surface tension and the capillary action of water. As water evaporates in the leaves, millions of menisci are formed in the tiny vascular bundles of the xylem tubes. As the surface tension of water works to reduce the surface area of these menisci, water molecules interconnected by hydrogen bonds pull each other up the full length of the plant by capillary action, even as high as the upper branches of a giant sequoia.

4.7 Review

Summary

- Intermolecular forces occur between, not within, molecules.
- The attraction between polar molecules is from electrostatic dipole–dipole forces. These forces attract oppositely charged and repel like charged ends of nearby molecules.
- Molecules in which a hydrogen atom is covalently bonded to nitrogen, oxygen, or fluorine form hydrogen bonds, which are unusually strong dipole–dipole interactions.
- Intermolecular forces caused by inducing temporary dipoles in atoms and molecules are called London dispersion forces. All molecules can produce London dispersion forces, but these forces are weak and tend to be important in interactions between non-polar molecules. London dispersion forces typically increase as a molecule's mass and size increase.
- Molecules that have stronger intermolecular forces have higher melting points, boiling points, viscosity, and surface tension than molecules with weaker intermolecular forces.

Questions

1. From the following groups, identify the substance that has the listed property. Explain your answer. K/U
   (a) highest boiling point: HBr, Kr, Cl_2
   (b) highest freezing point: H_2O, NaCl, HBr
   (c) lowest vapour pressure at 25 °C: Cl_2, Br_2, I_2
   (d) lowest freezing point: N_2, CO, CO_2
   (e) lowest boiling point: CH_4, CH_3CH_3, $CH_3CH_2CH_3$
   (f) highest boiling point: HF, HCl, HBr
2. From the following groups, identify the substance that has the listed property. Explain your answer. K/U
   (a) highest boiling point: CCl_4, CF_4, CBr_4
   (b) lowest freezing point: LiF, F_2, HCl
   (c) lowest vapour pressure at 25 °C: CH_3OCH_3, CH_3CH_2OH, $CH_3CH_2CH_3$
   (d) greatest viscosity: HF, H_2O_2
   (e) greatest heat of vaporization: H_2CO, CH_3CH_3, CH_4
3. (a) Why does ammonia have a very high solubility in water?
   (b) Draw a diagram of water interacting with ammonia molecules using Lewis structures. K/U C
4. Predict which substance in each of the following pairs has stronger intermolecular forces, and explain your reasoning: K/U T/I C
   (a) CO_2 or OCS
   (b) SeO_2 or SO_2
   (c) $CH_3CH_2CH_2NH_2$ or $H_2NCH_2CH_2NH_2$
   (d) CH_3CH_3 or H_2CO
   (e) CH_3OH or H_2CO
5. Consider the compounds Cl_2, HCl, F_2, NaF, and HF. Which compound has a boiling point closest to that of argon? Explain your reasoning. K/U T/I
6. The following compounds have boiling points (in no particular order) of −42.1 °C, −23 °C, and 78.5 °C. Match the boiling points to the correct compounds, and give reasons for your answer. K/U T/I
   (a) ethanol, CH_3CH_2OH
   (b) dimethyl ether, CH_3OCH_3
   (c) propane, $CH_3CH_2CH_3$
7. Molecular compounds can have London dispersion forces, dipole–dipole forces, and hydrogen bonding. Identify all the intermolecular forces present in each of the following compounds: K/U T/I
   (a) alcohols (for example, CH_3OH)
   (b) amines (for example, CH_3NH_2)
   (c) hydrocarbons (for example, CH_3CH_3)
   (d) carboxylic acids (for example, CH_3COOH)
   (e) ethers (for example, CH_3OCH_3)
8. For the compounds listed in Question 4, if the molecular masses of the substances were equal, which substance would you expect to have the highest boiling point? Why? K/U T/I

4.8

The Structure and Properties of Solids

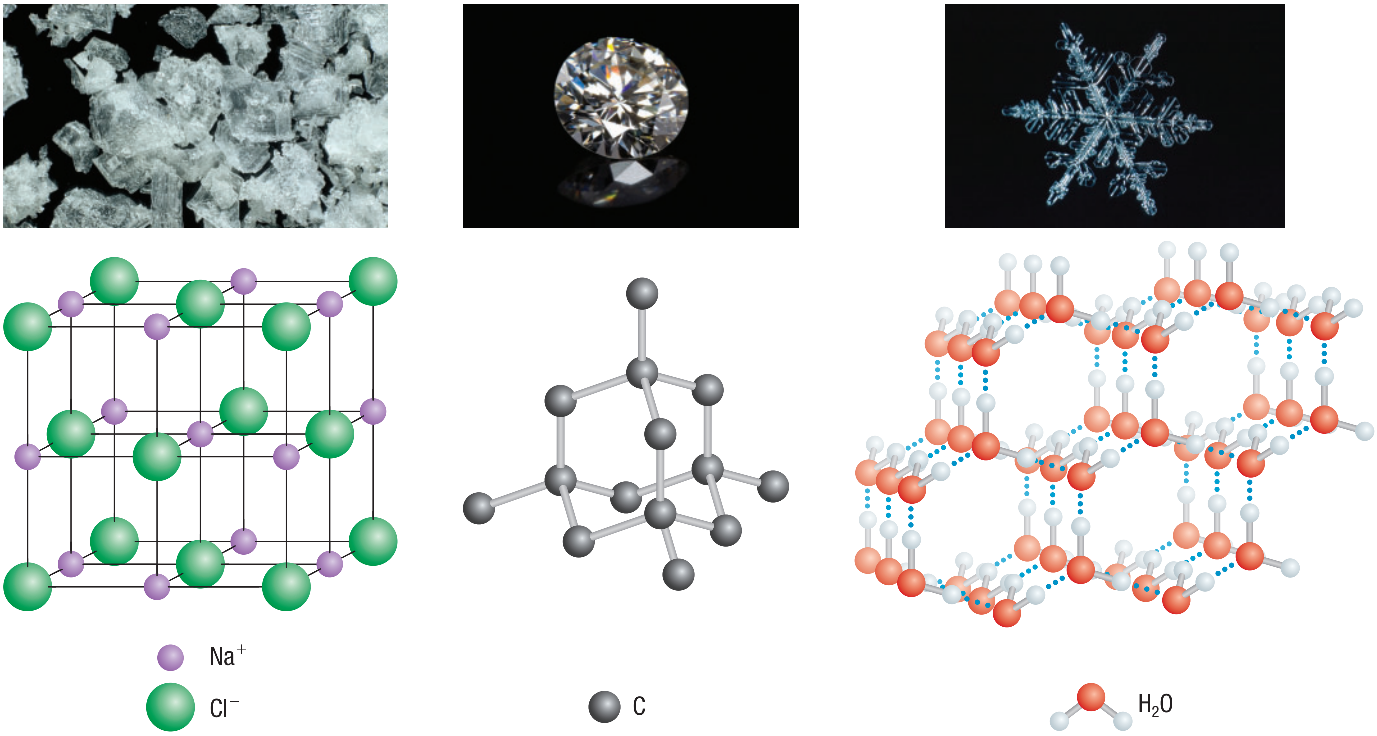
Figure 1 The Boeing 787 Dreamliner, made of composite materials, is more fuel-efficient than older aircraft.

composite material a material composed of two or more distinct materials that remain separate from each other in the solid phase

The rising cost of fuel has had a profound impact on the price we pay to travel. You are likely aware of how expensive gasoline is these days. Now imagine the cost of filling a commercial airplane's fuel tank, which is 3000 times larger than a car's gas tank! Given how much fuel an airplane consumes, it is not surprising that the cost of an airline ticket has increased substantially in recent years.

Because of high fuel prices, airplane designers have been working to develop lighter, quieter, and more fuel-efficient airplanes such as the Boeing 787 Dreamliner aircraft **(Figure 1)**. This model of plane uses approximately 20 % less fuel than a comparable Boeing 767 model. The 787 Dreamliner is the first major airplane to use **composite materials**—materials made from 2 or more substances that have significantly different chemical and physical properties. In composite materials, the substances remain separate and distinct from each other. Many common products, such as boats, bricks, surfboards, and even concrete, use composite materials. The 787 Dreamliner is made of at least 50 % composite materials, being mostly carbon and reinforced plastic. This combination provides a high strength-to-weight ratio and makes the airplane lighter than other models. Composite materials are also resistant to corrosion, heat, and chemicals—ideal for high-atmosphere travel. The properties of a composite material are determined by the structural and bonding characteristics of the substances from which it is made.

In this section, you will learn about the structural and bonding characteristics of substances in the solid phase. There are many different types of solids, such as ionic solids, metallic solids, molecular solids, and network solids. These are all crystalline solids. **Figure 2** shows three types of crystalline solids. You can see that the structural properties of each solid are different from each other.



(a) sodium chloride

(b) diamond

(c) ice

Figure 2 Examples of the different types of crystalline solids. (a) Sodium chloride is an ionic solid composed of alternating sodium, Na^+, and chloride, Cl^-, ions. (b) Diamond is a solid arrangement of carbon atoms. (c) Ice is the solid form of water. The blue dotted lines show hydrogen bonds between adjacent polar water molecules.

Ionic Crystals

You are already familiar with ionic crystals because you have studied the ionic bond that forms between Na^+ and Cl^- ions. This ionic crystal forms from the interaction of metal (sodium) and non-metal (chloride) ions. The ions arrange in a crystal lattice structure, with alternating packing of the positive and negative ions (Figure 2(a)).

Many of the physical properties of NaCl(s) are also characteristic of other ionic crystals. For example, NaCl(s) is a hard, brittle solid. When it dissolves in water, the solution conducts electricity, but solid NaCl does not conduct electricity. Ionic crystals tend to have high melting points. Magnesium oxide (used in antacid tablets) is an ionic solid that has a melting point of 2852 °C. This property is the result of the strong ionic bonds that hold the oppositely charged ions together.

Metallic Crystals

If you had the task of describing a metal, what words would you use? You might say that a metal is shiny or silvery. You may also describe a metal as a good conductor of thermal energy and electricity. In the solid state, metals form a **metallic crystal**, which is a structure composed of closely packed atoms held together by electrostatic interactions and free-moving electrons. Unlike ionic crystals, not all metallic crystals have similar properties. For example, solid gold is quite soft and easily moulded, making it useful in making jewellery. In contrast, solid aluminum, which is used to make items such as soft-drink cans, is much harder than gold so it keeps its shape better than gold. The melting points of metallic crystals also vary widely. Some metals, such as mercury, melt below room temperature, whereas others, such as tungsten, melt at temperatures higher than 3000 °C.

metallic crystal a solid with closely packed atoms held together by electrostatic interactions and free-moving electrons

What theory can explain these varied characteristics of metallic crystals? The **electron sea theory** postulates that metals are composed of closely packed atoms whose valence electrons are free to move. In this model, the positively charged nuclei of the atoms in the crystal remain at fixed points while the electrons are mobile (**Figure 3**). Imagine that you have placed several small marbles in a cup of water. The water (representing electrons) can move freely in the cup, but the marbles (representing nuclei) remain relatively fixed in place. The mobile electrons do not associate with 1 nucleus only, but move from nucleus to nucleus and thereby hold the positively charged nuclei together. This theory explains **metallic bonding**, the bonding that holds the nuclei and electrons of metals together.

electron sea theory a theory that states that the electrons in a metallic crystal move freely around the positively charged nuclei

metallic bonding the bonding that holds the nuclei and electrons of metals together

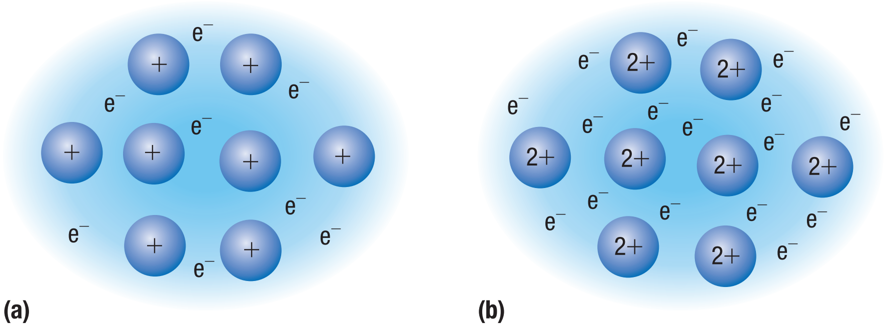


Figure 3 In the electron sea model of metallic solids the electrons are mobile. (a) Model of the Group 1 alkali metals with 1 valence electron (b) Model of the Group 2 alkaline earth metals with 2 valence electrons

The electron sea theory explains several properties of metallic crystals. The atoms within metallic crystals have low ionization energies because they possess loosely held electrons that can move freely outside their valence orbitals. The strong forces of attraction between the positive nuclei and the electrons result in closely packed metallic crystal structures.

Table 1 lists examples of common properties of metallic solids and an explanation of these properties.

Table 1 Properties of Metallic Solids

Property	Explanation
sheen	Mobile valence electrons absorb and emit light energy of many wavelengths of light.
malleability	The "electron sea" allows atoms to slide over each other.
electrical conductivity	Mobile valence electrons produce an electric current when a metal is connected to a battery.
hardness	The "electron sea" surrounding the positive nuclei produces strong electrostatic attractions that hold the nuclei together.

Molecular Crystals

molecular crystal a solid composed of individual molecules held together by intermolecular forces of attraction

Some substances, called **molecular crystals**, form crystal lattice structures when in the solid state, including sulfur, iodine, water, and carbon dioxide. Molecular crystals are similar to ionic crystal lattices except that they are often more complex. For example, the molecular crystal of water (ice) can form several different types of structures in the frozen form. **Figure 4** shows a symmetrical hexagonal structure that is often the form of ice in a snowflake.

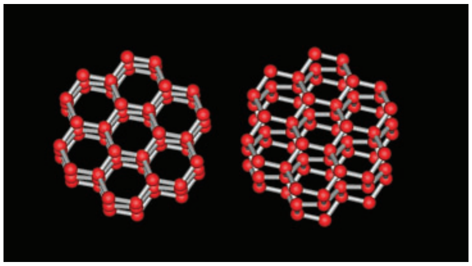


Figure 4 Two angles of the molecular model of a hexagonal lattice of solid water in a snowflake. In this illustration, atoms of both hydrogen and oxygen are red, covalent bonds between atoms are light grey, and hydrogen bonds between molecules are dark grey.

The intermolecular forces within a molecular crystal determine its structure and properties. Remember that intramolecular forces are much stronger than intermolecular forces. Intermolecular forces include London dispersion, dipole–dipole, and hydrogen bonding forces. Polar molecules exhibit both dipole–dipole forces and London dispersion forces, and non-polar molecules exhibit only London dispersion forces. The weak intermolecular forces help determine the properties of neutral molecules, which is why molecular crystals tend to have lower melting points and be less hard than ionic crystals. Molecular crystals contain neutral molecules, so they do not conduct an electric current very well, either in their pure form or in solution (**Table 2**). **Figure 5** shows a light micrograph of a crystal of iodine, $I_2(s)$, where molecules display a regular arrangement of equally spaced atoms within a lattice.

Table 2 Properties of Molecular Crystals

Property	Reason
low melting point	intermolecular interactions
little hardness	intermolecular interactions
electrical non-conductor	composed of neutral molecules

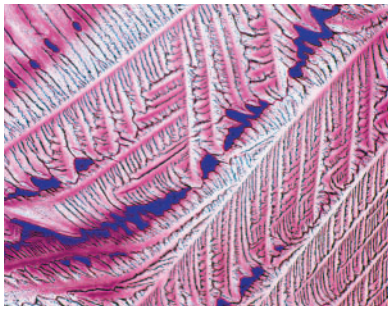


Figure 5 Polarized light micrograph of a crystal of iodine, I_2. The structure is a regular arrangement of iodine molecules.

Covalent Network Crystals

covalent network crystal a solid in which the atoms form covalent bonds in an interwoven network

A **covalent network crystal** is a solid in which the covalent bonds between atoms form an interwoven network. Diamond, the hardest naturally occurring substance on Earth, is an example of a covalent network crystal. The carbon atoms in a diamond molecule form a tetrahedral structure, as shown earlier, in Figure 2(b) on page 248. Each carbon atom forms 4 single covalent bonds to other carbon atoms by way of sp^3 hybrid orbitals. The network of covalent bonds is the source of the name for these crystals. You can predict some of the properties of covalent network crystals, using diamond as a model.

Covalent network crystals tend to have very high melting points and extreme hardness. The melting point of diamond is over 3500 °C. Therefore, the covalent bonding structure in a network solid must be very strong. You may have observed many hydrocarbon molecules that contain carbon–carbon covalent bonds, such as ethane and octane. The carbon–carbon bonds in diamond are no different than the carbon–carbon bonds in these molecules. However, the strength of diamond is a result of its interlocking network structure (**Figure 6**). Think of the strength of a braided rope. If you were to separate the individual strands, you would find that they are not very strong. Yet, when you braid the strands together, the rope is much stronger than any one strand.

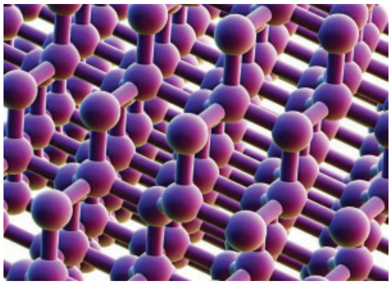
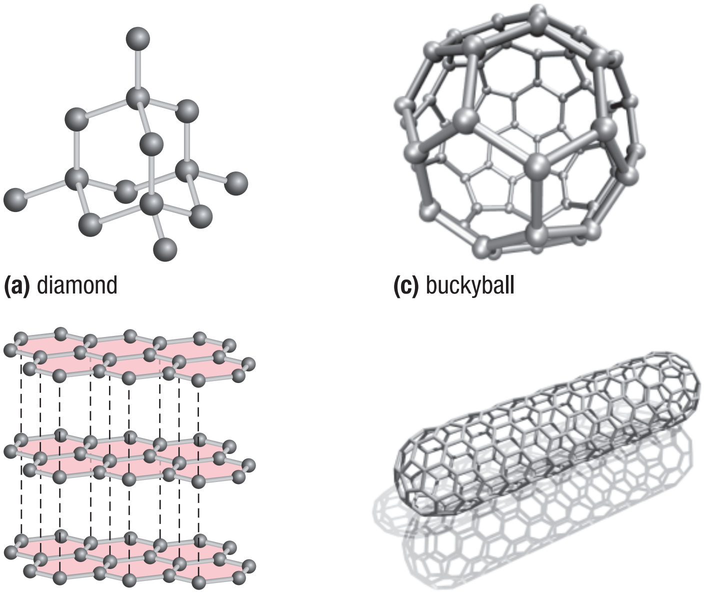


Figure 6 The covalent arrangement of carbon atoms in a solid diamond

Since the atoms in diamond interlock, they do not move around easily. This accounts for the extreme hardness of covalent network crystals. A large amount of energy is required to break the bonds in a covalent network crystal and melt it. The electrons in covalent network crystals do not move freely through the crystal because the atoms and covalent bonds hold the electrons in place. Thus, covalent network crystals are not good conductors of electricity.

Carbon atoms can form other structures in addition to the structure found in diamond (**Figure 7(a)**). Carbon atoms can form layers or sheets when in the solid phase, such as in graphite (**Figure 7(b)**), large spherical molecules in buckyballs (**Figure 7(c)**), and long, thin carbon nanotubes (**Figure 7(d)**). WEB LINK



(a) diamond

(c) buckyball

(b) graphite

(d) carbon nanotube

Figure 7 The different structures of solid carbon. (a) The tetrahedral arrangement of carbon atoms in a diamond. (b) The layered sheet structure of carbon atoms in graphite. A weak bonding interaction occurs between the layers of carbon sheets. (c) The ring-like arrangement of carbon atoms in a buckyball (d) The long, tube-like structure of carbon atoms in nanotubes

Graphite has very different properties from diamond. Graphite is slippery, black, and an electrical conductor. These differences are a result of the difference in bonding within graphite. The carbon atoms arrange in a hexagonal sheet. Each carbon atom in a sheet of graphite bonds to 3 other carbon atoms in a trigonal planar arrangement. Therefore, electrons in sp^2 hybrid orbitals form the covalent bonds in graphite. This arrangement results in delocalized electrons in *p* orbitals that can move from one side of the sheet to the other, which accounts for the electrical conductivity of graphite. Graphite has strong covalent bonds along the plane of the graphite sheet, and weaker London dispersion forces hold the graphite layers together (Figure 7(b)).

buckyball a spherical arrangement of carbon atoms that forms a hollow, cage-like structure

carbon nanotube a solid made of carbon atoms similar to graphite rolled into a cylinder

A **buckyball** consists of 60 carbon atoms arranged in a soccer ball–like structure. Its actual name is buckminsterfullerene, in honour of Richard Buckminster Fuller, who built architectural domes of this shape. The carbon atoms link together to form a hollow, dome-shaped cage. Buckyballs are extremely stable structures that have very high melting points. In the past 15 years, buckyballs have become popular because they have many different applications. Uses for buckyballs include chemical sensors, photovoltaic cells, cosmetics, and vehicles for delivering pharmaceutical drugs to cells. **Carbon nanotubes** are very similar in structure to buckyballs except that they have a cylindrical shape that is rolled at specific angles. The properties of nanotubes differ depending on their circumference, length, and twist. Nanotubes were discovered in 1991, and scientists are still learning more about the properties and applications of these structures.

Most covalent network crystals comprise the elements and compounds of carbon and silicon. The element silicon belongs to the same group (Group 14) as carbon in the periodic table. Silicon compounds make up most rocks, sand, and soil found on Earth. Crystalline quartz is a covalent network crystal of the silica molecule, SiO_2 (**Figure 8(a)**). Quartz forms a regular structure of molecules within the crystal.

When you heat solid silica above its melting point and then cool it rapidly, solid glass forms. Glass has a much more disordered structure than quartz (**Figure 8(b)**). Cooling molten glass quickly forms a structure that is not crystalline. In fact, glass more closely resembles a very viscous liquid than it does a crystalline solid. The properties of glass can change depending on the addition of different additives. For example, borosilicate glass, made of boron oxide and silica, produces a glass that does not expand or contract much when its temperature changes. Borosilicate glass is commonly used in labware and cookware because it resists breaking when heated or cooled rapidly.

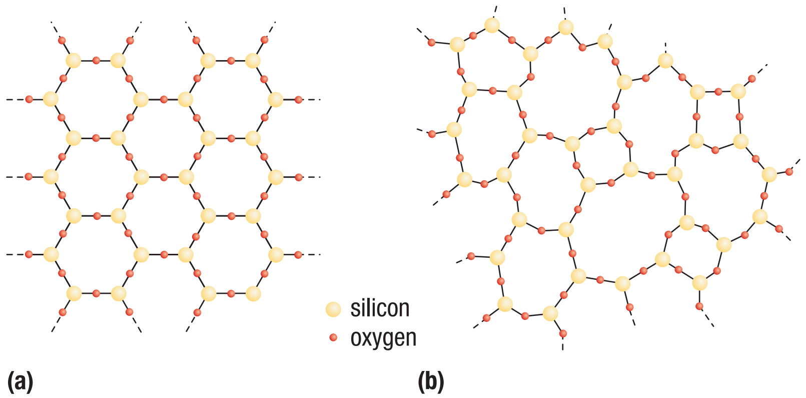


Figure 8 Two-dimensional representations of (a) a quartz crystal and (b) quartz glass. Note the irregular structure of the glass in contrast to the regular structure in the crystal.

semiconductor a substance that conducts a slight electric current at room temperature but has increasing conductivity at higher temperatures

Semiconductors

Transistors are essential components of electronic devices. As transistors have decreased in size, so has the size of electronic devices, while the capabilities of these devices have increased. You can listen to music, work at a computer, and watch television because of transistors. Transistors act as amplifiers and switches in electronic circuits. Semiconductors are essential components of transistors. **Semiconductors** consist of covalent crystals of elements such as silicon or germanium that conduct a small amount of electric current in standard conditions. When you increase the temperature slightly, the conductivity increases significantly. Engineers modify silicon or germanium by adding a small amount of an element such as arsenic or boron in a process called doping. This process allows engineers to create semiconductors with specific conductive properties (**Figure 9**).

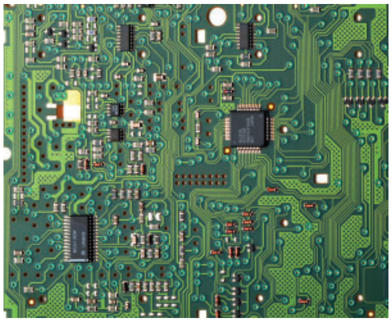
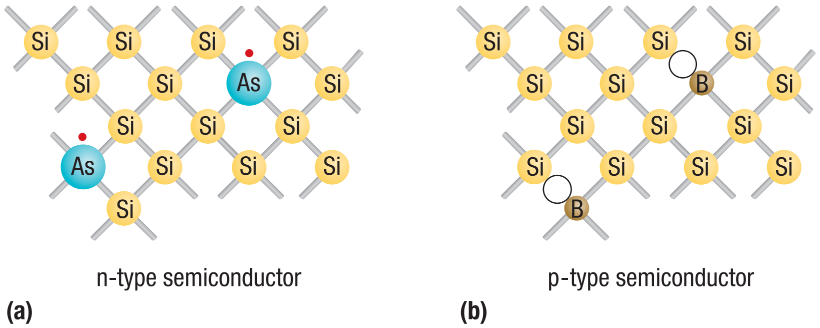


Figure 9 This microchip, which can contain millions of transistors, is built on a wafer of semiconductor material.

The atoms in a semiconductor have full valence electron shells, so electrons do not move from one atom to another. Thus, semiconductors are normally non-conductors. Semiconductors are sometimes doped with arsenic, which has 1 more valence electron than silicon. A slight increase in temperature causes these additional electrons in arsenic to jump to a higher energy level. When the electrons are in an excited state, they move from atom to atom easily and the semiconductor's conductivity increases (**Figure 10(a)**). This type of semiconductor is an n-type semiconductor. Silicon can also be doped with boron, which has 1 less valence electron than silicon. The missing electron creates a hole around the boron atoms that electrons from surrounding atoms move to fill, which also increases the semiconductor's conductivity (**Figure 10(b)**). This type of semiconductor is a p-type semiconductor.

CAREER LINK



n-type semiconductor

p-type semiconductor

Figure 10 (a) A silicon crystal can be doped with arsenic, which has one more valence electron than silicon. (b) A silicon crystal can also be doped with boron, which has one less valence electron than silicon.

Investigation 4.8.1

Identifying Solids (page 259)

Now that you know about the different types of solids, perform Investigation 4.8.1 to identify solids based on their physical and chemical properties.

Research This

3-D Photocopiers

Skills: Researching, Analyzing, Evaluating, Communicating

SKILLS HANDBOOK A5.1

Imagine that you are building a small bird feeder at home and you run out of nails. Typically, you would go to the store to purchase the nails. Now suppose you had a 3-D photocopier, or "fabricator"—a futuristic machine able to reproduce any three-dimensional object. Instead of going to the store, you could just reproduce the nails at home with the touch of a button. This idea may sound like science fiction to you, but scientists and engineers are beginning to develop such a machine (**Figure 11**).

Figure 11 A 3-D photocopier may one day allow you to create any object. Just design the object that you need from your computer and in a matter of seconds, a real-life replica is produced.

To design a machine like this, it is important to understand the structure of the atoms and molecules that comprise these objects, because this technology would rely on the concepts of chemical bonding and the structure of matter. Although the reality of such a machine may be many years into the future, the concept is interesting and a good topic of conversation.

1. Research 3-D photocopiers to find out the latest progress in their development.

A. In what ways could this machine change your life? A

B. What type of object do you think you would 3-D photocopy most often? A

C. What types of objects would be most difficult to 3-D photocopy? A

D. Are there any objects that you could not make with this machine? A

E. How could this machine promote green chemistry? A

F. Describe any drawbacks to using such a machine. A

WEB LINK

4.8 Review

Summary

- The four types of solids are ionic crystals, metallic crystals, molecular crystals, and covalent network crystals.
- Ionic crystals form when a metal reacts with a non-metal, producing oppositely charged ions that are electrostatically attracted to each other. An example of an ionic crystal is sodium chloride.
- Metallic crystals are bound by a sea of electrons. This region of negative charge explains the electrical conductivity, hardness, and flexibility of metals. An example of a metallic crystal is aluminum.
- The properties of molecular crystals are in part determined from the intermolecular dipole–dipole and hydrogen bonding forces in these substances. Lower melting points, less hardness, and electrical non-conductivity are characteristics of molecular crystals. Ice is an example of a molecular crystal.
- Hardness, electrical non-conductivity, and high melting point are characteristics of covalent crystals. Diamond is an example of a covalent crystal.
- Semiconductors are often made of silicon or germanium. Engineers modify silicon or germanium by doping it with a small amount of an element such as arsenic or boron.

Questions

1. Make a chart summarizing the properties of the four types of solids. Use the following headings: K/U C
    - Type of solid
    - Particles involved
    - Primary force of attraction
    - Boiling point
    - Electrical conductivity: solid, liquid, solution
    - Other physical properties of crystal
    - Conditions necessary for formation
    - Examples
2. Predict the type of solid that you would expect to have each of the following characteristics: K/U
    (a) greatest electrical conductivity
    (b) lowest melting point
    (c) highest conductivity when dissolved in water
    (d) lowest hardness
3. Provide an explanation for each of your answers in Question 2. K/U
4. Compare and contrast the structures of the following solids: K/U
    (a) $CO_2(s)$ versus $H_2O(s)$
    (b) NaCl(s) versus HCl(s)
5. Explain what the term "doping" means and why engineers dope semiconductor materials. K/U
6. What type of solid is a substance that
    (a) conducts electricity and has a high melting point?
    (b) does not conduct electricity as a solid but does when dissolved in water?
    (c) does not conduct electricity and has a high boiling point?
    (d) does not conduct electricity and has a low boiling point? K/U
7. Suggest a method to distinguish each of the following pairs of solids: T/I A
    (a) ionic crystal, molecular crystal
    (b) metallic crystal, covalent crystal
    (c) molecular crystal, metallic crystal
    (d) ionic crystal, covalent crystal
8. Explain how you could tell experimentally if titanium dioxide, TiO_2, is an ionic solid or a molecular solid. K/U T/I A
9. Switching salt and sugar on a table is a common prank. Since both substances look alike, they can be switched easily. Despite their similar appearance, salt and sugar differ in their properties because one is a molecular solid and the other is an ionic solid. Explain how and why their properties are different. K/U T/I A

CHAPTER 4 Investigations

Investigation 4.2.1 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Three-Dimensional Shape

Chemists use VSEPR theory to predict the structure of molecules. A molecule's structure can reveal important characteristics, such as its reactivity, behaviour, and electrical conductivity. Chemists also use molecular models to visualize the structure of a molecule. In this activity, you will use the VSEPR theory to predict the structure of different molecules, and then you will use a molecular modelling kit to visualize these molecules.

Purpose

To test your understanding of the VSEPR theory and observe the three-dimensional structure of molecules

Equipment and Materials

- molecular modelling kit
- guide of colour codes for atoms in kit

Procedure

SKILLS HANDBOOK A2.4

Part A: Three-Dimensional Structure

1. Use the VSEPR theory to predict the structures of the following molecules: C_2H_6, C_2H_4, C_2Cl_2, CH_3CH_2OH, NF_3, CCl_4, and OF_2.
2. Use the modelling kit to construct the molecules for the substances listed above.

Part B: Prediction of Molecular Polarity

3. Predict whether each of the molecules contains polar or non-polar covalent bonds.

Analyze and Evaluate

(a) What type of geometry does each molecule in this activity have? T/I

(b) In your prediction, which molecules contained bonds that were polar? T/I

(c) Which molecules are polar? T/I

(d) Explain why your answer to (c) may be different from your answer to (b). T/I

(e) Based on the results from the modelling kit, complete a table in your notebook using the headings shown in **Table 1**. K/U C

Table 1

Molecule	Shape	Bond angle	Are the bonds polar or non-polar?	Is the molecule polar or non-polar?

(f) Evaluate your predictions. T/I

Apply and Extend

(g) A student performed a similar analysis of the molecules PH_3, CH_3OH, CH_3COOH, and BF_3. Create a table like the one you completed in (e) for your structure predictions of these molecules. T/I C

(h) Which of the 4 molecules in (g) would orient in an electric field? Explain your reasoning. K/U

(i) State the geometry around each atom (excluding hydrogen) in the following compound, and indicate which areas of the molecule would be polar and which would be non-polar: K/U

$HC{\equiv}C{-}CH_2{-}CH{=}CH{-}CH_2{-}OH$

(j) Predict the shapes of the following molecules: K/U T/I

(i) $AsCl_5$

(ii) $AsOCl_3$

(iii) $AsCl_3$

(k) Determine the polarity of the molecules in (j). T/I

Investigation 4.5.1 CONTROLLED EXPERIMENT

Testing for Polar Molecules

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Polar molecules can be affected when you place them near a charged object. For example, a negatively charged balloon causes a stream of water to deflect toward the balloon. This occurs because of the polar nature of water. Water has 1 partial negatively charged oxygen atom and 2 partial positively charged hydrogen atoms. The partial positively charged hydrogen atoms in water are attracted to the negatively charged balloon. However, this attraction does not occur in all molecules. A non-polar molecule does not display partial charge distribution. Thus, non-polar molecules are not affected by a charged object.

In this investigation, you will determine the effect of placing a charged object in the vicinity of various liquids. From these data, you will be able to conclude which molecules are polar and which molecules are non-polar.

Testable Question

What effect does the polarity of a liquid have on the deflection that results from a nearby charged object?

Prediction

Predict which of the following molecules you expect to be polar: water, acetone, hexane, and ethanol

Variables

Identify the manipulated and responding variables and all variables that will be controlled in the experiment.

Experimental Design

A charged acetate strip and a charged vinyl strip will be held near a stream of polar and non-polar liquids. The effect of the charged acetate strip and the charged vinyl strip on the stream will be observed.

Equipment and Materials

SKILLS HANDBOOK A1.1

- chemical safety goggles
- lab apron
- paper towel
- beaker
- acetate strip (+)
- vinyl strip (−)
- dropper bottles or burettes filled with
  - water
  - acetone
  - hexane
  - ethanol

Acetone, hexane, and ethanol are flammable. Be sure there are no open flames nearby.

Hexane and ethanol are toxic. Be sure there is good ventilation in the lab. Do not pour the liquids down the sink. When you have finished with them, dispose of them in the containers provided.

Use glass burettes only. Some organic solvents break down plastic, ruining plastic burettes.

Procedure

SKILLS HANDBOOK A1.2, A2.1

1. Put on your eye protection and lab apron.
2. Rub the acetate strip with a paper towel.
3. Allow a stream of the first solution to flow from the dropper bottle or burette into the beaker.
4. Hold the acetate strip near the liquid stream as it falls from the dropper or burette. Observe any effect the acetate strip has on the solution.
5. Repeat Steps 2–4 with all solutions.
6. Repeat Steps 2–5 with the vinyl strip.
7. Dispose of the solutions as directed by your teacher.

Analyze and Evaluate

(a) What variables were measured, recorded, and/or manipulated in this investigation? T/I

(b) Draw the three-dimensional structures of the solvents tested in this experiment. Include their polarity. T/I C

(c) Identify the substances that were deflected when they dripped close to the charged acetate strip. T/I

(d) Would you expect polar or non-polar substances to be deflected by the charged acetate strip? Explain. T/I

(e) Describe any sources of experimental error. How might they have affected your results? T/I

Apply and Extend

(f) Predict the results of this investigation if you had used a stream of each of the following substances: methanol, cyclohexane, pentane, tetrahydrofuran (THF), and carbon tetrafluoride. Look up the structure of these compounds first, if necessary. T/I A

(g) At your 7-year-old sister's birthday party, you show her and her friends a "magic trick" by using a charged balloon to bend a stream of water. They ask you to explain what is happening. How could you explain this to them in a way they could understand? K/U T/I C

Investigation 4.7.1 CONTROLLED EXPERIMENT

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Hydrogen Bonding

Intermolecular forces are important in solids and liquids. When two pure substances mix in a chemical process, they either give off energy (exothermic reactions) or absorb energy (endothermic reactions). An exothermic reaction results in a temperature increase in the surroundings, whereas the surroundings experience a temperature decrease in endothermic processes. In this investigation, you will design a procedure to determine the effect of adding ethanol or glycerol (**Figure 1**) to water by measuring temperature change. After completing the investigation, you will be able to determine how hydrogen bonding affects a chemical reaction.

Figure 1 Dyed glycerol solution mixing with water

Testable Question

Will ethanol or glycerol undergo a greater increase in temperature when mixed with water?

Prediction/Hypothesis

Write a hypothesis relating changes in hydrogen bonding to temperature change. Based on your hypothesis, predict whether ethanol or glycerol will undergo a greater temperature change when mixed with water. Explain your reasoning.

Variables

Identify all variables that will be measured and/or controlled in the experiment. Specify the manipulated and responding variables.

Experimental Design

Equal amounts of ethanol and water, and glycerol and water, will be mixed. Then, the temperature changes that result from these reactions will be determined using a coffee-cup calorimeter.

Equipment and Materials

SKILLS HANDBOOK A1.1

- chemical safety goggles
- lab apron
- two 10 mL graduated cylinders
- polystyrene cup with lid (lid has centre hole for thermometer)
- 2 thermometers or temperature probes
- 250 mL beaker
- water
- ethanol
- glycerol

Ethanol is flammable and toxic. Be sure there are no open flames nearby.

Some people are allergic to glycerol and may feel irritation to the skin or eyes.

Procedure

SKILLS HANDBOOK A1.2, A2.1

1. Prepare a complete procedure as a series of numbered steps. Make sure that you clearly identify the masses, volumes, and equipment that you will use. Include any necessary safety precautions.
2. After your teacher approves your procedure, carry it out.

Analyze and Evaluate

(a) What variables were measured, recorded, and/or manipulated in each part of this investigation? T/I

(b) Which substance created the largest temperature change? Compare your results with your hypothesis. Give reasons for any differences. T/I

(c) Do you think that your results are accurate? Why or why not? T/I

(d) Evaluate your procedure. How can you improve it? T/I

Apply and Extend

(e) Propose a way to set up the reaction to produce a more representative experiment. If time allows, test this new experiment. T/I

Investigation 4.7.2 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Boiling Points and Intermolecular Forces

When you raise the temperature of a liquid to boiling, you put energy into the liquid. Strong intermolecular forces in a liquid require a large amount of energy (a high temperature) to make the liquid boil. Liquids that contain few intermolecular forces require less energy to boil and thus have a lower boiling point. In this investigation, you will determine the effect of dipole–dipole and London dispersion forces in different molecules on the boiling point of a liquid. You will use these data to compare and correlate polarity and molecular mass with the boiling point of a liquid.

Purpose

To determine the boiling points of various substances

Equipment and Materials

SKILLS HANDBOOK A1.1

- chemical safety goggles
- lab apron
- test tube
- 250 mL beaker
- thermometer
- hot plate
- 3 solvent dropper bottles of
  - butanol
  - propanol
  - isopropanol
- water

Butanol, isopropanol, and propanol are highly flammable and should be kept at a distance from any source of ignition. Do not use any open flames.

Do not aim test tubes with alcohol directly at yourself or your lab partner, because toxic fumes may be released.

People who have allergies to any of the chemicals may have irritations of the eyes or skin.

Procedure

SKILLS HANDBOOK A1.2, A2.3

1. Put on your eye protection and lab apron.
2. Place 5 drops of one alcohol into a test tube.
3. Put 150 mL of water into the 250 mL beaker. Put the thermometer into the beaker.
4. Place the test tube into the beaker, and put the beaker onto the hot plate.
5. Heat the water and test tube until the alcohol evaporates. You will need to watch closely to determine when this happens.
6. When the alcohol has evaporated, record the temperature of the water.
7. Carefully pour out the water in the beaker and replace it with 200 mL of fresh water.
8. Repeat Steps 2–7 with each of the other alcohols. If the alcohol does not evaporate within 10 min, record the temperature and note that it did not boil.
9. Dispose of solvents in the proper waste container or as instructed by your teacher.

Analyze and Evaluate

SKILLS HANDBOOK A6.5

(a) What variables were measured, recorded, and/or manipulated in each part of this investigation? T/I

(b) Graph your data in a table by plotting boiling point versus molar mass. T/I C

(c) Explain the graph of the molecules in terms of intermolecular forces. T/I

(d) Why is there a difference in boiling point between propanol and isopropanol? T/I

Apply and Extend

(e) The following molecules consisting of Group 2 atoms have the following melting points:

BeH_2 = 250 °C
MgH_2 = 327 °C
CaH_2 = 816 °C

Explain these results in terms of intermolecular forces. K/U T/I

(f) You want to use a solvent to rinse a beaker, but you want the solvent to evaporate quickly. Using information from this investigation, which solvent should you use? Can you think of a solvent that would be better? Explain why it would be better. K/U T/I A

Investigation 4.8.1 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Identifying Solids

You will design and carry out an investigation to use the physical properties of a substance to identify its classification.

Purpose

To determine the types of solids for 4 unidentified substances

Equipment and Materials

- chemical safety goggles
- lab apron
- four 250 mL beakers
- hot plate
- test tubes (number will be determined in your procedure)
- test-tube rack
- other equipment as determined in your plan
- 4 unidentified solids (obtained from your teacher)
- water

Tie back loose hair or clothing. Do not touch the test tubes after heating. Put them in a test-tube rack carefully after heating.

Procedure

SKILLS HANDBOOK A1.2, A2.3

1. Write a set of detailed steps to collect data that will help you to identify the types of solids for the 4 unidentified substances (ionic crystals, metallic crystals, molecular crystals, and covalent crystals). Include a detailed list of equipment and materials. Describe any safety precautions you will take.
2. Once your teacher has approved your design, carry out your procedure.

Analyze and Evaluate

(a) What variables were measured recorded, and/or manipulated in this investigation? T/I

(b) Identify the 4 solids and explain your reasoning. T/I

(c) Identify any sources of error in your investigation. What would you change to reduce this error if you were able to repeat this investigation? T/I

Apply and Extend

(d) Classify each of the following solids: $CO_2(s)$, $KCl(s)$, $SiO_2(s)$, and $Fe(s)$. T/I

(e) Copy **Table 1** into your notebook and complete it. T/I C

Table 1

Type of crystal	Is it soluble in water?	Will an aqueous solution be conductive?	Will the solid be conductive?	Will the liquid conduct?	Can it be easily crushed?
ionic					
metallic					
covalent					
molecular					

(f) Samples of sodium fluoride, copper shot, sugar, and graphite are placed on a metal plate, one in each corner. You heat the centre of the plate. In what order will the substances melt? Explain your answer. K/U T/I

CHAPTER 4 SUMMARY

Summary Questions

1. Create a quiz of 25 questions for this chapter based on the Key Concepts on page 192. Be sure to provide answers to the questions.
2. Look back at the Starting Points questions on page 192. Answer these questions using what you have learned in this chapter. Compare your latest answers with the answers that you wrote at the beginning of the chapter. Note how your answers have changed.

Vocabulary

ionic bond (p. 194)
isoelectronic (p. 195)
covalent bond (p. 195)
bonding electron pair (p. 195)
Lewis structure (p. 196)
duet rule (p. 196)
octet rule (p. 196)
lone electron pair (p. 197)
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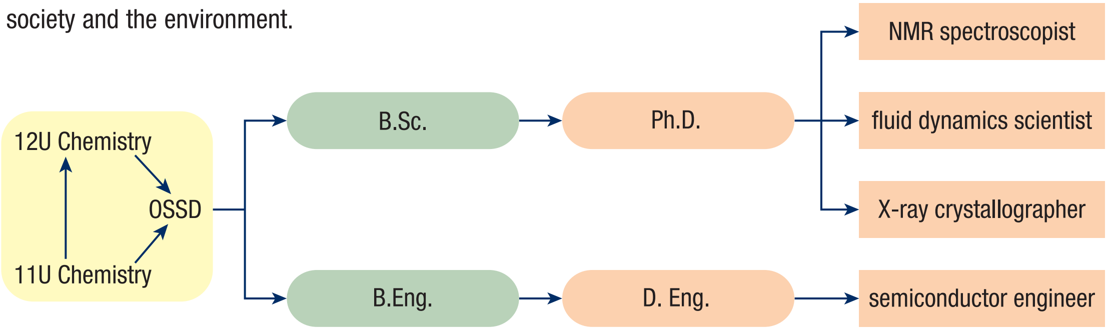
CAREER **PATHWAYS**

SKILLS HANDBOOK A7

Grade 12 Chemistry can lead to a wide range of careers. Some require a college diploma, a B.Sc. degree, or work experience. Others require specialized or postgraduate degrees. This graphic organizer shows a few pathways to careers mentioned in this chapter.

1. Select two careers related to Chemical Bonding that you find interesting. Research the educational pathways that you would need to follow to pursue these careers. What is involved in the required educational programs? Prepare a brief report of your findings.
2. For one of the two careers that you chose above, describe the career, main duties and responsibilities, working conditions, and setting. Also outline how the career benefits society and the environment.



CAREER LINK

CHAPTER 4 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. How many electrons surround the carbon atom in a molecule of carbon monoxide? (4.1) K/U
   (a) 2
   (b) 6
   (c) 8
   (d) 12
2. What is the geometry of carbon dioxide, CO_2? (4.2) K/U
   (a) linear
   (b) tetrahedral
   (c) trigonal planar
   (d) trigonal pyramidal
3. Which of the following bonds is the most ionic in character? (4.3) K/U
   (a) $S-P$
   (b) $N-C$
   (c) $Al-O$
   (d) $Si-P$
4. Which of the following molecules would you NOT expect to orient in an electric field? (4.3) K/U
   (a) NH_3
   (b) H_2O
   (c) CO
   (d) BH_3
5. Which of the following is a polar molecule? (4.5) K/U
   (a) BCl_3
   (b) CF_4
   (c) NCl_3
   (d) CO_2
6. What type of hybridization occurs in the carbon atoms of C_2F_2? (4.6) K/U
   (a) sp
   (b) sp^2
   (c) sp^3
   (d) no hybridization occurs
7. Which of the following affects the viscosity of a substance? (4.7) K/U
   (a) London dispersion forces
   (b) hydrogen bonding
   (c) dipole–dipole forces
   (d) all of the above
8. Which of the following substances has the lowest freezing point? (4.7) K/U
   (a) $NaCl$
   (b) H_2O
   (c) CH_4
   (d) Cl_2
9. Which type of solid has a low melting point, is a non-conductor of electricity, and is not very hard? (4.8) K/U
   (a) ionic crystal
   (b) metallic crystal
   (c) molecular crystal
   (d) covalent network crystal

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

10. Most Lewis structure drawings contain atoms that obey the octet rule. (4.1) K/U
11. Atoms that can be surrounded by more than 8 valence electrons have empty *d* orbitals. (4.1) K/U
12. The VSEPR theory determines molecular shape by maximizing repulsive forces between atoms bonded to a common central atom. (4.2) K/U
13. A diatomic molecule that contains chemical bonds between atoms having a large difference in electronegativity will orient in an electric field if the molecule's dipoles are not cancelled by symmetry. (4.3) K/U
14. Linus Pauling is best known for his VSEPR theory of molecular geometry. (4.4) K/U
15. A planar molecule with 3 identical bonds is a non-polar molecule. (4.5) K/U
16. A molecule of carbon tetrafluoride, CF_4, contains only sigma bonds. (4.6) K/U
17. A covalently bonded molecule that can form hydrogen bonds with other molecules is likely to have a higher boiling point than a covalently bonded molecule of similar molecular mass that cannot form hydrogen bonds. (4.7) K/U
18. Small molecules are usually more viscous than large, complex molecules. (4.7) K/U
19. Semiconductors can be doped to change the electrical conductivity of the material. (4.8) K/U

Go to Nelson Science for an online self-quiz.

WEB LINK

CHAPTER 4 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

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   (b) N–C
   (c) Al–O
   (d) Si–P
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   (c) CO
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   (a) BCl_3
   (b) CF_4
   (c) NCl_3
   (d) CO_2
6. What type of hybridization occurs in the carbon atoms of C_2F_2? (4.6) K/U
   (a) *sp*
   (b) sp^2
   (c) sp^3
   (d) no hybridization occurs
7. Which of the following affects the viscosity of a substance? (4.7) K/U
   (a) London dispersion forces
   (b) hydrogen bonding
   (c) dipole–dipole forces
   (d) all of the above
8. Which of the following substances has the lowest freezing point? (4.7) K/U
   (a) NaCl
   (b) H_2O
   (c) CH_4
   (d) Cl_2
9. Which type of solid has a low melting point, is a non-conductor of electricity, and is not very hard? (4.8) K/U
   (a) ionic crystal
   (b) metallic crystal
   (c) molecular crystal
   (d) covalent network crystal

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

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15. A planar molecule with 3 identical bonds is a non-polar molecule. (4.5) K/U
16. A molecule of carbon tetrafluoride, CF_4, contains only sigma bonds. (4.6) K/U
17. A covalently bonded molecule that can form hydrogen bonds with other molecules is likely to have a higher boiling point than a covalently bonded molecule of similar molecular mass that cannot form hydrogen bonds. (4.7) K/U
18. Small molecules are usually more viscous than large, complex molecules. (4.7) K/U
19. Semiconductors can be doped to change the electrical conductivity of the material. (4.8) K/U

Go to Nelson Science for an online self-quiz.

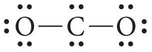
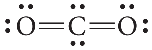
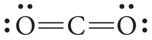
WEB LINK

CHAPTER 4 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Which is the correct Lewis structure of carbon dioxide? (4.1) K/U
   (a) O=C=O
   (b) 
   (c) 
   (d) 
2. Which of the following represents the molecular geometry of boron trifluoride, BF_3, and nitrogen trifluoride, NF_3, predicted by the VSEPR theory? (4.2) K/U
   (a) Both structures are trigonal planar.
   (b) Both structures are trigonal pyramidal.
   (c) BF_3 is trigonal planar, and NF_3 is trigonal pyramidal.
   (d) BF_3 is trigonal pyramidal, and NF_3 is trigonal planar.
3. Which of the following bonds is the least ionic in character? (4.3) K/U
   (a) S–P
   (b) N–C
   (c) Al–O
   (d) Si–P
4. Which of the following sets of bonds is listed in order of decreasing bond polarity? (4.3) K/U
   (a) H–H, H–O, H–N, H–F
   (b) H–F, H–N, H–O, H–H
   (c) H–F, H–O, H–N, H–H
   (d) H–O, H–F, H–N, H–H
5. To determine the polarity of a molecule, you need to know
   (a) the types of bonds in the molecule
   (b) the Lewis structure of the molecule
   (c) the geometry of the molecule
   (d) all of the above (4.5) K/U
6. Which of the following is a non-polar molecule? (4.5) K/U
   (a) $CFCl_3$ (c) NI
   (b) BI_3 (d) H_2O
7. A molecule has a central carbon atom with sp^3 orbitals. The bond angles are
   (a) 180° (c) 109.5°
   (b) 120° (d) 90° (4.6) K/U
8. Which of the following substances has the highest boiling point? (4.7) K/U
   (a) sodium chloride (c) methane
   (b) water (d) ammonia
9. Which of the following is NOT characteristic of London dispersion forces? (4.7) K/U
   (a) They are the weakest intermolecular forces.
   (b) They increase as the molecular mass of a substance increases.
   (c) They form when a hydrogen atom interacts with an electronegative atom.
   (d) They are weaker than intramolecular bonds.
10. Which of the following solids has the highest melting point? (4.7) K/U
    (a) sodium chloride
    (b) water
    (c) lead
    (d) diamond
11. Which of the following is NOT characteristic of semiconductors? (4.8) K/U
    (a) They are made of atoms with half-full valence shells.
    (b) They have a small energy gap between empty and valence orbitals.
    (c) They can be doped with arsenic to create n-type semiconductors.
    (d) They can be doped with boron to create p-type semiconductors.
12. To create an n-type doped silicon semiconductor, the doping agent should have the following number of valence electrons: (4.8) K/U
    (a) 2 (c) 3
    (b) 5 (d) 1

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

13. The most stable form of an atom exists when it has a full valence shell of electrons. (4.1) K/U
14. You can determine the molecular geometry of diborane, H_2BBH_2, by determining the geometry of each boron atom separately and then combining the structures. (4.2) K/U
15. A molecule that has two equal but oppositely pulling dipoles, such as carbon dioxide, will orient in an electric field. (4.3) K/U

16. Ronald Gillespie's VSEPR theory has helped chemists to understand the basic concepts of molecular geometry. (4.4) K/U
17. Nitrogen dioxide, NO_2, is a polar molecule. (4.5) K/U
18. Linear molecules with three different types of atoms are non-polar molecules. (4.5) K/U
19. A molecule of difluoroethyne, C_2F_2, contains only sigma bonds. (4.6) K/U
20. The smaller the molecular mass of a substance, the larger the London dispersion forces within it. (4.7) K/U
21. Hydrogen bonds are very strong dipole–dipole forces. (4.7) K/U
22. When ionic crystals dissolve in water, the resulting solution can conduct electricity. (4.8) K/U
23. The electrons in covalent network crystals move freely through the crystals. (4.8) K/U

Understanding

Write a short answer to each question.

24. Chemical bonds keep atoms together in a unit. In a short paragraph, compare and contrast the difference between ionic and covalent bonds. (4.1) K/U
25. Lewis structures provide information about chemical bonding and the electrons in molecules. (4.1) K/U C
    (a) Draw the Lewis structure of tetrabromomethane, CBr_4.
    (b) In a paragraph, describe the bonding and electrons in a molecule of tetrabromomethane.
26. For each of the following elements, explain what type of bond it will form and the reasons it forms this type of bond. Include a brief outline of the steps involved: hydrogen, carbon, sodium, and helium. (4.1) K/U
27. Sometimes atoms do not follow the octet rule. (4.1) K/U
    (a) Describe two cases where an atom in a molecule can have more or fewer than 8 valence electrons.
    (b) When a molecule has an atom with fewer than 8 valence electrons, would you expect it to be stable? Explain.
    (c) A molecule contains an atom with fewer than 8 valence electrons. What type of bond would you expect that atom to form?
28. (a) Compare and contrast the three-dimensional structure of methane and ammonia.
    (b) How are the angles in these molecules different?
    (c) Explain why these bond angles are not the same. (4.2) K/U
29. Describe the three-dimensional structure of boron tribromide, BBr_3. In your description, include a discussion about bonding electrons, identify the reason for the geometry, and describe the bond angle. (4.2) K/U
30. Describe the bond polarities of elemental bromine, Br_2; calcium oxide, CaO; and carbon monoxide, CO. Include a description of the electronegativity difference of each bond in your answer. What does the electronegativity difference tell you about the type of bond that forms? (4.3) K/U C
31. (a) Explain how bond polarity differs in the molecules hydrogen chloride, HCl, and elemental chlorine, Cl_2.
    (b) How would you expect these 2 molecules to behave if placed in an electric field? (4.3) K/U
32. Rank the following bonds in order of decreasing electronegativity difference: C–S, S–Cl, N–S, P–S, and S–O. (4.3) K/U
33. (a) Indicate which of the following molecules would NOT have a net dipole: water, carbon monoxide, carbon tetrachloride, boron trifluoride, and nitrogen tribromide.
    (b) Explain your answer to Part (a).
    (c) Indicate the direction of the dipole for the molecules from Part (a) that have a dipole. (4.5) K/U
34. Explain why methane is not a polar molecule but ammonia is a polar molecule. (4.5) K/U
35. Arrange the following molecules in terms of most polar to least polar and explain your order: (4.5) K/U

    CCl_2H_2, CCl_4, CF_2H_2, CF_2Cl_2
36. (a) Explain, using the valence bond theory, the orbitals involved in bonding in a molecule of carbon tetrafluoride, CF_4.
    (b) What type of bond is formed? (4.6) K/U
37. (a) Why are hybrid orbitals used to describe bonding in molecules?
    (b) What is the hybridization of the carbon atoms in a molecule of dibromoethyne, C_2Br_2?
    (c) What types of bonds form between all atoms in dibromoethyne, C_2Br_2? (4.6) K/U
38. The molecule ethanol is a common solvent in many chemistry applications. Why is ethanol a good solvent? (4.7) K/U A
39. (a) Which of the following molecules has physical properties that are primarily determined by London dispersion forces: phosphorus trichloride, PCl_3; sodium chloride, NaCl; silicon tetrachloride, $SiCl_4$; or methanol, CH_3OH?
    (b) Which of the molecules from Part (a) has the strongest forces of attraction? (4.7) K/U
40. Why is the shape of a meniscus of water in a glass cylinder different from the shape of a meniscus of mercury in a glass cylinder? (4.7) K/U

41. Relate the physical properties of each of the following compounds to the type of bonding that occurs in each: (4.8) K/U
    - (a) KBr(s)
    - (b) $H_2O(s)$
    - (c) C(s) (diamond)
    - (d) Cu(s)
42. Explain how doping silicon with either phosphorus or gallium increases the electrical conductivity of pure silicon. (4.8) K/U A
43. List three physical properties of
    - (a) metals
    - (b) ionic crystals
    - (c) molecular crystals of polar compounds
    - (d) molecular crystals of non-polar compounds
    - (e) network crystals (4.8) K/U

Analysis and Application

44. Draw the Lewis structure for each of the following molecules: (4.1) T/I C
    - (a) HF
    - (b) PBr_3
    - (c) CH_3OH
    - (d) H_2O_2
    - (e) SF_2
45. Draw the Lewis structure for each of the following ions: (4.1) T/I C
    - (a) PCl_2^-
    - (b) ClO_3^-
    - (c) ClO_2^-
46. How many lone pairs of electrons are on the central atom in each of the following molecules? (4.1) K/U
    - (a) SO_2
    - (b) NBr_3
    - (c) BF_3
    - (d) H_2O
47. (a) Draw the Lewis structure of the sulfate ion, SO_4^{2-}.
    (b) Sodium sulfate, Na_2SO_4, contains both ionic and covalent bonds. Identify the bonds. (4.1) T/I C
48. How many electrons surround the central atom in each of the following molecules? How many bonding pairs and lone pairs does each molecule have? (4.1) T/I
    - (a) SO_2
    - (b) NBr_3
    - (c) BF_3
    - (d) CO_2
    - (e) SCl_6
    - (f) $SiCl_4$
    - (g) H_2
    - (h) $AlBr_3$
49. Use the VSEPR theory to predict and draw the shape of each of the following molecules: (4.2) T/I C
    - (a) SCl_2
    - (b) AlF_3
    - (c) CH_3NBr_2
    - (d) CH_3BF_2
    - (e) $CH_3COCH_2CH_3$
50. Predict and draw the three-dimensional structure, including bond angles, for each of the following molecules: (4.2) T/I C
    - (a) SeO_3
    - (b) SeO_2
51. What is the shape of each of the following molecules? (4.2) T/I
    - (a) CS_2
    - (b) CH_3SH
    - (c) CH_3CN
    - (d) C_2F_4
52. Draw a Lewis structure for each of the following molecules or ions. Not all obey the octet rule. Indicate any coordinate bonds. (4.2) T/I C
    - (a) PH_4^+
    - (b) OH^-
    - (c) PO_4^{3-}
    - (d) SO_2
    - (e) O_3
    - (f) NO_2^-
53. Arrange the bonds in each of the following groups in order of increasing polarity: (4.3) T/I
    - (a) Li–H, Mg–H, B–H, N–H, O–H
    - (b) Al–F, Ga–Br, Ge–Cl, Sn–F
    - (c) P–S, P–Cl, P–O, P–F, P–H
54. Identify each of the following chemical bonds as ionic, covalent, or polar covalent: (4.3) K/U
    - (a) P–F
    - (b) Li–H
    - (c) Mg–Cl
    - (d) P–H
    - (e) Si–Br
    - (f) Ge–H
55. Indicate the bond polarity by determining the partial positive and partial negative charges on the atoms in each of the following bonds: (4.3) T/I
    - (a) Cl–Si
    - (b) Li–H
    - (c) Al–I
    - (d) Ge–H
56. Identify all atoms that can form a polar covalent bond with bromine such that the bromine atom has a partial positive charge. (4.3) T/I
57. Which of the following molecules would orient in an electric field? Explain why. (4.5) T/I
    - (a) CS_2
    - (b) CH_3OH
    - (c) C_5H_{12}
    - (d) SCl_2
    - (e) OF_2

58. Use partial charges to represent the dipole in the bonds of each of the following molecules: (4.5) T/I
   (a) B–B in B_2H_4
   (b) S–C in CH_3SH
   (c) H–C in C_5H_{12}
   (d) C–N in HOCN

59. Identify the molecules that have polar bonds but do not have a net dipole. State your reasoning. Then determine which molecules have a net dipole. State your reasoning. (4.5) T/I
   (a) $SiBr_4$
   (b) $SiHBr_3$
   (c) BH_2F
   (d) PH_3

60. Predict the polarity of each of the following molecules: (4.5) T/I
   (a) SeO_2
   (b) SBr_2
   (c) SiO_2
   (d) SeO_3
   (e) N_2O

61. When a negatively charged ebonite rod is brought close to a stream of water, the water will be attracted to the rod. When a positively charged glass rod is brought close to a stream of water, the water will also be attracted to the rod. (4.5) K/U C A
   (a) Explain why this is possible.
   (b) Draw a diagram for each situation, clearly showing the water molecules' dipole.

62. Predict the hybridization of the indicated atom in each of the following molecules: (4.6) T/I
   (a) C in CH_3OH
   (b) N in NCl_3
   (c) B in BBr_3
   (d) C in HCOH

63. What is the hybridization at the central atom in each of the following molecules? (4.6) T/I
   (a) SiF_4
   (b) $BeBr_2$
   (c) $AlCl_3$
   (d) C_2Cl_4
   (e) CO

64. Indicate the types of bonds formed in each molecule in Question 63. (4.6) T/I

65. (a) Draw the Lewis structure of an oxygen molecule, O_2.
   (b) Describe the bonds in the oxygen molecule. (4.6) T/I C

66. In graphite, the carbon atoms are joined together by covalent bonds formed from their sp^2 orbitals. (4.6) K/U T/I C A
   (a) Draw a diagram of what a layer of graphite would look like. Include at least 12 atoms of carbon.
   (b) Each sp^2 orbital contains 1 electron, which enters into a covalent bond. Since each carbon has 4 valence electrons, what orbital would the fourth electron be in?
   (c) Each layer in graphite is attracted to the layer above it and the layer below it. Based on what you know about orbitals, explain how this is possible.

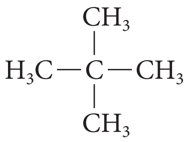
67. Why are triple bonds shorter and stronger than double or single bonds? Why are double and triple bonds more reactive than single bonds? Use diagrams to support your answer. (4.6) T/I C

68. Illustrate the bonding in the nitrogen molecule, N_2. Indicate sigma and pi bonds, and the orbitals used to make each. (4.6) T/I C

69. (a) Draw a Lewis structure of 1,3-butadiene, $CH_2CHCHCH_2$.
   (b) Determine the hybrid orbitals used by each carbon atom.
   (c) Draw the orbitals of the molecule before bonding and after the bonds have formed.
   (d) Label the sigma or pi bonds, and indicate the orbitals used in each bond.
   (e) Would the same orbitals be used in 1,2-butadiene, CH_2CCHCH_3? Why or why not? (4.6) T/I C

70. Ethanol and methoxymethane are isomers of each other (they have the same molecular formula, C_2H_6O). Ethanol, CH_3CH_2OH, boils at 78.4 °C, whereas methoxymethane, CH_3OCH_3, boils at −23.7 °C. Explain why their boiling points are different. (4.7) T/I

71. Indicate which compound in each of the following pairs has the higher boiling point: (4.7) T/I
   (a) *n*-pentane, $CH_3CH_2CH_2CH_2CH_3$, or neopentane,



$$H_3C-\overset{\displaystyle CH_3 \atop |}{\underset{| \atop \displaystyle CH_3}{C}}-CH_3$$

   (b) HF or HCl
   (c) HCl or LiCl
   (d) pentane, $CH_3CH_2CH_2CH_2CH_3$, or hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$

72. Predict which substance from each pair listed will have greater intermolecular forces: (4.7) T/I
   (a) propane (C_3H_8) or ethanol (C_2H_5OH)
   (b) SiH_4 or CH_4
   (c) H_2O or H_2S
   (d) C_2H_5OH or CH_3COH
   (e) C_2H_5OH or C_4H_9OH

73. **Table 1** shows the boiling points and the energy required to evaporate various substances. Explain explain each difference below. (4.7) T/I A

Table 1

Compound	Boiling point (°C)	ΔH_{vap} (kJ/mol)
benzene, C_6H_6	80	33.9
naphthalene, $C_{10}H_8$	218	51.5
carbon tetrachloride, CCl_4	76	31.8
acetone, CH_3COCH_3	56	31.8
benzoic acid, C_6H_5COOH	249	68.2

(a) Acetone has a lower boiling point than carbon tetrachloride.
(b) Naphthalene has a higher ΔH_{vap} than benzene.
(c) Benzoic acid has a higher boiling point than benzene.
(d) Naphthalene has a lower ΔH_{vap} than benzoic acid.

74. Identify the type of solid that each of the following substances forms: (4.8) T/I
(a) $CaSO_4$
(b) NaOH
(c) U
(d) PH_3

75. What type of bonding would you expect for each of the following solids? (4.8) T/I
(a) K2S
(b) SiH_4
(c) Zn
(d) SiO_2

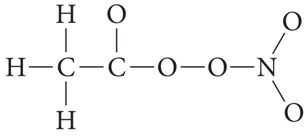
76. What type of bonding would you expect for each of the following substances? List one additional property that you would expect each substance to have. (4.1, 4.8) K/U A
(a) a molecular element that is a gas at room temperature
(b) a hard, silver-grey solid that conducts electricity as a solid
(c) a very hard, insoluble crystal that does not conduct electricity as a solid or a liquid
(d) a hard, brittle solid that dissolves in water

77. Compare and contrast the chemical properties you would expect for the solids aluminum and aluminum oxide. (4.8) T/I

78. Which of the solid substances in each pair has a higher melting point? Explain your answer. (4.8) T/I
(a) SiC and Pb
(b) I_2 and Na_3PO_4
(c) H_2O and H_2Se

Evaluation

79. Peroxyacetylnitrate (PAN) is present in photochemical smog. Draw a Lewis structure for PAN. The arrangement of atoms is

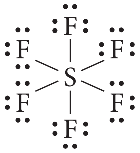


(4.1) T/I C

80. (a) Many different types of animals (including mollusks, bivalves, corals, and snails) have protective shells made from calcium carbonate, $CaCO_3$. Draw a Lewis structure of calcium carbonate. Include charges in your drawing.
(b) Predict the shape and bond angles of the carbonate ion.
(c) Which orbital is used by the carbon atom to form each type of bond? (4.1, 4.6) T/I C

81. Your classmate was reviewing notes on bonding, and said, “A bond is either purely covalent, polar, or purely ionic. It is all very black and white.” Do you agree or disagree with this statement? Justify your answer. Are there any exceptional cases where it could be true or untrue? (4.3) K/U T/I C

82. Molecules with *d* orbitals can have more than 8 electrons around the central atom. The Lewis structure for sulfur hexafluoride, SF_6, is



(a) State the orientation that would allow the greatest separation between bonding electrons in sulfur hexafluoride, and state the shape of this molecule.
(b) Draw the three-dimensional structure of phosphorus pentachloride, PCl_5. (4.2) K/U T/I C

83. Which of the following substances would you expect to be the most polar: carbon dioxide, CO_2; carbonate ion, CO_3^{2-}; methanol, CH_3OH; or methyl mercaptan, CH_3SH? Explain your answer. (4.3, 4.5) T/I A

84. A capacitor is a device that stores electrical energy. Which of the following substances, water or hexane, $C_6H_{14}(l)$, would be a better choice for use in a capacitor? Explain. (4.5) T/I A

85. For each molecule below, draw the Lewis structure, predict the geometry, determine the bond angle and polarity, and indicate the hybridization. (4.1, 4.2, 4.3, 4.5, 4.6) K/U T/I C
   (a) OF_2
   (b) CF_4
   (c) BeF_2
   (d) C_2F_2

86. The molecule $H_2C{=}CHCH{=}CH_2$ is a 4-carbon hydrocarbon molecule with 2 double bonds. (4.1, 4.2, 4.3, 4.5, 4.6) K/U T/I C
   (a) Draw the Lewis structure for this molecule.
   (b) Determine the structure and hybridization around each carbon atom, including bond angles.
   (c) State whether the molecule is polar.

87. Explain the geometry and shape of the phosphate ion, PO_4^{3-}. Include bond angles and hybridization. (4.2, 4.6) T/I

88. Propyne, $C_3H_4(g)$, is a 3-carbon hydrocarbon with multiple bonds. Propose a structure for propyne, describing angles, hybridization, and types of bonds. (4.2, 4.3, 4.6) T/I

89. Consider the three-dimensional structure of iodine pentafluoride, IF_5, according to the VSEPR theory. (4.2, 4.3, 4.6) T/I
   (a) Does this molecule follow the octet rule?
   (b) How many electrons are in the valence shell of iodine?

90. Hydrogen peroxide, H_2O_2, is a viscous liquid with a relatively low vapour pressure and a boiling point of 152.2 °C. Explain why this molecule's physical properties are different from those of water. (4.7) A

91. Use intermolecular forces to account for the trends in melting points in **Table 2**. (4.7, 4.8) K/U T/I

Table 2

Compound	Melting point (°C)
NaCl	801
$MgCl_2$	708
$AlCl_3$	190
$SiCl_4$	−70
PCl_3	−91
SCl_2	−78
Cl_2	−101

Reflect on Your Learning

92. You have studied different types of chemical bonds in this chapter. Write a one-page report about the topic and why it is important to you. What else would you like to know about this topic? How could you go about acquiring this knowledge? C

93. When studying this chapter, you first read about types of chemical bonds and then about VSEPR theory. Write a paragraph explaining why it was helpful to learn about these topics in this order instead of in the reverse order. C

94. How did the information you learned in this chapter affect your thinking about the structure and properties of solids? C

95. How would you explain the concepts of molecular polarity, intermolecular forces, and structure of solids to a fellow student who has not taken chemistry? K/U C

Research

WEB LINK

96. Vitamin C is an essential nutrient that we need to protect us against oxidation. This molecule is also a cofactor, which means it is used in chemical reactions and changes slightly during a chemical reaction. Research and draw the Lewis structure of vitamin C. Include molecular polarity in your analysis. T/I C A

97. Intermolecular forces are common in biological molecules. Investigate the intermolecular forces in DNA, including base pairing. Describe structures and the number of hydrogen bonds that form per base pair. Use this information to describe the stability and structure of DNA. T/I A

98. Many common household cleaners, such as stain removers, are based on the use of polar and non-polar molecules. Investigate the ingredients in some stain removers, and determine how polar and non-polar molecules are involved in these cleaners. T/I A

99. Research carbon nanotubes and their chemical and physical properties. How does the bonding in carbon nanotubes differ from other substances made of carbon? What are some applications of carbon nanotubes? T/I A

100. Asbestos is a naturally occurring fibre that has amazing fire-resistant properties. T/I A
   (a) Research the bonding in asbestos.
   (b) What type of structure is asbestos? Explain how its structure determines its fire-resistant properties.
   (c) Why has asbestos been important to the Canadian economy in the past?
   (d) What are the health concerns with asbestos? How are the health concerns related to its structure?
   (e) There are still places in Canada where asbestos is mined and then exported to other countries. Do you think this practice should continue? Give reasons for your answer.

Altered Reality

In our universe, the arrangement of the elements in the periodic table is a direct consequence of their four quantum numbers: n, l, m_l, and m_s. For example, all Group 1 elements have a similar electron configuration of 1 electron in the outermost *s* orbital. This configuration determines many of the group's chemical properties. The following is a description of each quantum number:

- n: main energy level, $n = 1, 2, 3, 4, \ldots$
- l: shape of the orbitals (*s*, *p*, *d*, *f*, etc.), $l = 0$ to $n - 1$
- m_l: magnetic quantum number for orbital orientation, where $m_l = -l$ to $+l$
- m_s: spin quantum number, $m_s = -\frac{1}{2}, +\frac{1}{2}$

Imagine a new universe in which this chemical reality has changed, and the universe now follows a different set of quantum number rules—the old rules no longer apply. In the new universe, the following change occurred:

$$m_l = -(n + 1) \text{ to } (n + 1)$$

All of the other quantum numbers, n, l, and m_s, remain the same.

This change in one quantum number changes not only the laws of physics, but the periodic table as well—the chemical properties of the elements change. Your new universe is made of elements that are arranged differently and follow a different set of fundamental standards from the elements in this universe (**Figure 1**).

Task

In this Unit Task, you are a chemist who is responsible for developing a new periodic table of the first 40 elements. You will need to compile this new periodic table based on the new definition of the magnetic quantum number. This exercise will help you understand how chemists developed the original periodic table that we use today. In this task, you will test your understanding of the use of quantum numbers to describe the organization of elements in the periodic table.

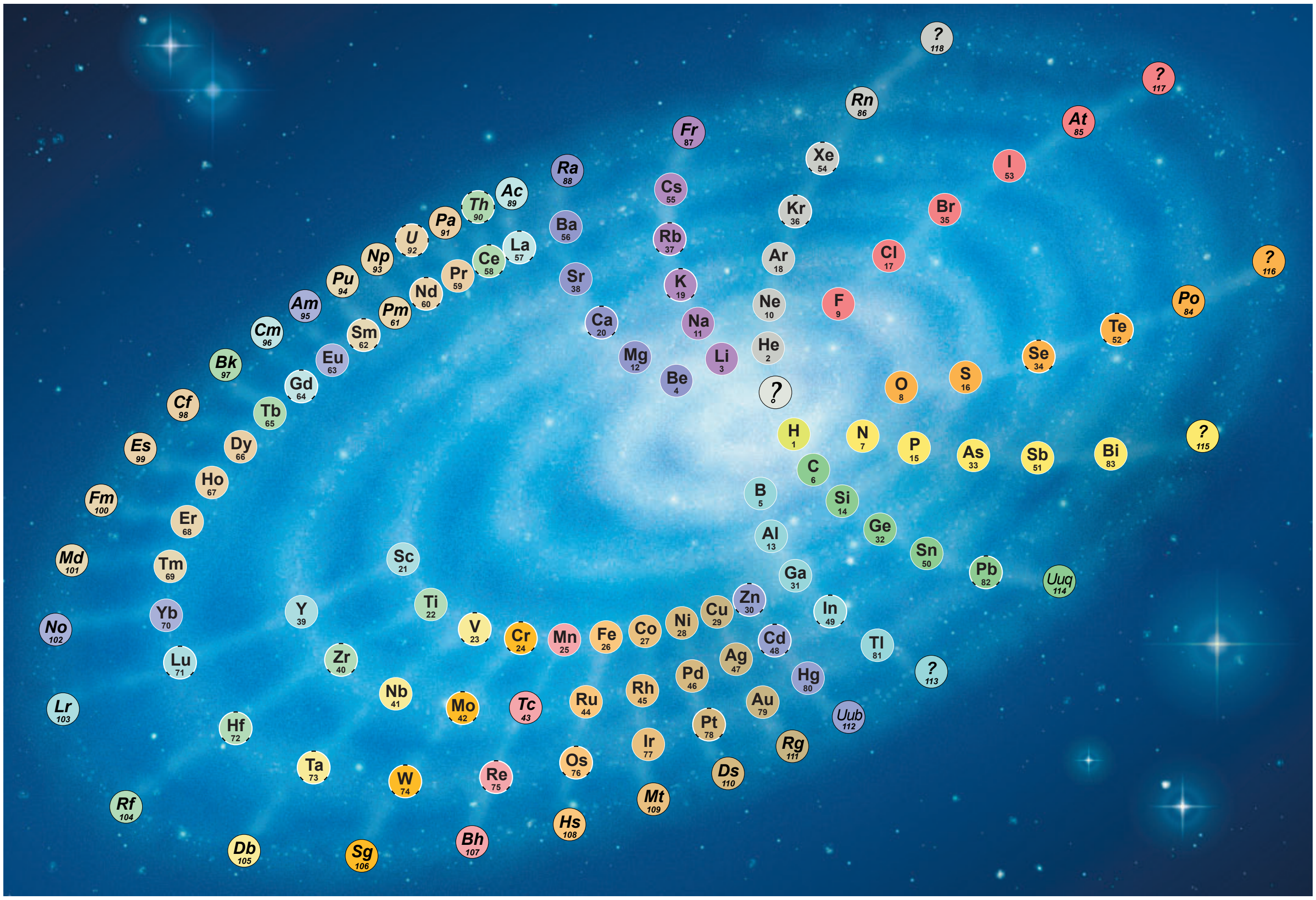


Figure 1 The new universe has a different set of rules for the magnetic quantum number m_l.

Purpose

To understand the relationship between quantum numbers and periodic trends among the elements by creating a new periodic table of the elements based on a hypothetical change to the magnetic quantum number

Procedure

1. Using enough space for 40 elements, draw the outline of your new periodic table in which elements have a magnetic quantum number $m_l = -(n+1)$ to $(n+1)$.
2. Identify the groups and periods in your new periodic table.
3. Add the elements to your new table. You can use the names of the current first 40 elements, or you can create your own element names.

Analyze and Evaluate

(a) What variables did you use in this activity? What did you change? What was the result of each change? T/I

(b) Explain how the number of electrons allowed into the *s*, *p*, *d*, and *f* orbitals has changed from the real periodic table. T/I

(c) In your new periodic table, why is there a different number of groups compared to the real periodic table? T/I

(d) In your new periodic table, why is there a different number of elements in a given period compared to the real periodic table? T/I

(e) What are the atomic numbers of the elements in the new universe that are likely to have properties similar to the alkali metals in our universe? Why? T/I

(f) How many of the first 40 elements are probably non-metals? Why? T/I

(g) What is the electron configuration of element number 20 in the new periodic table? T/I

(h) How do you think chemical bonding would be different in this new universe? T/I

(i) Copy **Table 1** into your notebook and complete it with the allowed values for all four quantum numbers for the elements in your new periodic table. T/I C

Table 1 Quantum Numbers for New Periodic Table

Principal quantum number (n)	Secondary quantum number (l)	Magnetic quantum number (m_l)	Spin quantum number (m_s)
1	0 (*s*)		
2	0 (*s*)		
	1 (*p*)		
3	0 (*s*)		
	1 (*p*)		
	2 (*d*)		

Apply and Extend

(j) Imagine that you have just made a purchase and the company from which you have bought your item is ready to send it to you. Explain how quantum numbers are similar to your address. C A

(k) What would happen if you only gave the store your street address? Compare this situation to knowing only one quantum number. C A

ASSESSMENT **CHECKLIST**

Your completed Unit Task will be assessed according to the following criteria:

Knowledge/Understanding

✓ Identify the manipulated and controlled variables.

Thinking/Investigation

✓ Develop a plan to determine the arrangement of elements in your new periodic table.

✓ Correctly use the variables in the activity.

✓ Fill out the new periodic table correctly.

✓ Analyze the results.

✓ Evaluate the new periodic table.

Communication

✓ Effectively illustrate the new periodic table.

✓ Prepare a suitable lab report that includes the complete procedure for creating the new periodic table, the completed new periodic table, a summary of the new periodic table, and your analysis and evaluation of the new periodic table.

Application

✓ Analyze the new table and compare it to the current periodic table.

UNIT 2 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Which of the following is true about the proton? (3.1) K/U
   (a) It is negatively charged.
   (b) It was the last subatomic particle to be discovered.
   (c) Its mass is less than that of an electron.
   (d) It is located in the nucleus.
2. How many neutrons does the argon isotope $^{37}_{18}\text{Ar}$ contain? (3.1) K/U
   (a) 18
   (b) 19
   (c) 37
   (d) 55
3. Which subatomic particles are located in the nucleus of the atom? (3.1) K/U
   (a) protons and neutrons
   (b) protons and electrons
   (c) neutrons and electrons
   (d) protons, neutrons, and electrons
4. What happened when Ernest Rutherford fired alpha particles at a thin piece of gold foil? (3.1) K/U
   (a) Most of the alpha particles bounced straight back, and a few went straight through.
   (b) All of the alpha particles were scattered at different angles.
   (c) Most alpha particles went straight through, a few were scattered at different angles, and some bounced straight back.
   (d) All of the alpha particles went straight through.
5. What is the mass number of an atom that contains 3 protons and 4 neutrons? (3.1) K/U
   (a) 1
   (b) 3
   (c) 4
   (d) 7
6. What are isotopes? (3.1) K/U
   (a) atoms with the same number of protons but a different number of electrons
   (b) atoms with the same number of protons but a different number of neutrons
   (c) atoms with the same mass number but a different number of neutrons
   (d) atoms with the same mass number but different atomic numbers
7. The Bohr model of the atom
   (a) applies to all atoms except hydrogen
   (b) explains the hydrogen emission spectrum
   (c) explains continuous spectra
   (d) is the current model of the atom (3.2) K/U
8. When is a line spectrum produced? (3.2) K/U
   (a) when white light is passed through a prism
   (b) when excess energy is released by the emission of light of various wavelengths
   (c) when electrons are emitted from the surface of a material
   (d) when electromagnetic energy is emitted from a black object that has been heated
9. How many sublevels can be present in the third principal energy level? (3.4) K/U
   (a) 3
   (b) 6
   (c) 9
   (d) 12
10. What are the possible values of m_l for $l = 1$? (3.4) K/U
    (a) 0
    (b) $-1, 0, 1$
    (c) $-2, -1, 0, 1, 2$
    (d) $-3, -2, -1, 0, 1, 2, 3$
11. Which of the following lists the allowed subshells for $n = 3$? (3.4) K/U
    (a) 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*
    (b) 3*s*, 3*p*
    (c) 3*s*, 3*p*, 3*d*
    (d) 3*s*, 3*p*, 3*d*, 3*f*
12. According to the aufbau principle,
    (a) it is impossible to know the exact position of an electron
    (b) electrons are added to the lowest-energy orbital available
    (c) the lowest energy configuration for an atom is the one that has the maximum number of unpaired electrons
    (d) energy can exist only in discrete amounts (3.5) K/U
13. What is the electron configuration of the sodium atom? (3.5) K/U
    (a) $1s^2 2s^2 2p^6 3s^1$
    (b) $1s^2 2s^2 2p^6 3s^2$
    (c) $1s^2 2s^2 2p^2 3s^2 3p^2$
    (d) $1s^2 2s^2 2p^1$
14. Which of the following elements has 3 valence electrons? (3.5) K/U
    (a) lithium
    (b) magnesium
    (c) titanium
    (d) aluminum

15. Which element has the electron configuration $1s^22s^22p^63s^23p^64s^23d^{10}4p^5$? (3.5) K/U
    (a) Br
    (b) Cl
    (c) Pb
    (d) Kr
16. Which of the following correctly matches the group name and the group label on the periodic table? (3.5) K/U
    (a) noble gases — 18
    (b) alkali metals — 2
    (c) halogens — 16
    (d) alkaline earth metals — 13
17. The sodium ion, Na^+, has
    (a) 11 protons and 11 electrons
    (b) 11 protons and 10 electrons
    (c) 12 protons and 11 electrons
    (d) 10 protons and 11 electrons (4.1) K/U
18. A bromide ion has the same number of electrons as
    (a) I
    (b) Cl
    (c) Ar
    (d) Kr (4.1) K/U
19. What type of bond is formed by the transfer of electrons between atoms? (4.1) K/U
    (a) ionic bond
    (b) polar covalent bond
    (c) non-polar covalent bond
    (d) coordinate covalent bond
20. Which of the following compounds would you expect to have covalent bonds? (4.1) K/U
    (a) KCl
    (b) Na_2O
    (c) CO_2
    (d) BaS
21. What type of molecular geometry results from 4 shared electron pairs around the central atom? (4.2) K/U
    (a) linear
    (b) bent
    (c) trigonal planar
    (d) tetrahedral
22. From its Lewis structure, how many lone electron pairs are there on nitrogen in nitric acid, $HNO_3(aq)$? (4.2) K/U C
    (a) 0
    (b) 1
    (c) 2
    (d) 3
23. Which of the following molecules has a linear shape? (4.2) K/U
    (a) $BeCl_2$
    (b) H_2O
    (c) H_2S
    (d) CCl_4
24. Which element has the lowest electronegativity? (4.3) K/U
    (a) F
    (b) H
    (c) At
    (d) Fr

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

25. The electron is the most massive particle in an atom. (3.1) K/U
26. The neutron is a negatively charged subatomic particle. (3.1) K/U
27. A radioisotope is an isotope that emits subatomic particles. (3.1) K/U
28. Most of the mass of an atom is concentrated in a positive, dense centre called the nucleus. (3.1) K/U
29. A line spectrum results when white light is passed through a prism. (3.2) K/U
30. The movement of an electron to a different energy level is called a transition. (3.2) K/U
31. John Dalton originated the idea that the electron also exhibits wave properties. (3.3) K/U
32. The Heisenberg Uncertainty Principle states that it is impossible to know the speed and position of an electron at the same time. (3.3) K/U
33. According to the Pauli exclusion principle, in a given atom, 2 electrons can have the same set of four quantum numbers. (3.4) K/U
34. The valence electrons are the electrons in an atom that can be gained or lost in a chemical reaction. (3.5) K/U
35. Ionic compounds are electrically charged. (4.1) K/U
36. Most ionic compounds are crystalline solids at room temperature. (4.1) K/U
37. Three-dimensional structure describes the three-dimensional arrangement of atoms in a pure substance. (4.2) K/U
38. Carbon dioxide molecules have a bent shape. (4.2) K/U
39. In a polar covalent bond, electrons are shared equally between atoms. (4.3) K/U
40. Electronegativity is the ability of an atom in a molecule to attract electrons to itself. (4.3) K/U
41. A molecule is polar if it contains at least one polar bond and is not symmetrical about the central atom. (4.5) K/U
42. Hybridization is based on the concept that all hybridized orbitals are identical. (4.6) K/U
43. Semiconductors are doped with atoms that have the same number of valence electrons as the semiconductor atoms. (4.8) K/U

UNIT 2 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Which of these statements correctly describes the nucleus of an atom? (3.1) K/U
   (a) It is neutral.
   (b) It is positively charged and very dense.
   (c) It contains protons and electrons.
   (d) It has a small mass compared to the rest of the atom.
2. Which of the following correctly describes a neutron? (3.1) K/U
   (a) It is located in the nucleus.
   (b) It has no charge.
   (c) It has approximately the same mass as a proton.
   (d) all of the above
3. The mass number of an atom is
   (a) the number of protons in the nucleus
   (b) the sum of the protons and electrons
   (c) the sum of the protons and neutrons
   (d) the sum of the protons, neutrons, and electrons (3.1) K/U
4. Which of the following pairs of symbols represents isotopes of the same element? (3.1) K/U
   (a) $^{12}_{6}$C and $^{12}_{7}$C
   (b) $^{12}_{6}$C and $^{13}_{7}$C
   (c) $^{12}_{6}$C and $^{12}_{6}$C
   (d) $^{12}_{6}$C and $^{13}_{6}$C
5. A neutral atom has an atomic number of 26 and a mass number of 58. How many protons, neutrons, and electrons does the atom have? (3.1) K/U
   (a) 26 protons, 26 neutrons, and 26 electrons
   (b) 58 protons, 26 neutrons, and 26 electrons
   (c) 26 protons, 32 neutrons, and 26 electrons
   (d) 26 protons, 58 neutrons, and 32 electrons
6. What is the name given to the observation that electrons are emitted from matter after the matter absorbs energy from short waves of electromagnetic radiation? (3.2) K/U
   (a) the photoelectric effect
   (b) blackbody radiation
   (c) quantum theory
   (d) the Pauli exclusion principle
7. What can happen when a substance absorbs energy? (3.2) K/U
   (a) Electrons in the substance transition from their ground state to an excited state.
   (b) Excess energy is released by the emission of light of various wavelengths.
   (c) Electrons are emitted from the surface of the material.
   (d) all of the above
8. Which of the following is included in quantum theory? (3.1) K/U
   (a) Light has properties of waves.
   (b) Light has properties of particles.
   (c) Particles have properties of waves.
   (d) all of the above
9. According to Heisenberg's uncertainty principle,
   (a) atomic orbitals can be described by a set of quantum numbers
   (b) electrons travel in distinct paths called orbits
   (c) it is impossible to know the exact position and speed of an electron at the same time
   (d) in a given atom, no 2 electrons can have the same set of four quantum numbers (3.3, 3.4) K/U
10. What is the maximum number of electrons that can occupy the second energy level? (3.4) K/U
   (a) 1
   (b) 2
   (c) 4
   (d) 8
11. Which of the following orbitals is the highest in energy? (3.4) K/U
   (a) 3*p*
   (b) 3*d*
   (c) 4*s*
   (d) 4*p*
12. Which of the following orbital designations is incorrect? (3.4) K/U
   (a) 1*p* (c) 3*f*
   (b) 2*d* (d) all of the above
13. Which is the electron configuration for the element gallium? (3.5) K/U
   (a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5 4p^6$
   (b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
   (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
   (d) $1s^2 1p^6 2s^2 2p^6 3s^2 3p^6 4s^2 4p^4$

14. Which of the following correctly matches the group name with the number of valence electrons? (3.5) K/U
(a) noble gases — 3
(b) alkali metals — 4
(c) halogens — 5
(d) alkaline earth metals — 2

15. What is the basis of ionic bonding? (4.1) K/U
(a) the equal sharing of bonding electrons
(b) the transfer of an electron from a non-metal to a metal
(c) the electrostatic attraction between oppositely charged ions
(d) the unequal sharing of bonding electrons

16. Which of the following describes how an atom can obtain an octet of electrons? (4.1) K/U
(a) by gaining electrons until it has 8 valence electrons
(b) by losing electrons until it has 8 valence electrons
(c) by sharing electrons until it has 8 valence electrons
(d) all of the above

17. A fluoride ion has
(a) 9 protons and 10 electrons
(b) 9 protons and 9 electrons
(c) 10 protons and 9 electrons
(d) 9 protons and 8 electrons (4.1) K/U

18. Which of the following contains a coordinate covalent bond? (4.1) K/U
(a) NH_4^+
(b) Cl_2
(c) H_2O
(d) NaCl

19. How many electrons are in a typical calcium ion? (4.1) K/U
(a) 2
(b) 18
(c) 20
(d) 22

20. In reactions with non-metals, metals tend to
(a) gain electrons and become negative ions
(b) gain electrons and become positive ions
(c) lose electrons and become negative ions
(d) lose electrons and become positive ions (4.1) K/U

21. Which of the following pairs of elements would most likely form a covalent compound? (4.1) K/U
(a) aluminum and silicon
(b) calcium and oxygen
(c) hydrogen and sulfur
(d) calcium and potassium

22. Which of the following molecules has a triple bond? (4.2) K/U
(a) NH_3
(b) HF
(c) CO_2
(d) C_2H_2

23. What is the shape of a molecule of carbon tetrachloride, CCl_4? (4.2) K/U
(a) linear
(b) trigonal planar
(c) tetrahedral
(d) octahedral

24. How many lone electron pairs does the Lewis structure for the ammonia molecule have on the central atom? (4.2) K/U
(a) 0
(b) 1
(c) 2
(d) 3

25. In a polar covalent bond, valence electrons are
(a) equally shared between atoms
(b) unequally shared between atoms
(c) transferred from a metal to a non-metal
(d) transferred from a non-metal to a metal (4.3) K/U

26. Which element has the highest electronegativity? (4.3) K/U
(a) I
(b) Br
(c) Cl
(d) F

27. If the difference in the electronegativity between 2 atoms is less than 0.5, then the bond between them is
(a) polar covalent
(b) non-polar covalent
(c) ionic
(d) none of the above (4.3) K/U

28. What type of orbital hybridization is present in a water molecule? (4.6) K/U
(a) sp
(b) sp^2
(c) sp^3
(d) sp^3d

29. Hydrogen bonding is the strong intermolecular force between hydrogen atoms and
(a) oxygen atoms
(b) fluorine atoms
(c) nitrogen atoms
(d) all of the above (4.7) K/U

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

30. A proton is a negatively charged subatomic particle. (3.1) K/U
31. Radiation is the travel of particles or energy waves through a medium or in space. (3.1) K/U
32. Electrons are attracted to protons but repel each other. (3.1) K/U
33. The atomic number of an atom is the sum of the protons and neutrons in the nucleus. (3.1) K/U
34. The nucleus accounts for most of an atom's mass. (3.1) K/U
35. Each element has a unique number of protons. (3.1) K/U
36. A quantum is a packet of energy. (3.1) K/U
37. If an electron emits a photon, it can drop to a lower energy level. (3.2) K/U
38. The highest energy state for an atom is its ground state. (3.2) K/U
39. Spectroscopy of excited gaseous elements led to the discovery of line spectra. (3.2) K/U
40. Blackbody radiation is the energy that would be emitted from an ideal blackbody. (3.1) K/U
41. Quantum theory is the theory that energy can exist only in discrete amounts. (3.3) K/U
42. An orbit is the region around the nucleus where there is a high probability of finding an electron. (3.3) K/U
43. The principal quantum number indicates the main energy level of an electron in an atom. (3.4) K/U
44. The electron configuration for the element calcium is $[\text{Ar}]4s^1$. (3.5) K/U
45. A magnesium atom has 3 valence electrons. (3.5) K/U
46. A lithium atom has 2 electrons in its second energy level. (3.5) K/U
47. Ionic bonds are formed by a transfer of electrons from metal atoms to non-metal atoms. (4.1) K/U
48. The bond between 2 chlorine atoms is ionic. (4.1) K/U
49. Lewis structures show the arrangement of electrons in a molecule. (4.1) K/U
50. Ionic compounds are composed of 2 or more non-metal ions. (4.1) K/U
51. A triple bond contains 3 shared pairs of electrons. (4.2) K/U
52. The Lewis structure for a water molecule has 1 lone pair of electrons on the central atom. (4.2) K/U
53. The valence shell electron-pair repulsion (VSEPR) theory describes how atomic orbitals and hybrid orbitals overlap to form a new orbital with a pair of opposite-spin electrons. (4.2) K/U
54. The polarity of a bond decreases as the electronegativity difference increases. (4.3) K/U
55. The end-to-end overlap of orbitals forms a pi bond. (4.6) K/U
56. Intramolecular forces occur between molecules. (4.7) K/U

Match the scientist on the left with the most appropriate discovery on the right.

57. (a) Max Planck
    (b) Albert Einstein
    (c) Louis de Broglie
    (d) Niels Bohr
    (e) Wolfgang Pauli
    (f) Werner Heisenberg
    (g) Erwin Schrödinger
    (h) James Chadwick
    (i) J.J. Thomson
    (j) Ernest Rutherford

    (i) idea that energy from a blackbody is quantized
    (ii) discovery of the neutron
    (iii) discovery of the nucleus
    (iv) idea that the energy of electrons is quantized
    (v) the photoelectric effect
    (vi) discovery of the electron
    (vii) the exclusion principle
    (viii) equation describing the energy and location of an electron in a hydrogen atom
    (ix) uncertainty principle
    (x) quantum theory (3.1, 3.2, 3.3) K/U

Match the term on the left with the most appropriate description on the right.

58. (a) linear
    (b) trigonal planar
    (c) tetrahedral
    (d) octahedral

    (i) has four bond angles of 90° in a plane and two bonds at 90° to the plane
    (ii) has a bond angle of 180°
    (iii) has bond angles of 109.5°, each equally positioned in four locations around the central atom
    (iv) has bond angles of 120° and all of the atoms are found in the same plane (4.2) K/U

Understanding

Write a short answer to each question.

59. Explain J.J. Thomson's "blueberry muffin model" of the atom. (3.1) K/U
60. What was Robert Millikan's contribution to atomic theory? (3.1) K/U
61. Explain how and why the results of Rutherford's gold foil experiment differed from his expectations. (3.1) K/U
62. What was the problem with the Rutherford atomic model? (3.1) K/U
63. How do isotopes of a given element differ? How are they similar? (3.1) K/U
64. How do the numbers of protons and electrons in a neutral atom compare? (3.1) K/U
65. What is the relationship between an isotope and a radioisotope? (3.1) K/U
66. What part of Dalton's atomic theory did Thomson disprove with the discovery of electrons? (3.1) K/U
67. According to Dalton's atomic theory, all atoms of a given element are identical in mass and other properties. Is this correct? Explain. (3.1) K/U
68. The three mass numbers of the three isotopes of neon are 20, 21, and 22. How many neutrons does each isotope have? (3.1) K/U
69. What is a cathode ray tube? (3.1) K/U
70. How does the mass of the nucleus compare with the mass of the rest of the atom? (3.1) K/U
71. Name two phenomena that support the concept that light is a packet of energy. (3.1) K/U
72. Why was the Bohr atomic model, although incorrect, a significant contribution to atomic theory? (3.2) K/U
73. How are scientists able to determine what elements are present in distant stars? (3.2) K/U
74. Draw an illustration that describes the relationships among emission spectra, line spectra, and continuous spectra. (3.2) K/U C
75. What conclusions did scientists draw from each of the following observations? (3.1, 3.2) K/U
    (a) An atom emits a specific set of frequencies of light when it is excited by thermal energy or electricity.
    (b) A beam of electrons is deflected by an electric field toward a positively charged plate.
76. What is an atomic orbital? (3.3) K/U
77. Why is it impossible to determine both the exact location and the velocity of an electron? (3.3) K/U
78. What information is given by the solutions to Schrödinger's equation? (3.3) K/U
79. Using n to represent the principal energy level number, write equations that show the relationship between
    (a) the principal energy level number and the number of sublevels (subshells)
    (b) the principal energy level number and the number of orbitals
    (c) the principal energy level number and the maximum number of electrons in an energy level (3.4) K/U T/I
80. Explain why the following set of quantum numbers is not possible: $n = 3$; $l = 3$; $m_l = 0$ (3.4) K/U
81. What is the maximum number of electrons that can have the same
    (a) n, l, m_l, and m_s quantum numbers?
    (b) n, l, and m_l quantum numbers?
    (c) n and l quantum numbers? (3.4) K/U
82. Identify the elements with these electron configurations: (3.5) K/U
    (a) $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$
    (b) $1s^22s^22p^63s^2$
    (c) $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^75s^1$
    (d) $1s^22s^22p^63s^23p^6$
83. An orbital representation uses circles or lines to represent atomic orbitals, and arrows to represent electrons. The direction of the arrow (up or down) represents the electron spin direction. For example, the orbital representation of a 3p sublevel consists of three lines or circles with each line or circle representing an orbital. Draw an orbital representation of a 3p sublevel that
    (a) shows a violation of Hund's rule
    (b) shows a violation of the Pauli exclusion principle
    (c) is a correct representation of a 3p sublevel with 3 electrons (3.5) K/U C
84. Write the name of the element that fits each description. (3.5) K/U
    (a) has 5 valence electrons in its third energy level
    (b) noble gas with 2 valence electrons
    (c) non-metal with 1 valence electron
    (d) semiconductor with 3 valence electrons
85. State the number of valence electrons in an atom of each element below. (3.5) K/U
    (a) aluminum
    (b) oxygen
    (c) helium
    (d) bromine

86. The term "isoelectronic" refers to entities that have the same electron configuration. For example, the magnesium ion, Mg^{2+}, and the fluoride ion, F^-, are isoelectronic. Write the formulas for two other atoms or ions that are isoelectronic with the magnesium and fluoride ions. (3.5) K/U

87. Why are there no transition elements in periods 1, 2, and 3? (3.5) K/U

88. Write the electron configuration of
    (a) the element with the highest electronegativity
    (b) the non-metal element in Group 4A
    (c) the transition element with the lowest atomic number
    (d) the noble gas that has 2 valence electrons (3.5) K/U

89. How many electrons are transferred from the beryllium atom to the sulfur atom when they form an ionic bond? (4.1) K/U

90. Explain why a fluoride ion is larger than a fluorine atom. (4.1) K/U

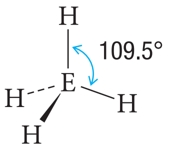
91. Indicate whether each of the following atoms is more likely to form a cation (a positively charged ion) or an anion (a negatively charged ion): (4.1) K/U
    (a) calcium
    (b) chlorine
    (c) lithium
    (d) oxygen

92. Indicate the most likely number of electrons each of the following atoms will gain or lose in forming ionic bonds: (4.1) K/U
    (a) sodium
    (b) phosphorus
    (c) chlorine
    (d) strontium

93. Draw a Venn diagram to compare and contrast ionic bonding and covalent bonding. (4.1) K/U T/I C

94. Why are ionic compounds electrically neutral? (4.1) K/U

95. Consider the following Lewis structure, where E is an unknown element. What are some possible identities for element E? (4.2) K/U



96. What is the difference between a bonded electron pair and a lone pair? (4.2) K/U

97. What is electron-pair repulsion? (4.2) K/U

98. How does electron-pair repulsion affect the shape of a molecule? (4.2) K/U

99. The molecule with the chemical formula $HOOCCH_2COCH_3$ is a 4-carbon chain with 1 oxygen atom (carbonyl group) double-bonded to carbon 3 and 1 oxygen atom (carboxylic acid) double-bonded to carbon 1. Use the VSEPR theory to describe the geometry around each of the carbon atoms. (4.2) T/I

100. What happens when the electronegativity difference between 2 atoms is very large? (4.3) K/U

101. Place the following elements in order of increasing electronegativity: K, Br, Na, O, S. (4.3) K/U

102. Choose the element in each of the following pairs that has the highest electronegativity: (4.3) K/U
    (a) K and Ca
    (b) O and F
    (c) S and Si
    (d) Ga and Ge

103. The electronegativity of the element hydrogen is the same as that of the element phosphorus, greater than that of the element boron, and less than that of the element carbon. List the following bonds in order of decreasing polarity: P–H, O–H, N–H, F–H, C–H. (4.3) K/U

104. Predict the type of bond—ionic, non-polar covalent, or polar covalent—that forms between the following pairs of elements: (4.3) K/U
    (a) Rb and Cl
    (b) S and S
    (c) C and F
    (d) Ba and S
    (e) N and P
    (f) B and H

105. Write Lewis structures, and predict the molecular structures of oxygen dichloride, OCl_2; krypton difluoride, KrF_2; beryllium hydride, BeH_2; sulfur dioxide, SO_2; sulfur trioxide, SO_3; nitrogen trifluoride, NF_3; iodine trifluoride, IF_3; tetrafluoromethane, CF_4; selenium tetrafluoride, SeF_4; krypton tetrafluoride, KrF_4; iodine pentafluoride, IF_5; and arsenic pentafluoride, AsF_5. Which of these molecules are polar? (4.1, 4.2, 4.5) K/U C

106. (a) Determine the electron configuration of each of the following atoms:
        (i) P
        (ii) S
        (iii) Br
        (iv) Si
    (b) Use your answers from (a) to draw the orbital diagram of the valence electrons for each of the above atoms. (4.6) K/U C

107. For each of the atoms in Question 106, determine the orbital it would use to bond with hydrogen atoms to form the following compounds: (4.6) K/U

(a) PH_3

(b) H_2S

(c) HBr

(d) SiH_4

108. Each of the following atoms reacts with hydrogen: (i) boron; (ii) nitrogen; (iii) carbon; and (iv) fluorine. (4.6) K/U T/I C

(a) Write the electron configuration for each atom.

(b) Draw the orbital diagrams, showing the valence electrons for each atom.

(c) Determine whether any electrons need to be promoted. If so, draw a new orbital diagram showing the excited-state atom.

(d) Hybridize the orbitals as needed. Draw the orbital diagrams, showing the hybrid orbitals.

(e) How many half-empty orbitals does each atom have? How many orbitals are available for bonding?

(f) State the orbital each atom would use to form a sigma bond with a hydrogen atom.

(g) Draw the resulting molecule.

109. Predict the hybridization of each atom, and describe the three-dimensional structure of each of the following molecules: (4.6) K/U T/I

(a) $BeCl_2$

(b) H_2S

(c) H_2CO

(d) SiF_4

110. Which liquid would have the greater surface tension: butane, $CH_3CH_2CH_2CH_3$, or 1-propanol, $CH_3CH_2CH_2OH$? Why? (4.7) K/U

111. Discuss the similarities and differences between

(a) polar bonds and hydrogen bonds

(b) dipole–dipole interactions and London dispersion forces (4.7) K/U T/I

112. Explain how the properties of each solid allow it to be used as described: (4.8) K/U A

(a) Copper is the most common metal used in electrical wires.

(b) Diamonds are used in industry as abrasives and drill tips.

(c) Liquid nitrogen (boiling point −196 °C) is used as a refrigerant.

113. Explain the difference between intramolecular forces and intermolecular forces. (4.8) K/U

114. (a) Characterize each of the following forces as intramolecular or intermolecular:

(i) van der Waals

(ii) London dispersion

(iii) dipole–dipole

(iv) hydrogen bonds

(v) covalent bonds

(b) Arrange the forces in (a) from strongest to weakest. (4.8) K/U

115. Why does molten potassium chloride, KCl(l), conduct electricity even though solid potassium chloride does not? (4.8) K/U A

116. Draw a chart showing the similarities and differences between

(a) metallic and ionic bonds

(b) network solids and covalent molecules (4.8) K/U C

117. What type of substance is each of the following? (4.8) K/U T/I

(a) Gallium crystals are shiny and silver-coloured. They are good conductors of electricity. Gallium metal melts at 29.8 °C.

(b) This compound has a very high melting point, is hard and brittle, and conducts electricity as a liquid but not as a solid.

(c) Liquid tin(IV) chloride does not conduct electricity. It forms crystals that are soft, and it has a melting point of −33 °C.

(d) Paradichlorobenzene is one of the main ingredients in mothballs. It has a melting point of 54 °C and crushes fairly easily.

(e) Mica is an unusual rock that cleaves (breaks) in very thin layers. It has a melting point of 1378 °C. It is chemically unreactive, and is stable when exposed to electricity, light, moisture, and extreme temperatures.

(f) Some semiconductors are made of the transition metal boron. Boron is very hard and has a melting point of 2349 °C.

(g) Hydrargyrum is a name once used for one of the elements. It is a shiny silver liquid at room temperature that conducts electricity very well.

118. How could you tell experimentally whether titanium dioxide, TiO_2, is an ionic solid or a network solid? (4.8) K/U T/I

119. What type of solid does each of the following substances form? (4.8) K/U T/I

(a) CO_2
(b) SiO_2
(c) Si
(d) CH_4
(e) Ru
(f) I_2
(g) KBr
(h) H_2O
(i) NaOH
(j) U
(k) $CaCO_3$
(l) PH_3

120. Identify the four substances in **Table 1** as ionic, network, metallic, or molecular solids. (4.8) K/U T/I

Table 1

Compound	Conducts electricity as a solid	Other properties
diborane, B_2H_6	no	gas at 25 °C
silicon dioxide, SiO_2	no	high melting point
cesium iodide, CsI	no	aqueous solution conducts electricity
tungsten, W	yes	high melting point

121. Briefly describe lattice structures. (4.8) K/U

122. Explain why ionic compounds are brittle. (4.8) K/U

123. Indicate whether each of the following is a property of ionic compounds or covalent compounds: (4.8) K/U

(a) form crystal lattices
(b) low melting and boiling points
(c) tend to be brittle solids
(d) tend to be soluble in water
(e) tend to have low solubility in water
(f) have high melting and boiling points

Analysis and Application

124. **Figure 1** shows how the electron clouds of 2 hydrogen atoms interact as a covalent bond forms. (4.1) K/U T/I C

(a) Draw a similar diagram showing how hydrogen and chlorine atoms will react to form a covalent bond. Show the attractive and repulsive forces.
(b) Draw a similar diagram showing how 2 fluorine atoms will react.

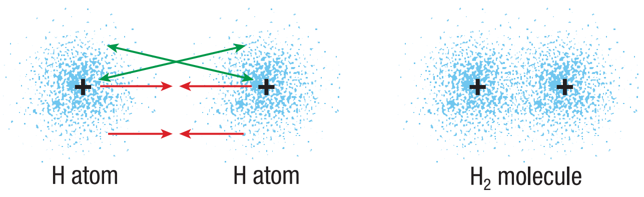
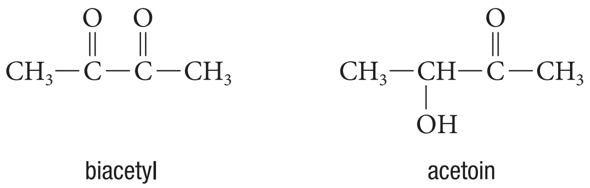


Figure 1

125. Using what you know about the structure of metals, covalent crystals and ionic substances, and the quantization of light, explain why the photoelectric effect is best demonstrated using metal. (3.1, 4.8) K/U A

126. Water is an unusual molecule. It has high melting and boiling points that are uncharacteristic and can dissolve many ionic compounds. As a result, it is the solvent of life. Biological life without water is difficult to imagine. Indeed, recent evidence of liquid water on Mars has sparked new interest in whether life has existed there in the past or currently exists. Based on your understanding of the structure of water predicted by VSEPR theory, suggest why water's structure is ultimately responsible for its remarkable properties. (4.2) K/U T/I A

127. Biacetyl and acetoin are added to margarine to make it taste more like butter. The structures of both compound s are shown in **Figure 2**. (4.3, 4.5, 4.6) T/I C A



$CH_3-C(=O)-C(=O)-CH_3$

$CH_3-CH(OH)-C(=O)-CH_3$

biacetyl acetoin

Figure 2

(a) Draw the Lewis structure for each compound and indicate the hybridization of the carbon atoms.
(b) Predict values for all C–C–O bond angles.
(c) How many sigma bonds and how many pi bonds are there in biacetyl and acetoin molecules?

128. Illustrate the bonding using diagrams of the orbitals for each of the following. Show the bonding orbitals formed. (4.6) K/U T/I C

(a) HF
(b) F_2
(c) BCl_3
(d) NF_3
(e) C_2Cl_4

129. Water is an extremely effective solvent for dissolving polar and ionic compounds. To work as a cleaning agent, the water first has to reach the "dirt." This can become a problem. The same property of water that makes it such a good solvent—its ability to form strong dipole–dipole interactions—also makes it difficult to get into the small spaces where dirt lingers. Water would rather interact with other water molecules than leave its neighbouring molecules in search of dirt. This tendency to be attracted to other similar molecules is called surface tension. Water's surface tension is extremely high. Surface tension is the enemy of cleaning systems. Special chemicals called surfactants are added to detergents specifically to lower the surface tension of water so it can penetrate small spaces and dislodge and dissolve

dirt. If you were asked to design a surfactant, what chemical properties would you want your surfactant molecule to have? How would you explain to a consumer how your surfactant works? (4.7) T/I C A

130. Hydrogen peroxide (H_2O_2) is a syrupy liquid with a relatively low vapour pressure and a boiling point of 152.2 °C. Explain the differences of these physical properties from those of water. (4.7) K/U A

131. Hydrogen bonds greatly affect the properties of water. In a format of your choice, describe how the world around us would be different if water did not have hydrogen bonds. (4.7) K/U T/I C A

132. The element selenium is a semiconductor used in photocopiers. What type of semiconductor would be formed if a small amount of indium impurity were added to pure selenium? (4.8) T/I A

Evaluation

133. Evaluate the benefits to society of nanoparticles used in medicine. What impact would the widespread use of nanoparticles have on the environment? (3.7) T/I C A

134. Cyclotrons, synchrotrons, and linear accelerators have been used to discover new subatomic particles. What social benefits are associated with these discoveries? (3.7) T/I C A

135. Evaluate the cost and environmental impact of several types of light bulbs. Include the advantages and disadvantages of each type. (3.7) T/I C A

Reflect on Your Learning

136. Many of the concepts in this unit are abstract. Describe some of the strategies you have used to understand these concepts. C

137. What information in this unit did you find most interesting? Why? What information did you find least interesting? Why? C

138. Think about what you already knew about atomic structure and bonding before beginning this unit. What misconceptions did you have? Where did they come from? How has working through this unit helped you identify and correct your misconceptions? C

139. How would you explain to a friend or family member who does not have any chemistry training what you learned in this unit? C

WEB LINK

Research

140. Many specialized materials have been created on the basis of scientific research into the structure of matter and chemical bonding. Research disposable diapers. T/I C A
    (a) What properties of disposable diapers enable them to hold so much liquid?
    (b) What impact has the widespread use of such diapers had on the environment?

141. An amorphous solid has no specific arrangement of its atoms or ions. Tar and wax are amorphous solids. Glass is also an amorphous solid. Most glass contains silicon dioxide, SiO_2, as the main ingredient. C A
    (a) Based on its chemical structure, is silicon dioxide an ionic or covalent compound?
    (b) Research the properties of glass. Do the properties of glass more closely match those of an ionic compound or a covalent compound? Discuss the structure and properties of glass. Give details to support your opinion on whether glass is an ionic or covalent compound.

142. Technological devices that are based on the principles of atomic and molecular structures can have societal benefits and costs. Discuss a technology that is based on the principles of atomic emission. Describe the social and economic implications of the technology. Share your findings in a written report. A C

143. The colours observed in fireworks displays are produced by heating metal salts. Use Internet resources to determine how salts are used in fireworks displays and the processes that cause these salts to emit light. Create a poster or electronic slideshow to share your findings. C A

144. What is known about the atom is due to contributions from several disciplines. Describe the contributions to atomic theory of at least eight philosophers, chemists, physicists, and mathematicians, choosing two people from each category. Prepare a timeline to display what you learned. C A

145. (a) What types of metals are used in dental amalgams? What properties of these metals allow them to be used for this purpose?
    (b) What metals are used to make coins? What are the properties of these metals? Why are they used instead of other metals? C A

146. Hair is composed mainly of a protein called keratin. What types of chemical bonds are present in hair? How do chemical processes such as perming and colouring affect these bonds? Use Internet resources to answer these questions. Prepare an advertisement or an electronic slideshow to share your findings. T/I A

147. Choose a radioisotope that is used in the diagnosis of disease. Explain what care must be taken in the storage, use, and disposal of this material. Prepare a workplace training brochure from the information you find. T/I A

UNIT 3

Energy Changes and Rates of Reaction

OVERALL EXPECTATIONS

- analyze technologies and chemical processes that are based on energy changes, and evaluate them in terms of their efficiency and their effects on the environment
- investigate and analyze energy changes and rates of reaction in physical and chemical processes, and solve related problems
- demonstrate an understanding of energy changes and rates of reaction

BIG IDEAS

- Energy changes and rates of chemical reaction can be described quantitatively.
- The efficiency of chemical reactions can be improved by applying optimal conditions.
- Technologies that transform energy can have societal and environmental costs and benefits.

UNIT TASK PREVIEW

In this Unit Task, you will quantitatively analyze the rate of a chemical reaction. You will compare the effectiveness of the addition of different catalysts to changing the rate at which hydrogen peroxide is broken down into simpler substances. The Unit Task is described in detail on page 402. As you work through the unit, look for Unit Task Bookmarks to see how information in the section relates to the Unit Task.

ARTIFICIAL PHOTOSYNTHESIS

Imagine if you could use solar energy to convert carbon dioxide gas and liquid water into fuel that could be used in place of fossil fuels. That is exactly what researchers at the Lawrence Berkeley National Laboratory in California are trying to do. These researchers are trying to develop an artificial version of photosynthesis. Photosynthesis is a chemical process that occurs in green plants. During photosynthesis, plants capture solar energy and use it to convert carbon dioxide gas and liquid water into energy-rich molecules such as glucose.

Artificial photosynthesis offers the promise of a renewable alternative to fossil fuels. Another important potential advantage of fuels produced through artificial photosynthesis is that they would be "carbon neutral". A carbon neutral fuel neither contributes to nor reduces the concentration of carbon in the atmosphere, making it environmentally friendly. Increases in atmospheric carbon dioxide gas concentration are a primary cause of global warming, which can lead to global climate change. For this reason, alternative fuels that do not increase atmospheric carbon concentrations are in demand. The carbon dioxide required to produce artificially photosynthesized fuel is readily available and very inexpensive. Atmospheric carbon dioxide is continually replenished by many activities, such as respiration of organisms and by burning hydrocarbon fuels to heat our homes and power our vehicles.

A key step in photosynthesis involves breaking down water molecules into hydrogen and oxygen atoms. To do this requires energy. In green plants, this reaction occurs at room temperature, using the energy of sunlight. Early attempts to mimic this reaction in the lab resulted in reactions that were too slow to be a practical way of producing fuels. That may soon change. Berkeley researchers have found that adding cobalt oxide crystals to the reaction mixture makes the breakdown of water occur much faster. Although this compound is not a reactant in artificial photosynthesis, it causes the reaction to occur faster. Next, scientists must find ways to mimic the many other steps in the complex process of photosynthesis. This ambitious goal will involve considerable research and development.

Questions

1. Give an example of a fuel that is renewable and a fuel that is non-renewable. Justify your choices.
2. Explain what is meant when we describe a process as being "carbon neutral."
3. Berkeley researchers found that the reaction in which water is broken down into hydrogen and oxygen atoms occurred much faster after they added cobalt oxide that had been ground into a fine powder. Suggest an explanation to account for this observation.
4. Scientific research can be very expensive. If you were the director of a lab conducting research into artificial photosynthesis, what organizations or companies would you approach to fund your research, and why? Are there any groups or organizations that you think would be likely to turn down your request? Explain.

UNIT 3 ARE YOU READY?

CONCEPTS

- describe the particle theory of matter
- understand the properties and behaviour of gases in terms of molecular motion
- describe various types of chemical reactions, including synthesis, decomposition, and combustion reactions
- understand a variety of energy transfers and transformations, and explain them using the law of conservation of energy
- distinguish, qualitatively, the relationship between efficiency and thermal energy transfer

SKILLS

- write balanced chemical equations
- perform stoichiometric calculations
- use significant digits
- identify safe laboratory procedures
- draw Lewis structures to represent the bonds in ionic and molecular compounds
- use appropriate terminology related to chemical reactions

Concepts Review

1. **Figure 1** shows three devices whose functions involve energy transformations. Identify the type of energy transformation(s) occurring in each case. K/U

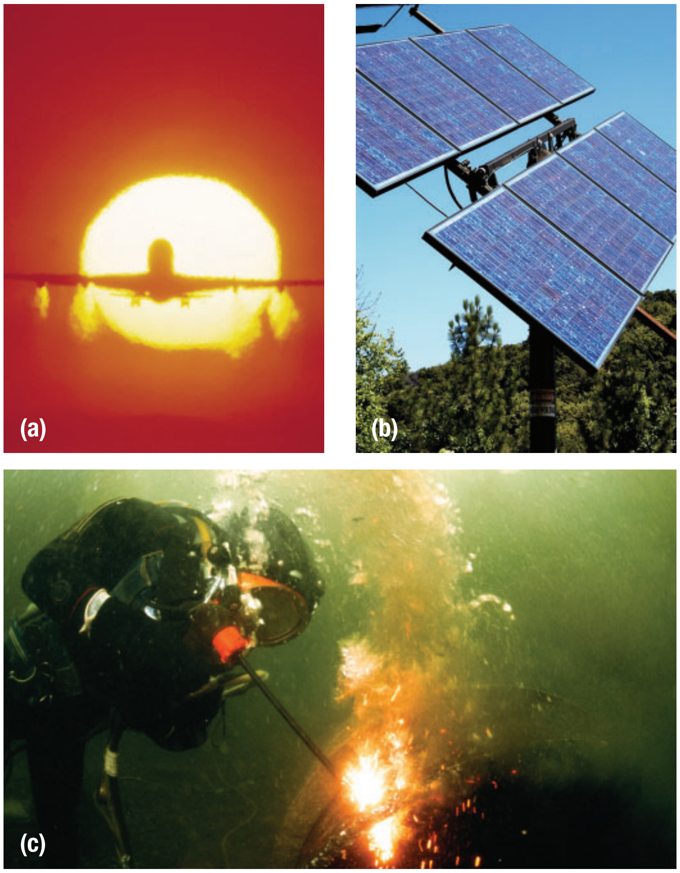


Figure 1 Examples of devices that involve the transformation of energy from one form to another: (a) A jet taking off (b) A solar panel generating electricity (c) An electric arc torch melting metal

2. A cold pack used for first-aid treatment is activated when two substances mix. Does the reaction between these substances absorb energy or release energy? Explain your reasoning. K/U
3. Explain why sodium metal reacts violently in water, while gold metal is inert. K/U
4. The kinetic molecular theory states that all matter is made up of particles that are in constant motion. Draw a diagram to illustrate the arrangement of particles in each of the different states of matter. Use arrows to show how the particles are moving. K/U C
5. For each example shown in **Figure 2**, state whether the water molecules release or absorb energy. K/U

Figure 2 Examples of water (a) melting, (b) condensing, (c) boiling, and (d) freezing

6. The following equation represents the decomposition of hydrogen peroxide:

   $$2\ H_2O_2(aq) \longrightarrow 2\ H_2O(l)\ +\ O_2(g)$$

   Predict whether the reaction absorbs energy or releases energy. Explain your reasoning. K/U T/I
7. Outline the changes in molecular motion that are predicted to occur when a sample of ice is heated until it is converted to steam. Explain your reasoning, using the particle theory of matter. Assume that the ice turns to liquid before it becomes steam. K/U A

Skills Review

8. Identify the variable that causes each of the following effects: K/U T/I
   (a) Sugar dissolves in hot water faster than in an equal volume of cold water.
   (b) Vinegar, 0.8 mol/L acetic acid, is safe to consume while lab-grade acetic acid, 15.0 mol/L, is corrosive.

9. Draw a Lewis structure for each of the following substances: K/U T/I C
   (a) chlorine, Cl_2
   (b) nitrogen, N_2
   (c) water, H_2O
   (d) carbon tetrachloride, CCl_4
   (e) carbon dioxide, CO_2
   (f) ethene, C_2H_4

10. (a) Write the chemical equation representing the complete combustion of octane, $C_8H_{18}(l)$.
   (b) Calculate the volume of carbon dioxide that would be produced by the combustion of 1.00 g of octane at SATP.
   (c) What volume of oxygen would be required to react with the 1.00 g of octane? K/U T/I

11. Write a balanced chemical equation to represent the following chemical reactions. Classify these reactions as being synthesis, decomposition, single displacement, or combustion. K/U T/I C
   (a) Solid potassium chlorate breaks down into solid potassium chloride and gaseous oxygen when heated.
   (b) Iron(III) oxide reacts with aluminum to produce iron and aluminum oxide. Assume all reactants and products are solids.
   (c) Gaseous butane, C_4H_{10}, burns in air to produce gaseous carbon dioxide and water vapour.
   (d) Potassium metal corrodes in air to form solid potassium oxide.

12. If pure carbon, C(s), undergoes combustion in the presence of a limited amount of oxygen gas, $O_2(g)$, carbon monoxide gas, CO(g), is produced. Carbon monoxide gas can react with oxygen gas to produce carbon dioxide gas, $CO_2(g)$. K/U T/I A
   (a) Write a balanced chemical equation to represent each of these changes.
   (b) If 2.0 mol of carbon were reacted, what volume of carbon monoxide would be produced at SATP? What volume of carbon dioxide?
   (c) Write the balanced chemical equation for the combustion reaction between solid carbon and oxygen gas to produce carbon dioxide gas.
   (d) If 2.0 mol of solid carbon were reacted, what volume of carbon dioxide gas would be produced?
   (e) Compare your answers from (b) and (d). Explain the similarities and differences.

13. For each of the following, convert between the specified units: K/U T/I
   (a) 24 400 J = ____________ kJ
   (b) 0.48 kg = ____________ g
   (c) 1.52×10^{-5} g = ____________ mg

14. (a) Write the balanced chemical equation for the complete combustion reaction of propane, $C_3H_8(g)$ (**Figure 3**).

Figure 3 Combustion of propane gas in a camp stove

   (b) What mass of carbon dioxide gas will be produced if 6.11 g of propane gas reacts with excess oxygen gas? K/U T/I

15. Solve the following problems. Express the answer to the correct number of significant digits. K/U T/I
   (a) $$\frac{45\ \text{J}}{2.46\ \frac{\text{J}}{\text{mol}}}$$
   (b) $$(50.00\ \text{g})\left(4.18\ \frac{\text{J}}{{}^\circ\text{C}\cdot\text{g}}\right)(0.33\ {}^\circ\text{C})$$
   (c) $$\frac{(2.100\ \text{g})\left(0.891\ \frac{\text{J}}{{}^\circ\text{C}\cdot\text{g}}\right)(245.4\ {}^\circ\text{C} - 225.0\ {}^\circ\text{C})}{1.65\ \text{mol}}$$

16. You are writing a procedure for an investigation that involves a burning candle. Identify four safety precautions related to the burning candle that should be including in the procedure. K/U T/I

CAREER PATHWAYS **PREVIEW**

Throughout this unit you will see Career Links. Go to the Nelson Science website to find information about careers related to Energy Changes and Rates of Reaction. On the Chapter Summary page at the end of each chapter you will find a Career Pathways feature that shows you the educational requirements of the careers. There are also some career-related questions for you to research.

CHAPTER

5 Thermochemistry

KEY CONCEPTS

After completing this chapter you will be able to

- compare the energy changes of different substances, perform calorimetry calculations, and describe the relationship between reactions using enthalpy terms
- represent thermochemical equations using different methods, and determine whether a reaction is exothermic or endothermic
- calculate and use bond energies to estimate the enthalpy change of a reaction
- define and solve problems using Hess's law
- write formation reactions and calculate enthalpy changes using standard enthalpy of formation values
- describe current and future energy sources and explain their advantages and disadvantages

What Is the Relationship between Chemical Reactions and Energy?

A fundamental characteristic of energy is that it is never destroyed; it is transformed from one form to another. All your energy needs are met by energy transformations. For example, when you use a cellphone, chemical energy in the battery is first transformed into electrical energy and then into sound energy. If you go for a run, the cells in your body transform some of the chemical energy associated with glucose molecules into the kinetic energy of moving muscles. Some of this chemical energy is also transformed into thermal energy, so your body temperature increases and you start to sweat.

Similarly, some quantity of chemical energy is transformed to another form of energy whenever reactants are converted to products during a chemical reaction. For example, consider the combustion reactions that take place in a campfire. These reactions convert stored energy found in cellulose and other substances found in wood into thermal energy, light energy, and sound energy. When you are camping, you might use the thermal energy to cook your food and warm your body while you enjoy the sound energy of the crackling fire. You might use the light energy to help you see after sundown.

A chemical reaction either releases or absorbs energy in some form, depending on the specific reactants and products. For example, cellular respiration is the process used by your body to provide chemical energy that you can transform to the kinetic energy of moving muscles. During cellular respiration, energy is released as your cells break down glucose and form carbon dioxide gas and water vapour. In contrast, during the process of photosynthesis, energy in sunlight is absorbed to form glucose from carbon dioxide gas and liquid water.

The study of energy transformation in chemical reactions is a major field of chemistry. Understanding energy transformations helps chemists to predict how much energy a chemical reaction will release or absorb. These predictions can then be applied to finding new and more efficient methods of harnessing energy. In this chapter, we will explore different ways in which the quantity of energy associated with a chemical reaction can be determined.

STARTING **POINTS**

Answer the following questions using your current knowledge. You will have a chance to revisit these questions later, applying concepts and skills from the chapter.

1. What forms of energy do you use in your everyday life? What are some sources of this energy?
2. Provide some examples from your daily life of chemical reactions that release energy and others that absorb energy.
3. Why do some reactions release energy while others absorb energy?
4. How do chemical reactions and nuclear reactions differ? How are they similar?
5. Suggest some new or alternative sources of energy that we may use in the future, and briefly describe their advantages and disadvantages.

Mini Investigation

Measuring Temperature Change

Skills: Performing, Observing, Evaluating, Communicating

SKILLS HANDBOOK **A1, A2, A3**

In this investigation, you will observe and measure the temperature changes that occur when various substances dissolve in water.

Equipment and Materials: chemical safety goggles; gloves; 100 mL graduated cylinder; 100 mL beaker; alcohol thermometer; electronic balance; stirring rod; weighing boats or papers; water; sodium hydroxide, $NaOH(s)$; ammonium chloride, $NH_4Cl(s)$; sodium chloride, $NaCl(s)$; calcium chloride, $CaCl_2(s)$; urea, $CO(NH_2)_2(s)$; calcium acetate, $Ca(C_2H_3O_2)_2(s)$

Sodium hydroxide and calcium acetate are corrosive. Avoid skin and eye contact. If you spill these chemicals on your skin, wash the affected area with a lot of cool water.

Ammonium chloride and calcium chloride can be toxic if ingested and may cause skin or eye irritation. Avoid skin and eye contact. In the case of contact, wash the affected area with plenty of cool water. Inform your teacher.

1. Put on your safety goggles and gloves.
2. Using the graduated cylinder to measure 25 mL of water. Pour the water into the 100 mL beaker.
3. Measure and record the initial temperature of the water.
4. Using the electronic balance, weigh out 0.5 g of any one of the compounds listed under Equipment and Materials.
5. Add the compound you chose in Step 4 to the water in the beaker (from Step 2). Stir with the stirring rod.
6. Measure and record the final temperature of the mixture.
7. Repeat Steps 1 to 5 with two other substances.
8. Dispose of the mixtures as directed by your teacher.

A. Which substance caused the greatest change in temperature when dissolved in the water? T/I

B. Which of the substances released energy when dissolved in the water? What evidence supports this? T/I

C. Which of the substances you used absorbed energy when they dissolved in the water? What evidence supports this? T/I

5.1 Energy Changes in Chemical and Nuclear Reactions

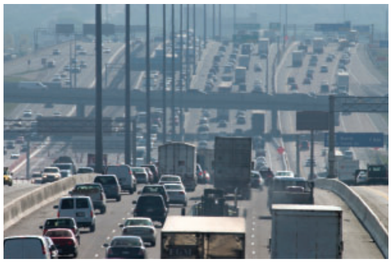


Figure 1 Our use of fossil fuels is unsustainable. New sources of green, sustainable energy are needed to meet the world's growing demand.

Our ability to harness energy has contributed greatly to the development of human civilization. For most of human history, the only way to transport people and things over land was by walking or through animal labour. Then, during the Industrial Revolution of the 1800s, inventors found ways to harness thermal energy to do work. Energy released by burning coal was used to heat water, releasing steam fast enough to move mechanical parts in machines. People and goods could then be moved long distances by steam-powered locomotives and boats. The next advance took place in the late 1800s in the form of the internal combustion engine, which produces energy by burning gasoline. Today, there are more than half a billion vehicles that are powered by the internal combustion engine (**Figure 1**). As this number grows, the demand for inexpensive and reliable sources of fuel also increases. Most of these vehicles use fossil fuels, which are non-renewable and negatively effect the environment. How will we meet our energy needs for transportation and other activities in more sustainable ways? To answer this challenge, we need to understand the energy changes that take place in chemical and nuclear reactions.

The Nature of Energy

thermochemistry the study of the energy changes that accompany physical or chemical changes in matter

energy the ability to do work; SI units joules (J)

work the amount of energy transferred by a force over a distance; SI units joules (J)

The study of energy changes during physical or chemical changes in matter is called **thermochemistry**. The study of thermochemistry uses some familiar terms in very precise ways. Scientists define **energy** as the ability to do work. **Work** is the energy transferred to an object by a force that causes the object to move. For example, the energy to lift satellites into orbit comes from simple chemical reactions that release huge quantities of thermal energy. The hot expanding gases released during the rocket launch do work on the rocket by pushing it into the sky. No work is done, however, if the force of the gases is inadequate to get the rocket off the ground. Both energy and work are measured in joules (J).

potential energy the energy of a body or system due to its position or composition

kinetic energy the energy of an object due to its motion

All forms of energy can be classified as either kinetic energy or potential energy. **Potential energy** is energy due to the position or composition of an object. **Kinetic energy** is the energy of motion. For example, the water behind a dam has a great deal of potential energy because of its elevation. This energy can be used to do work on the blades of turbines in a hydroelectric generating station. As the water falls, the potential energy is transformed into kinetic energy. The falling water causes the turbine blades to spin. The kinetic energy of the spinning turbines is transferred to a generator and transformed into electrical energy, another form of potential energy.

The energy associated with chemical bonds is also potential energy. Chemical bonds are the result of attractive forces between the nucleus of one atom or ion and the negative charges of electrons in the other atom or ion. The amount of energy released or absorbed in a chemical reaction equals the difference between the potential energy of the bonds in the reactants and the potential energy of the bonds in the products. For example, energy is released during the combustion of gasoline because the products have less potential energy than the reactants. In an internal combustion engine, the products of this combustion reaction are hot gases. The molecules in the hot gases that are produced by the engine move much faster than the molecules in the incoming cool air. Therefore, the combustion gases have more kinetic energy. This energy is used to do work on the mechanical parts inside the engine that eventually make the car move.

Thermal Energy, Heat, and Temperature

The total quantity of potential energy and kinetic energy of a substance is called **thermal energy**. In general, the quantity of thermal energy of a substance depends on how fast its entities—atoms, ions, molecules, or polyatomic ions—are moving. When a substance absorbs thermal energy, its entities move at a greater speed, and the substance warms up. When a substance releases thermal energy to its surroundings, its entities move more slowly, and the substance cools. In science, **heat** is a verb that refers to the transfer of thermal energy from a warm object to a cool object. So, when you heat water in a kettle on a stove, you transfer thermal energy from the burner to the kettle to the water. Similarly, when an object cools, it transfers thermal energy to its surroundings.

Temperature is a measure of the average kinetic energy of the entities in a substance. As a substance is warmed, some of its particles move faster. The average kinetic energy of the substance's entities increases and so does the temperature of the substance. For example, a cup of hot water has a higher temperature than an iceberg. The average water molecule in the hot water has more kinetic energy than the average water molecule in the iceberg. However, an iceberg contains billions more water molecules than a cup of hot water. Therefore, the total quantity of thermal energy of an iceberg is greater than that of a cup of hot water.

thermal energy the total quantity of kinetic and potential energy in a substance

heat the transfer of thermal energy from a warm object to a cooler object

temperature a measure of the average kinetic energy of entities in a substance

Law of Conservation of Energy

One important characteristic of energy is that it is always conserved. We cannot create new energy nor can we destroy energy by using it. Energy can only be converted from one form into another. Think about the combustion of propane in a barbecue (**Figure 2**). Chemical energy stored in propane is converted into thermal energy and light energy. However, the total amount of energy before and after the combustion reaction occurs remains constant. These ideas are summarized in the law of conservation of energy:

Figure 2 The potential energy of the propane fuel in the barbecue is converted to thermal energy.

Law of Conservation of Energy
Energy cannot be created or destroyed.

To help analyze energy conversions involving chemical reactions, chemists find it useful to divide the universe into two parts: the chemical system and its surroundings. A **chemical system** is composed of the reactants and products being studied. The **surroundings** are all the matter that is not part of the system. In the propane gas barbecue, the chemical system is composed of the reactants (propane gas, $C_3H_8(g)$, and oxygen gas, O_2 (g)), and the products (carbon dioxide gas, $CO_2(g)$, and water vapour, $H_2O(g)$). The surroundings include the barbecue and the food on the grill.

Chemical systems can be classified as being open or closed. An **open system** can exchange both energy and matter with its surroundings. An operating propane barbecue is an example of an open system. Propane gas flows into the burner and thermal energy and the products of combustion flow out. A chemical reaction that produces a gas in a solution in an unsealed beaker is also an open system, since energy and matter can flow into or out of the system to the surroundings. The surroundings include the beaker and the air around the beaker. A **closed system** can exchange energy, but not matter, with its surroundings. A glow stick (**Figure 3**) is an example of a closed system. Light energy released when chemicals inside the stick are mixed flows out into the surroundings. The matter (that is, the chemicals) remain sealed inside.

A third kind of system exists, called an isolated system. In an **isolated system**, neither matter nor energy can move into or out of the system. However, it is impossible to set up a true isolated system on Earth.

chemical system a group of reactants and products being studied

surroundings all the matter that is not part of the system

open system a system in which both matter and energy are free to enter and leave the system

closed system a system in which energy can enter and leave the system, but matter cannot

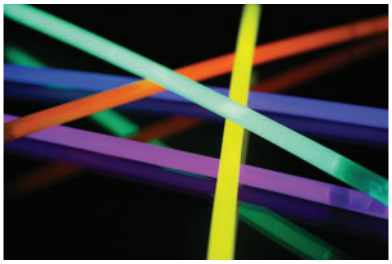


Figure 3 Each of these glow sticks forms a closed system. Matter cannot escape; only light energy.

isolated system an ideal system in which neither matter nor energy can move in or out

Endothermic and Exothermic Reactions

During a chemical reaction, the chemical bonds in the reactant(s) are broken, and new bonds are formed to produce the product(s). The potential energy of the entities in a stable structure, such as the atoms in a molecule or the ions in an ionic compound, is lower than the potential energy of the individual isolated atoms. Therefore, bond breaking requires energy, while bond formation releases energy.

From the law of conservation of energy, you know that the total energy in a chemical system and its surroundings must be the same before and after a chemical reaction occurs. If more energy is released from the formation of new bonds in the products than is required to break bonds in the reactants, then the chemical reaction will release some energy to the surroundings. A chemical reaction system that releases energy to the surroundings is **exothermic** (the prefix *exo-* means "out of"). The products of an exothermic reaction have lower potential energy (and stronger bonds on average) than the reactants.

exothermic releasing energy to the surroundings

For example, the combustion of methane is an exothermic reaction. The balanced chemical equation for this reaction is

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) + \text{energy}$$

Notice that an energy term is included on the product side of the equation to show that energy is released. This energy is the difference between the energy absorbed by breaking bonds in the reactants and the energy released by forming bonds in the products. The quantity of this energy is the difference in potential energy between the reactants and products and has the symbol ΔE_p. Since the combustion of methane is exothermic, energy is released to the surroundings, mainly as thermal energy and light energy. **Figure 4** illustrates the changes that occur during this reaction in an open system. The quantity of matter in the system (represented by the tan box) remains the same, and the released energy (the large arrow) flows to the surroundings (the yellow area). When an exothermic reaction releases thermal energy, the temperature of the surroundings increases.

Energy Changes during an Exothermic Reaction in an Open System

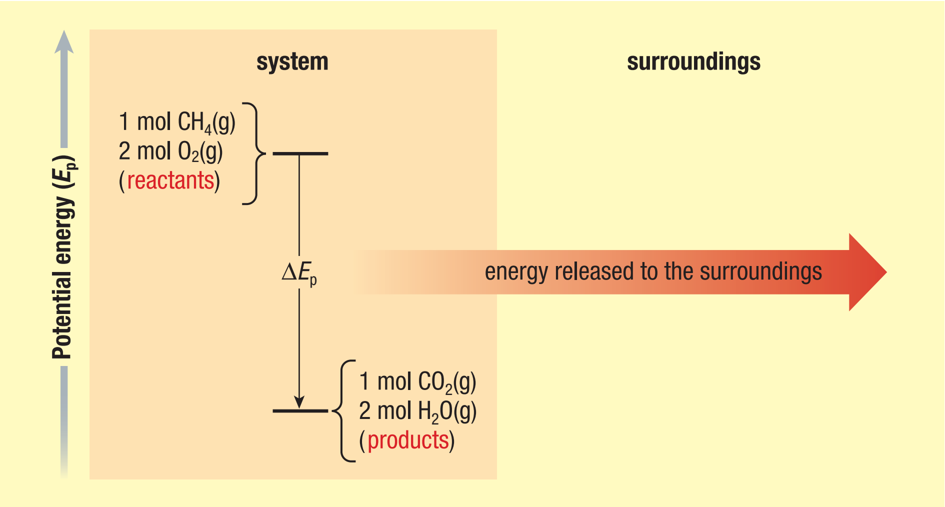


Figure 4 The combustion of methane releases a quantity of energy with the magnitude ΔE_p, which flows to the surroundings, mainly as thermal energy and light energy. This is an exothermic reaction.

endothermic absorbing energy from the surroundings

A reaction that absorbs thermal energy from its surroundings is **endothermic** (the prefix *endo-* means "inside"). During an endothermic reaction, the chemical system absorbs energy from the surroundings and increases its potential energy. This means that the products have higher potential energy (and weaker bonds on average) than the reactants. The synthesis of nitric oxide from its elements is an example of an endothermic reaction, represented by the equation

$$N_2(g) + O_2(g) + \text{energy} \rightarrow 2\,NO(g)$$

Notice that, for an endothermic reaction, the energy term is included on the reactants side of the equation. **Figure 5** illustrates the changes that occur during this reaction in an open system. The quantity of matter in the system again remains the same, but now energy flows from the surroundings to the system.

Energy Changes during an Endothermic Reaction in an Open System

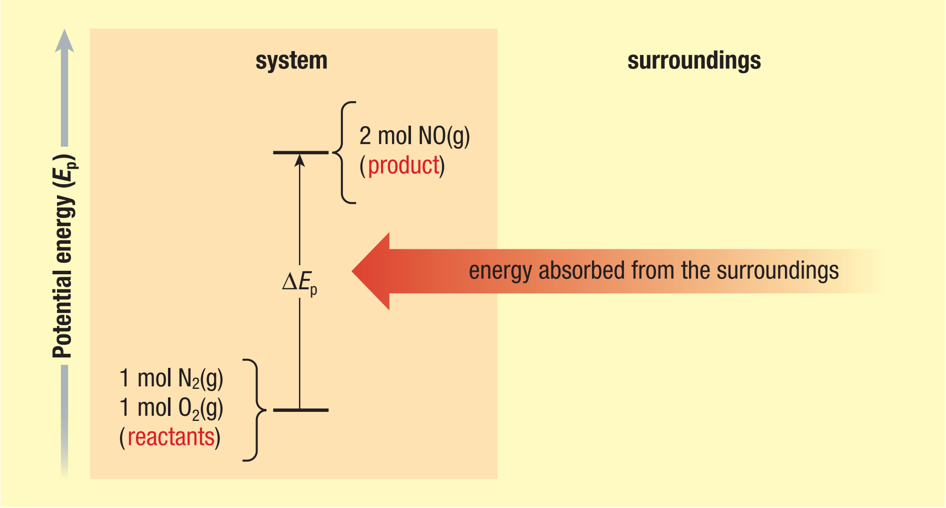


Figure 5 The synthesis of nitric oxide from its elements absorbs a quantity of thermal energy with the magnitude ΔE_p from the surroundings. This is an endothermic reaction.

UNIT TASK **BOOKMARK**

How can you apply what you have learned about endothermic and exothermic reactions in your Unit Task (on page 402)?

Nuclear Energy

Unlike chemical reactions, all nuclear reactions are exothermic. Per unit of mass, nuclear reactions release much more energy than exothermic chemical reactions. Two nuclear reactions involving large quantities of energy are fission and fusion.

A **fusion** reaction occurs when nuclei of small atomic mass combine to form larger, heavier nuclei. Fusion reactions are responsible for the release of vast amounts of energy in stars, including the Sun (**Figure 6**). The Sun consists of 73 % hydrogen, 26 % helium, and 1 % other elements. Hydrogen nuclei under immensely high pressure in the Sun undergo fusion and form helium nuclei. The fusion process releases energy, some of which reaches Earth. The fusion of hydrogen atoms produces 1.7×10^9 kJ of energy for each mole of helium produced.

fusion the process of combining two or more nuclei of low atomic mass to form a heavier, more stable nucleus

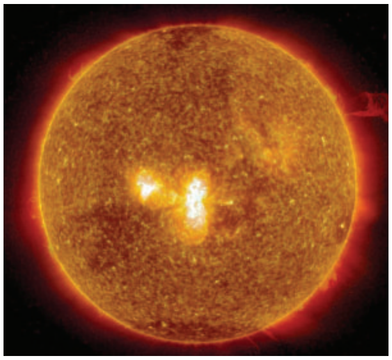


Figure 6 The most common fusion reactions that occur in the Sun involve hydrogen atoms.

Let us review nuclear notation. An element with the chemical symbol *X* is represented as ${}^{A}_{Z}\mathrm{X}$, where *A* is the mass number (number of protons plus number of neutrons) and *Z* is the atomic number (number of protons). A neutron is a subatomic entity, and the symbol ${}^{1}_{0}\mathrm{n}$ is used to show that a neutron has a mass number of 1 and an atomic number of 0. Using nuclear notation, the equation for the fusion reaction of hydrogen atoms is

$$ {}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} $$

Scientists have worked for decades to find a way to develop fusion reactors to generate energy, but the intense pressure and heat needed for fusion to occur have made this difficult to achieve to date. CAREER LINK

During **fission**, large nuclei with high atomic mass are split into smaller, lighter nuclei by collision with a neutron. The nuclei of all elements above atomic number 83 are unstable and can undergo fission. Fission does not normally occur in nature. Fission reactions produce vast quantities of energy—millions of times more than is released in chemical reactions.

fission the process of using a neutron to split a nucleus of high atomic mass into two nuclei with smaller masses

Nuclear power plants use the fission of uranium-235 to produce electricity. When a neutron collides with a $^{235}_{92}U$ nucleus, the uranium nucleus splits into smaller nuclei and releases energy and additional neutrons (**Figure 7**). These neutrons collide with more uranium nuclei, causing these nuclei to split and release more energy and even more neutrons.

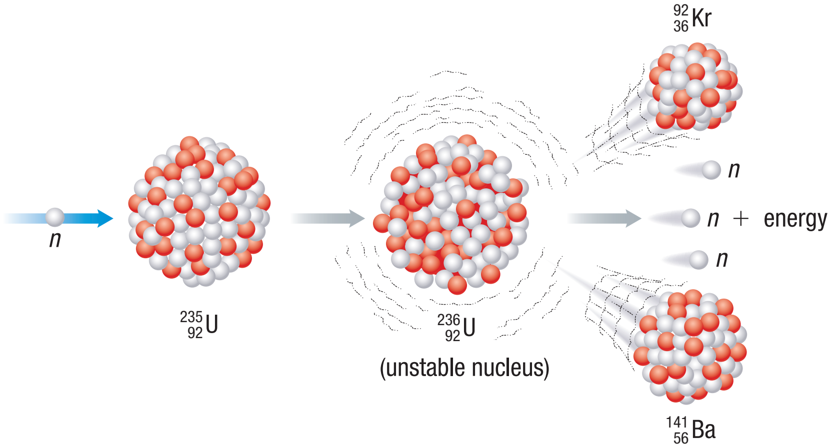


Figure 7 The uranium-235 nucleus undergoes fission when a neutron strikes it. The fission produces two lighter nuclei, free neutrons, and a large amount of energy.

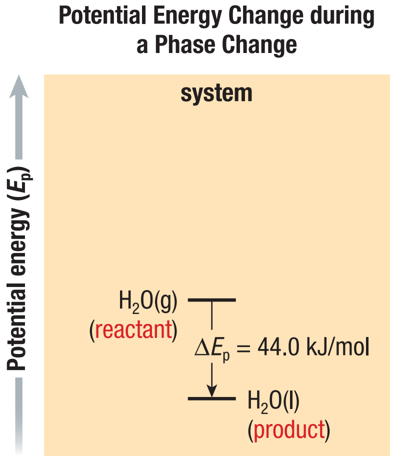
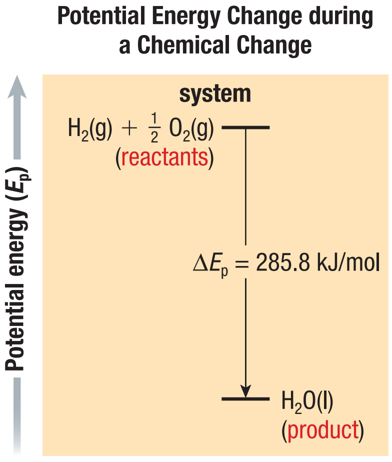
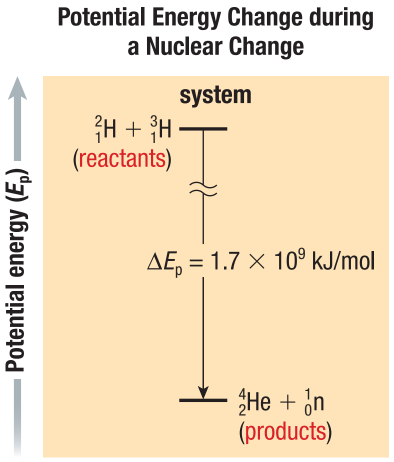
The equation for the fission of uranium is

$$^{1}_{0}n + ^{235}_{92}U \rightarrow ^{92}_{36}Kr + ^{141}_{56}Ba + 3\,^{1}_{0}n$$

Uranium is used in nuclear power plants because it undergoes a fission chain reaction. About 15 % of all electrical energy in Canada is produced by the fission of uranium in nuclear power plants. Nuclear power plants can generate much more electricity from a small amount of fuel than can power plants that use fossil fuels. For example, uranium fission can produce about 26 million times more energy than the combustion of an equal mass of methane. WEB LINK

Energy changes occur during any physical, chemical, or nuclear change. **Table 1** gives an example of each of these types of energy changes, and the magnitude of the potential energy change in the system. Notice that the potential energy change varies considerably. For example, to show the graph of the nuclear change on the same scale as the other changes would require a textbook about 1000 km long!

Table 1 Examples of Magnitudes of Potential Energy Changes during a Phase Change, Chemical Change, and Nuclear Change

Phase change	Chemical change	Nuclear change
$H_2O(g) \rightarrow H_2O(l)$	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	$^{2}_{1}H + ^{3}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n$
		

5.1 Review

Summary

- Energy is the ability to do work.
- Potential energy is the energy of position or composition.
- Kinetic energy is the energy of motion.
- Thermal energy is the sum of the potential and kinetic energy in a substance.
- Heat is the transfer of thermal energy from a warmer object to a cooler object.
- Temperature is a measure of the average kinetic energy of the particles in a substance.
- The law of conservation of energy states that energy cannot be created or destroyed but can be converted from one form to another.
- An open system can exchange both energy and matter with its surroundings. A closed system can exchange energy, but not matter, with its surroundings.
- An exothermic reaction releases energy to its surroundings. An endothermic reaction absorbs energy from its surroundings.
- Fusion is a nuclear reaction in which two or more nuclei of low atomic mass combine to form a heavier nucleus.
- Fission is a nuclear reaction in which a neutron collides with a nucleus of high atomic mass and splits it into nuclei with smaller masses.

Questions

1. For each of the following, describe which is greater—the potential energy or the kinetic energy. K/U
   (a) a stick of dynamite prior to exploding
   (b) a space shuttle before launch
   (c) the soot rising above a campfire
   (d) the chemicals inside a new battery
2. For each of the following, identify whether the reaction process is exothermic or endothermic. K/U
   (a) water evaporating into steam
   (b) a candle burning
   (c) the combustion of gasoline
   (d) the melting of ice
   (e) the splitting of a nitrogen molecule, N_2, into individual atoms
   (f) dissolving barium hydroxide, $Ba(OH)_2$, in water and observing a temperature decrease in the surroundings
3. Consider the following statement: "The law of conservation of energy states that energy cannot be created or destroyed. Therefore, when thermal energy is transferred from a system to the surroundings, the quantity of thermal energy lost by the system must be equal to the amount of thermal energy gained by the surroundings." Does this statement accurately describe what happens to the thermal energy? Explain why or why not. K/U A
4. Distinguish between heat, thermal energy, and temperature using examples from your experience. K/U A
5. Compare and contrast nuclear fission and fusion. K/U T/I
6. The law of conservation of energy can be stated as "the total energy of the universe is constant." Explain how this is a restatement of the definition given in the text. K/U T/I
7. A fire is started in a fireplace by striking a match and lighting crumpled paper under some logs. Explain all the energy transfers in this scenario using the terms "exothermic," "endothermic," "system," "surroundings," "potential energy," and "kinetic energy." K/U T/I A
8. Explain why the water in a swimming pool at 24 °C has more thermal energy than a cup of boiling water at 100 °C. K/U T/I A
9. Liquid water at 0 °C turns to ice. Is this process endothermic or exothermic? Explain what is occurring using the terms "system," "surroundings," "thermal energy," "potential energy," and "kinetic energy." K/U T/I A

5.2 Calorimetry and Enthalpy

Firefighters risk their lives every day when they enter burning buildings. To help reduce this risk, they wear suits that protect them from the high temperatures of fire (**Figure 1**). The temperature inside a protective suit remains in a range that allows the firefighter to continue working. The heat-resistant fibres used to construct these suits protect firefighters from high temperatures while still allowing them to move. Most protective clothing worn by firefighters is constructed with a fabric called Nomex. When Nomex is exposed to high temperatures, the fibres absorb thermal energy and swell, which prevents the firefighter's skin from increasing in temperature and burning. Obviously, fibres such as the cotton in a T-shirt cannot absorb enough thermal energy to protect a person from fire. What chemical property describes the ability of a substance to absorb thermal energy? WEB LINK

Figure 1 To stay safe, firefighters rely on insulated suits that protect them from thermal energy.

Heat Capacity

Have you ever dashed across hot beach sand so you could stand comfortably in the cool water? Both the water and the sand are heated by the same energy source—the Sun—and yet the sand feels so much hotter. Both substances have been heated by the Sun for the same amount of time, so why is the temperature of the sand so much higher? This difference in temperature is caused by a difference in the specific heat capacity of water and sand. **Specific heat capacity (*c*)** is the quantity of thermal energy required to raise the temperature of 1 g of a substance by 1 °C. The SI units for specific heat capacity are J/g·°C. It takes a lot of thermal energy to raise the temperature of a substance with a high specific heat capacity, such as water, but relatively little to raise the temperature of a substance with a low specific heat capacity, such as sand.

specific heat capacity (*c*) the quantity of thermal energy required to raise the temperature of 1 g of a substance by 1 °C; SI units J/(g·°C)

Table 1 shows the specific heat capacities of some common substances. Note that water's specific heat capacity is more than five times that of sand. This means that the amount of thermal energy required to raise the temperature of water by 1 °C is five times the amount of thermal energy required to raise the temperature of sand. The high specific heat capacity of water is the reason the temperature of a lake remains cool well into the summer while the surrounding land is warm. Substances with a high specific heat capacity also take longer to cool. A lake, for example, remains warm into autumn, long after the land temperature has decreased. It will also remain cool in the spring longer than the surrounding land.

Table 1 Specific Heat Capacities of Some Common Substances

Substance	Specific heat capacity in J/(g·°C)
liquid water, $H_2O(l)$	4.18
ice, $H_2O(s)$	2.03
aluminum, Al(s)	0.900
iron, Fe(s)	0.444
solid carbon graphite, C(s)	0.710
liquid methanol, $CH_3OH(l)$	2.92
solid silicon dioxide (sand), $SiO_2(s)$	0.835

Calorimetry and Thermal Energy Transfer

Heating water on a gas stove transfers thermal energy from the natural gas to the water. This energy transfer increases the kinetic energy of the water molecules, which makes them move faster. As a result, the average kinetic energy, or temperature, of the water increases. One way that scientists can study thermal energy transfers is by calorimetry. **Calorimetry** is the process of measuring energy changes during a physical or chemical change.

calorimetry the experimental process of measuring the thermal energy change in a chemical or physical change

calorimeter a device that is used to measure thermal energy changes in a chemical or physical change

A **calorimeter** is a device used to measure energy changes during a physical or chemical change. The design of calorimeters varies (**Figure 2** shows three examples of calorimeters). In general, a calorimeter consists of a well-insulated reaction chamber, a tight-fitting cover with insulated holes for a thermometer, and some mechanism to stir the calorimeter contents. Using an insulated chamber minimizes energy losses to the surroundings. A tight lid prevents matter from leaving or entering the calorimeter. A simple calorimeter can be made from two nested polystyrene foam cups and a lid to hold a stirrer and thermometer, as shown in Figure 2(a). The inner cup is where the chemical system being studied (for example, a chemical reaction) is placed. The inner cup also holds a liquid, usually water. Any change in the thermal energy of the system is detected as a temperature change of the water. The outer cup provides additional insulation. If you have ever kept a hot or cold liquid in a foam cup for a long time, you know that thermal energy eventually escapes. That is why more elaborate calorimeters are used, such as the model in Figure 2(b), when precise measurements are required.

Reactions carried out in calorimeters like those in Figure 2(a) or 2(b) take place under constant pressure, since a small amount of gas will always escape. As a result, the volume of the contents will change, which keeps the pressure constant. Therefore, to study a physical or chemical change involving a gas or gases, chemists use a bomb calorimeter (Figure 2(c)). A bomb calorimeter is a very rigid, tightly sealed vessel that prevents almost all gas from escaping while maintaining a constant volume. If a physical or chemical change produces gas(es), the pressure in the bomb calorimeter will increase. If a change consumes gas(es), the pressure will decrease. A bomb calorimeter is particularly useful for studying the energy changes of combustion reactions, since one reactant is always oxygen gas and the products always include one or more gases.

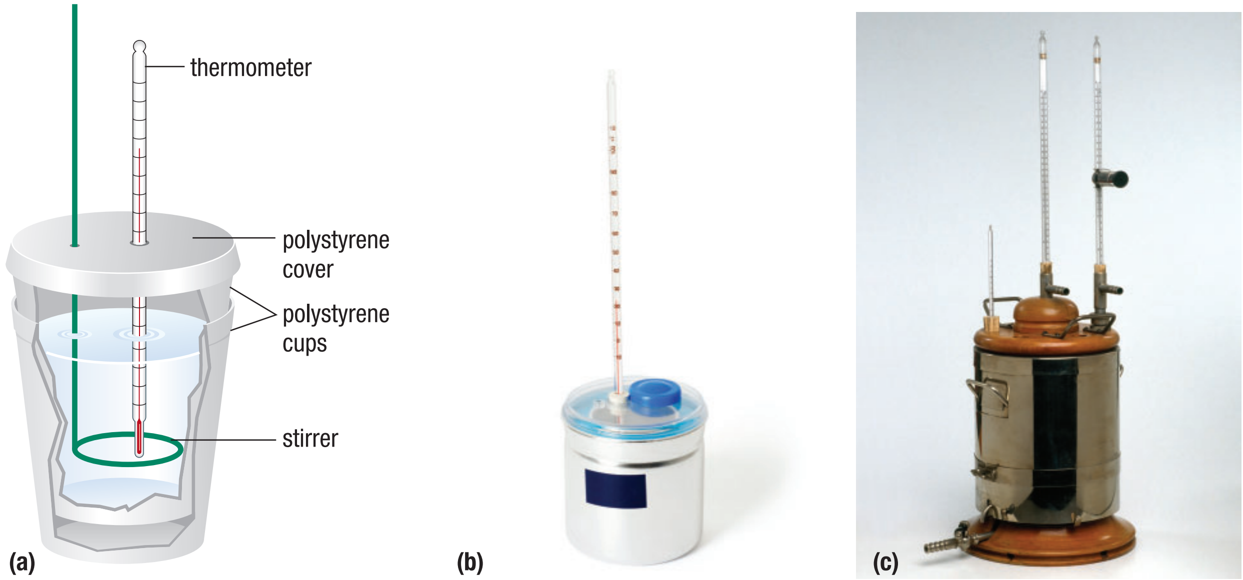


Figure 2 (a) A coffee-cup calorimeter can provide reasonably accurate data. (b) A laboratory calorimeter can provide precise data for changes of state or chemical reactions that do not involve gases. (c) A bomb calorimeter can provide precise data for changes of state or chemical reactions that involve gases.

Calorimetry Calculations

For the investigations provided in this text, you will use a coffee-cup calorimeter. When analyzing data obtained using a coffee-cup calorimeter, make these assumptions:

- Any thermal energy transferred from the calorimeter to the outside environment is negligible.
- Any thermal energy absorbed by the calorimeter itself is negligible.
- All dilute, aqueous solutions have the same density (1.00 g/mL) and specific heat capacity (4.18 J/(g·°C)) as water.

These assumptions are valid only for physical or chemical changes that take place in water or a dilute aqueous solution.

In calorimetry, the total amount of thermal energy absorbed or released by a chemical system is given the symbol q. The magnitude of q depends on three factors:

- the mass of the substance
- the specific heat capacity of the substance
- the temperature change experienced by the substance as it warms or cools

The value of q is calculated using the equation

$$q = mc\Delta T$$

where m is the mass of the substance, c is the specific heat capacity of the substance, and ΔT is the change in temperature of that substance. The change in temperature is the difference between the final temperature, T_{final}, and the initial temperature, T_{initial}, which can be written as

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

The value of q has two parts: the magnitude of q tells you how much energy is involved, and the sign tells you the direction of energy transfer.

The transfer of energy from a system to the surroundings in a coffee-cup calorimeter is illustrated in **Figure 3**. The system is composed only of the components of the physical or chemical change that occurs. The water in a coffee-cup calorimeter is the surroundings, and all energy transfers are assumed to take place between the system and the water. The calorimeter itself is assumed not to be involved in these energy transfers. You can use the value of q for the surroundings (the water) to predict whether a change will be exothermic or endothermic.

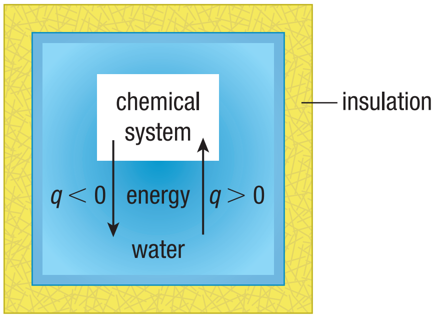


Figure 3 The chemical system undergoes either a physical change or a chemical change. Energy is either absorbed from, or released to, the surroundings (the water in the calorimeter). An increase in the temperature of the water indicates an exothermic reaction, whereas a decrease in the temperature of the water indicates an endothermic reaction.

If q has a negative value, the system transfers thermal energy to its surroundings and the change is exothermic. The temperature of the water (the surroundings) in the calorimeter increases. If q has a positive value, the system absorbs thermal energy from its surroundings and the change is endothermic. The temperature of the water in the calorimeter decreases.

Since energy cannot be destroyed, the total thermal energy of the system and its surroundings remains constant. Therefore, the sum of q_{system} plus $q_{\text{surroundings}}$ should equal zero, since these symbols represent equal quantities but with opposite signs:

$$q_{\text{system}} + q_{\text{surroundings}} = 0 \qquad \text{or} \qquad q_{\text{system}} = -q_{\text{surroundings}}$$

Tutorial 1 Calculations Involving Thermal Energy Transfer

In this tutorial, you will use calorimetry data to determine the quantity of thermal energy released or absorbed during a reaction when the specific heat capacity of a substance is known, and to determine the specific heat capacity of a substance.

Sample Problem 1: Thermal Energy Transfer Involving a Metal in Water

A student places 50.0 mL of liquid water at 21.00 °C into a coffee-cup calorimeter. She places a sample of gold at 100.00 °C into the calorimeter. The final temperature of the water is 21.33 °C. The specific heat capacity of water is 4.18 J/g·°C and the density of water, *d*, is 1.00 g/mL. Calculate the quantity of thermal energy, *q*, absorbed by the water in the calorimeter.

Given: $V_{H_2O(l)} = 50.0\text{ mL}$; $c = 4.18\text{ J/(g·°C)}$; $d_{H_2O(l)} = 1.00\text{ g/mL}$; $T_{\text{initial}} = 21.00\text{ °C}$;
$T_{\text{final}} = 21.33\text{ °C}$

Required: quantity of thermal energy absorbed, *q*

Analysis: $m = Vd$; $\Delta T = T_{\text{final}} - T_{\text{initial}}$; $q = mc\Delta T$

Solution:

Step 1. Determine the mass of water, *m*, in the calorimeter.

$$\begin{aligned} m &= Vd \\ &= 50.0\ \cancel{\text{mL}} \times \frac{1.00\text{ g}}{1\ \cancel{\text{mL}}} \\ m &= 50.0\text{ g} \end{aligned}$$

Step 2. Determine the change in temperature, ΔT, of the water in the calorimeter.

$$\begin{aligned} \Delta T &= \Delta T_{\text{final}} - T_{\text{initial}} \\ &= 21.33\text{ °C} - 21.00\text{ °C} \\ \Delta T &= 0.33\text{ °C} \end{aligned}$$

Step 3. Calculate the quantity of thermal energy, *q*, transferred to the water in the calorimeter.

$$\begin{aligned} q &= mc\Delta T \\ &= (50.0\ \cancel{\text{g}})\left(4.18\frac{\text{J}}{\cancel{\text{g}}\cdot\cancel{°\text{C}}}\right)(0.33\ \cancel{°\text{C}}) \\ q &= 69\text{ J} \end{aligned}$$

Step 4. Check that the sign of *q* makes sense.

Since the temperature in the water increased, water absorbed energy. Therefore, *q* should be positive.

Statement: The quantity of thermal energy absorbed by the water was 69 J.

Sample Problem 2: Determining Specific Heat Capacity of a Substance from Calorimetric Data

Using the value for *q* that you calculated in Sample Problem 1, calculate the specific heat capacity, *c*, of the sample of gold if its mass is 6.77 g. Assume that the final temperature of the gold sample was the same as the final temperature of the water in the calorimeter.

Given: $m_{\text{Au}} = 6.77\text{ g}$; $q = 69\text{ J}$; $T_{\text{initial}} = 100.00\text{ °C}$; $T_{\text{final}} = 21.33\text{ °C}$

Required: specific heat capacity of the gold sample, *c*

Analysis: $\Delta T = T_{\text{final}} - T_{\text{initial}}$; $q = mc\Delta T$

Solution

Step 1. Determine the change in temperature, ΔT, of the gold sample.

$$\begin{aligned}\Delta T &= \Delta T_{\text{final}} - T_{\text{initial}} \\ &= 21.33\ °\text{C} - 100.00\ °\text{C} \\ \Delta T &= -78.67\ °\text{C}\end{aligned}$$

Step 2. Determine if q should be positive or negative.

You know from Sample Problem 1 that 69 J of thermal energy was absorbed by the water (the surroundings). The quantity of thermal energy lost by the gold sample (the system) must be of the same magnitude but opposite in sign:

$$q = -69\ \text{J}$$

Step 3. Rearrange $q = mc\Delta T$ to solve for c.

$$\begin{aligned}q &= mc\Delta T \\ c &= \frac{q}{m\Delta T} \\ &= \frac{-69\ \text{J}}{(6.77\ \text{g})(-78.67\ °\text{C})} \\ c &= 0.13\ \text{J/(g·°C)}\end{aligned}$$

Statement: The specific heat capacity of the sample of gold is 0.13 J/(g · °C).

Sample Problem 3: Calculating the Thermal Energy Transfer during a Neutralization Reaction

A 50.0 mL sample of a 1.0 mol/L aqueous solution of hydrochloric acid, HCl(aq), was mixed with 50.0 mL of a 1.0 mol/L aqueous solution of sodium hydroxide, NaOH(aq), at 25.0 °C in a calorimeter. After the solutions were mixed by stirring, the temperature was 31.9 °C.
(a) Determine the quantity of thermal energy transferred by the reaction to the water, q, and state whether the reaction was endothermic or exothermic. Assume that the specific heat capacity and density of both solutions is the same as that of liquid water ($c_{H_2O(l)} = 4.18\ \text{J/(g·°C)}$ and $d_{H_2O(l)} = 1.00\ \text{g/mL}$).
(b) State if the reaction is exothermic or endothermic.

Given: $V_{\text{NaOH(aq)}} = 50.0\ \text{mL}$; $V_{\text{HCl(aq)}} = 50.0\ \text{mL}$;
$d_{H_2O(l)} = 1.00\ \text{g/mL}$; $T_{\text{initial}} = 25.0\ °\text{C}$;
$T_{\text{final}} = 31.9\ °\text{C}$; $c_{H_2O(l)} = 4.18\ \text{J/(g·°C)}$

Required: q

Analysis: $m = Vd$; $q = mc\Delta T$; $m_{\text{total}} = m_{\text{NaOH(aq)}} + m_{\text{HCl(aq)}}$; $\Delta T = T_{\text{final}} - T_{\text{initial}}$

Solution

Step 1. Determine the mass of the solution, m.

Since 50.0 mL of the first solution was combined with 50.0 mL of the second solution, the total volume in the calorimeter is 100.0 mL. Assuming these solutions have the same density as liquid water, then use the equation

$$\begin{aligned}m &= Vd \\ &= (100.0\ \cancel{\text{mL}})\left(1.00\ \frac{\text{g}}{\cancel{\text{mL}}}\right) \\ m &= 100\ \text{g}\end{aligned}$$

Step 2. Calculate the change in temperature, ΔT.

$$\begin{aligned}\Delta T &= T_{\text{final}} - T_{\text{initial}} \\ &= 31.9\ °\text{C} - 25.0\ °\text{C} \\ \Delta T &= 6.9\ °\text{C}\end{aligned}$$

Step 3. Calculate the quantity of thermal energy absorbed by the water, q, and determine if the reaction is exothermic or endothermic.

$$q = mc\Delta T$$

$$= (100\ \cancel{\text{g}})\left(4.18\frac{\text{J}}{\cancel{\text{g}}\cdot\cancel{°\text{C}}}\right)(6.9\ \cancel{°\text{C}})$$

$$= 2.9 \times 10^3\ \text{J}$$

$$q = 2.9\ \text{kJ}$$

Therefore, the thermal energy transferred by the reaction to the water is −2.9 kJ. Since the value of q is negative, the reaction is exothermic.

Statement: The quantity of thermal energy transferred was −2.9 kJ, and the reaction was exothermic.

Practice

1. How much thermal energy is required to raise the temperature of 6.0 mL of water from 25 °C to 75 °C in a calorimeter or other closed system? T/I [ans: 1.3 kJ]
2. Aqueous ethylene glycol is commonly used in car radiators as an antifreeze and coolant. A 50 % ethylene glycol solution in a radiator has a specific heat capacity, c, of 3.5 J/(g · °C). If a 4.0 kg quantity of ethylene glycol absorbs 250 kJ of thermal energy, what was the temperature change, ΔT, of the solution? Assume the radiator is a closed system. T/I [ans: 18 °C]
3. When 50.0 mL of 1.0 mol/L hydrochloric acid is neutralized completely by 75.0 mL of 1.0 mol/L sodium hydroxide in a coffee-cup calorimeter, the temperature of the total solution changes from 20.2 °C to 25.6 °C. Determine the quantity of energy transferred, q, and state whether the reaction was endothermic or exothermic. T/I [ans: 2800 J; exothermic]

Mini **Investigation**

Thermal Energy Transfer in a Coffee-Cup Calorimeter

Skills: Performing, Observing, Analyzing, Evaluating, Communicating

SKILLS HANDBOOK **A1, A2.1, A3**

In this activity, you will place a heated piece of metal into water in a coffee-cup calorimeter. You will then calculate the quantity of thermal energy, q, that is transferred for both the system and the surroundings.

Equipment and Materials: balance; coffee-cup calorimeter; graduated cylinder; thermometer; 250 mL beaker; kettle; tongs; glass rod; sample of metal; hot water

1. Using the balance, determine and record the mass of your assigned metal.
2. Use the tongs to place your metal in a hot water bath for a minimum of 2 minutes.
3. Use the graduated cylinder to measure out 100 mL of tap water. Pour the measured tap water into the calorimeter.
4. Measure and record the initial temperature of the water in the calorimeter using the thermometer.
5. Use the thermometer to measure the temperature of the hot water in the hot water bath.
6. Use the tongs to carefully transfer the hot metal into the calorimeter containing the 100 mL of tap water. Close the lid of the calorimeter.
7. Insert the glass rod into the calorimeter lid and stir the water in the calorimeter. Do not open the calorimeter.
8. Remove the glass rod. Insert the thermometer into the calorimeter, taking care not to strike the metal with the thermometer. Measure and record the final temperature of the water.

A. Calculate the quantity of thermal energy gained by the water. T/I

B. Assume that the initial temperature of the metal was the temperature of the hot water bath and the final temperature was the temperature of the warm water in the calorimeter. Calculate the quantity of thermal energy lost by the metal, using the specific heat capacity given in Table 1 (page 292). T/I

C. Compare your answers to A and B. Explain any differences. T/I

D. What were some sources of experimental error? How would you improve this investigation? T/I

Enthalpy Change

enthalpy (*H*) the total amount of thermal energy in a substance

enthalpy change (Δ*H*) the energy released to or absorbed from the surroundings during a chemical or physical change

Every substance undergoing a chemical or physical change contains a certain amount of thermal energy. The total amount of thermal energy is sometimes called **enthalpy (*H*)**. Chemists have yet to find a way of measuring the enthalpy of a given substance. However, the energy change that occurs in a system during a reaction, called the **enthalpy change (Δ*H*)**, can be measured using calorimetry data. Let us examine why this is possible.

Chemists have found that as long as pressure remains constant, the enthalpy change of the chemical system is equal to the flow of thermal energy in and out of the system, or

$$\Delta H_{\text{system}} = |q_{\text{system}}|$$

For a chemical reaction, the enthalpy change, ΔH, is given by the equation

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

When the products of a reaction have a greater enthalpy than the reactants, ΔH will be positive. The system absorbs thermal energy from its surroundings and the reaction is endothermic. On the other hand, if the enthalpy of the products is less than that of the reactants, ΔH will be negative. In this case, the system releases thermal energy to its surroundings and the reaction is exothermic.

$\Delta H > 0$, endothermic reaction
$\Delta H < 0$, exothermic reaction

For example, suppose we use a bomb calorimeter to determine the enthalpy of the reaction in which magnesium metal, Mg(s), reacts with an aqueous solution of hydrochloric acid, HCl(aq), according to the net ionic equation

$$\text{Mg(s)} + 2\,\text{H}^+\text{(aq)} \rightarrow \text{Mg}^{2+}\text{(aq)} + \text{H}_2\text{(g)}$$

The chemical system consists of solid magnesium, aqueous hydrochloric acid, magnesium ions, and hydrogen gas. The surroundings are the liquid water in the calorimeter. During the reaction, the water temperature increases. You can infer from the temperature increase that energy is transferred from the chemical system to the surroundings (**Figure 4**). Therefore, the products have a lower enthalpy than the reactants, so $\Delta H < 0$ and this is an exothermic reaction.

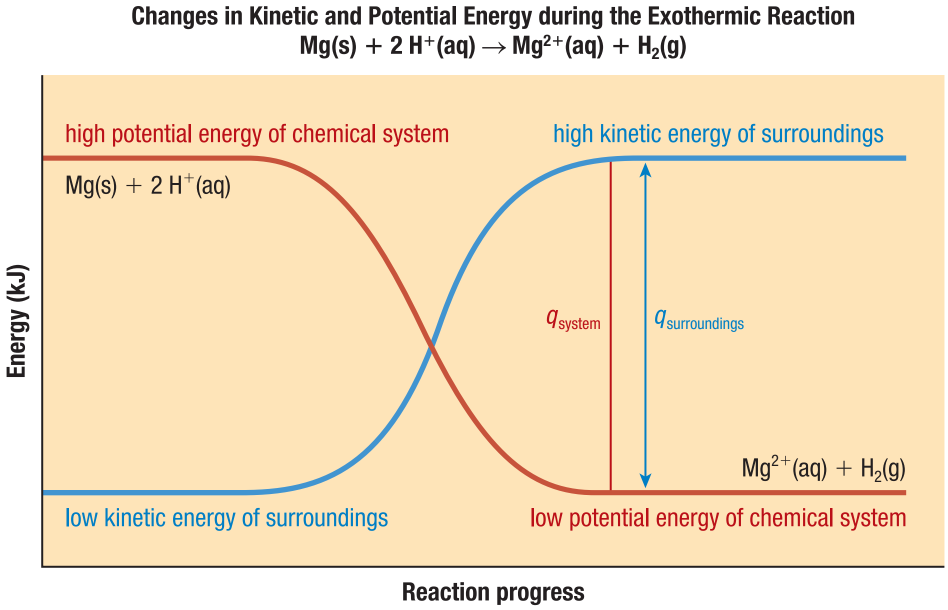


Figure 4 As this exothermic reaction progresses, the quantity of energy in the chemical system, q_{system}, decreases as the system releases energy to the surroundings. Consistent with the law of conservation of energy, this same quantity of energy, $q_{\text{surroundings}}$, is absorbed by the surroundings.

Molar Enthalpy Change

The **molar enthalpy change (ΔH_r)** of reaction for a substance is the energy change that occurs when 1 mol of that substance undergoes a physical, chemical, or nuclear change. The SI unit for molar enthalpy change is joules per mole (J/mol). In the symbol ΔH_r, the subscript "r" indicates the chemical reaction type. **Table 2** shows how the symbol for molar enthalpy change is written for various types of chemical reactions and gives examples of balanced equations for each. Notice that when you write the balanced equation for the molar enthalpy change of *formation* of a product, the coefficient of that product must always be 1. Other substances in the equation may have fractional coefficients as a result (see the equation for the formation of methanol, CH_3OH).

molar enthalpy change (ΔH_r) the enthalpy change associated with a physical, chemical, or nuclear change involving 1 mol of a substance; SI units J/mol

Table 2 Molar Enthalpies of Reaction

Type of molar enthalpy change (ΔH_r)	Example of change (relevant substance shown in red)
solution (ΔH_{sol})	$NaBr(s) \rightarrow Na^+(aq) + Br^-(aq)$
combustion (ΔH_c)	$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + H_2O(l)$
vaporization (ΔH_{vap})	$CH_3OH(l) \rightarrow CH_3OH(g)$
formation (ΔH_f)	$C(s) + 2\,H_2(g) + \frac{1}{2}\,O_2(g) \rightarrow CH_3OH(l)$
neutralization (ΔH_{neut})*	$2\,NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2\,H_2O(l)$
neutralization (ΔH_{neut})*	$NaOH(aq) + \frac{1}{2}\,H_2SO_4(aq) \rightarrow \frac{1}{2}\,Na_2SO_4(aq) + H_2O(l)$

*Enthalpy of neutralization can be written per mole of base or acid.

Investigation 5.2.1

Molar Enthalpy of a Chemical Change (page 333)

In this investigation, you will use a calorimeter to determine an experimental value for the molar enthalpy change of the neutralization of a base by an acid, ΔH_{neut}.

The quantity of energy involved in a change (the enthalpy change, ΔH, expressed in kJ) depends on the quantity of matter that undergoes the change. For example, it takes twice the quantity of energy to convert 1 L of liquid water to water vapour as it does to convert 500 mL. To calculate an enthalpy change, ΔH, for some amount of substance other than 1 mol, you need to obtain the molar enthalpy value, ΔH_r, from a reference source, and then use the formula

$$\Delta H = n\Delta H_r$$

where n is the amount and ΔH_r is the molar enthalpy change of the reaction.

Tutorial 2 Molar Enthalpy Calculations

In this tutorial, you will use molar enthalpy change of a reaction, ΔH_r, data to predict the enthalpy change for a physical or chemical change.

Sample Problem 1: Calculate ΔH for Vaporization Reactions

Ethanol, $CH_3CH_2OH(l)$, is used to disinfect the skin prior to an injection. If a 1.00 g sample of ethanol is spread across the skin and evaporated, what is the expected enthalpy change? The molar enthalpy of vaporization of ethanol is 38.6 kJ/mol.

Given: $m_{ethanol} = 1.00$ g; $\Delta H_{vap} = 38.6$ kJ/mol

Required: ΔH

Analysis: $\Delta H = n\Delta H_{vap}$

Solution:

Step 1. Calculate the amount of ethanol in 1.00 g.

$$M_{CH_3CH_2OH(l)} = 46.08 \text{ g/mol}$$

$$n_{CH_3CH_2OH(l)} = \frac{m_{CH_3CH_2OH(l)}}{M_{CH_3CH_2OH(l)}}$$

$$= \frac{1.00\ \cancel{\text{g}}}{46.08\ \cancel{\text{g}}/\text{mol}}$$

$$n_{\text{CH}_3\text{CH}_2\text{OH(l)}} = 0.021701\ \text{mol (2 extra digits carried)}$$

Step 2. Solve for the change in enthalpy using $\Delta H = n\Delta H_{\text{vap}}$.

$$\begin{aligned}\Delta H &= n\Delta H_{\text{vap}}\\ &= 0.021701\ \cancel{\text{mol}} \times \frac{38.6\ \text{kJ}}{1\ \cancel{\text{mol}}}\\ &= 0.838\ \text{kJ}\\ \Delta H &= 838\ \text{J}\end{aligned}$$

Step 3. Determine whether the enthalpy change is positive or negative.

In this case, ethanol must absorb energy to evaporate. Therefore, evaporation is endothermic and $\Delta H > 0$.

Statement: The enthalpy change for the evaporation of 1.00 g of ethanol is $+838$ J.

Sample Problem 2: Calculate ΔH for Dissolution Reactions

An energy change called enthalpy of solution, ΔH_{sol}, occurs when a substance dissolves in water. A student places 125 g of liquid water, $H_2O(l)$, at 24.2 °C into a coffee-cup calorimeter, and then adds 10.5 g of solid potassium bromide, KBr(s), also at 24.2 °C. He stirs the liquid until the potassium bromide dissolves, and then determines that the temperature has changed to 21.1 °C. Calculate the molar enthalpy change for this dissolution reaction, ΔH_{sol}. Assume that the specific heat capacity, c, of the liquid in the calorimeter is the same as the specific heat capacity of water, 4.18 J/(g·°C).

Given: $m_{\text{H}_2\text{O(l)}} = 125$ g; $m_{\text{KBr(s)}} = 10.5$ g; $T_{\text{initial}} = 24.2$ °C; $T_{\text{final}} = 21.1$ °C

Required: ΔH_{sol}

Analysis: $q = mc\Delta T$; $\Delta T = T_{\text{final}} - T_{\text{initial}}$

Solution:

Step 1. Calculate $q_{\text{surroundings}}$.

$$\begin{aligned}q_{\text{surroundings}} &= mc\Delta T\\ &= (m_{\text{H}_2\text{O(l)}})(c)(T_{\text{final}} - T_{\text{initial}})\\ &= (125\ \text{g})\left(4.18\frac{\text{J}}{\text{g·°C}}\right)(21.1 - 24.2\ \text{°C})\\ &= (125\ \cancel{\text{g}})\left(4.18\frac{\text{J}}{\cancel{\text{g}}\cdot\cancel{\text{°C}}}\right)(-3.1\ \cancel{\text{°C}})\\ q_{\text{surroundings}} &= -1.620 \times 10^3\ \text{J (2 extra digits carried)}\end{aligned}$$

Step 2. Determine ΔH_{system}.

Since the final temperature is lower than the initial temperature, the surroundings lose thermal energy to the system. Therefore, the system absorbs energy and so the reaction is endothermic.

$$\Delta H_{\text{system}} = 1.620 \times 10^3\ \text{J}$$

Step 3. Convert enthalpy change to molar enthalpy change using the molar mass, M. Use the periodic table to determine the molar mass of potassium bromide, $M_{\text{KBr(s)}}$, and then convert the mass of potassium bromide, $m_{\text{KBr(s)}}$, to amount, $n_{\text{KBr(s)}}$. Then, use this amount to convert the enthalpy change to the molar enthalpy change.

$$M_{\text{KBr(s)}} = 119.00\ \text{g/mol}$$

$$n_{\text{KBr(s)}} = \frac{m_{\text{KBr(s)}}}{M_{\text{KBr(s)}}}$$

$$= \frac{10.5\ \cancel{g}}{119.00\ \cancel{g}/\text{mol}}$$

$$n_{\text{KBr(s)}} = 0.088235\ \text{mol (two extra digits carried)}$$

$$\Delta H = n\Delta H_{\text{sol}}$$

$$\Delta H_{\text{sol}} = \frac{\Delta H}{n}$$

$$= \frac{1.620 \times 10^3\ \text{J}}{0.088235\ \text{mol}}$$

$$\Delta H_{\text{sol}} = 18\ \text{kJ/mol}$$

Statement: The molar enthalpy change of the dissolution reaction of potassium bromide in water is 18 kJ/mol.

Practice

1. Calculate the enthalpy change expected when 50.0 g of water vaporizes, if the molar enthalpy of vaporization of water is 44.0 kJ/mol. T/I [ans: 122 kJ]
2. Some ionic compounds are hydrates—solid compounds to which is bound a specific percentage of water. Some hydrates melt when heated and release energy when they solidify. For example, at 32 °C, liquid Glauber's salt—sodium sulfate decahydrate, $Na_2SO_4 \cdot 10\ H_2O(l)$—solidifies and releases 78.0 kJ/mol of energy. Calculate the enthalpy change when 2.50 kg of Glauber's salt enters the solid state? T/I [ans: −605 kJ]
3. Propane, C_3H_8, is a liquid in a pressurized barbecue tank but vaporizes instantly as it flows out of the tank. Calculate the mass of propane that would vaporize as a result of absorbing 100.0 kJ of energy. The molar enthalpy of vaporization of propane is 15.7 kJ/mol. T/I [ans: 281 g]
4. Sodium hydroxide, NaOH, is the active ingredient in some brands of drain openers. A temperature increase of 10.6 °C is observed when 4.00 g of sodium hydroxide is dissolved in 100.0 mL of water. Calculate the molar enthalpy of dissolution of sodium hydroxide. T/I [ans: -44.3×10^3 J/mol or −44.3 kJ/mol]

Representing Molar Enthalpy Changes

All chemical reactions undergo a change in enthalpy. Spectacular reactions such as the combustion of the highly flammable liquid ethanol are obviously exothermic (**Figure 5**). In most chemical reactions, however, the enthalpy change is more subtle. In fact, it is often difficult to tell whether a reaction is exothermic or endothermic. Therefore, it is important to have a clear way of communicating this information in the chemical equation for the reaction. A chemical equation that describes the enthalpy change of a reaction is called a thermochemical equation.

Figure 5 A flambé involves burning an alcoholic beverage, such as brandy, mixed with food.

For example, the synthesis of water from its elements is an exothermic reaction and can be represented by the two thermochemical equations

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) + 285\ \text{kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H = -285\ \text{kJ}$$

In the first thermochemical equation, an energy term is on the product side to indicate that energy is released by the chemical system. In the second thermochemical equation, the enthalpy change, ΔH, is written after the balanced chemical equation. In this example, the enthalpy change is negative, indicating that the process is exothermic. Notice that both equations indicate that 1 mol of hydrogen reacts to release 285 kJ of thermal energy. The only difference is how this energy change is communicated.

Now consider the reverse of this synthesis reaction. Electricity can be used to decompose water into its elements. For this reaction to occur, water must absorb 285 kJ/mol of energy. This reaction can be represented by the following two thermochemical equations:

$$H_2O(l) + 285\text{ kJ} \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g) \quad \Delta H = 285\text{ kJ}$$

In the first equation, the energy term is on the reactant side, indicating that energy is absorbed by the system. In the second equation, the molar enthalpy term has a positive sign, indicating that the decomposition reaction is endothermic.

potential energy diagram a graphical representation of the energy transferred during a physical or a chemical change

You can also represent the enthalpy change of a reaction using a potential energy diagram. In a chemical reaction, both reactants and products have potential energy. In a **potential energy diagram**, you express the potential energy (y-axis) as a function of the reaction progress (x-axis). For an exothermic reaction, the reactants have more potential energy than the products. Therefore, you will draw the line for the potential energy of the reactants higher than the line drawn for the products (**Figure 6(a)**). In an endothermic reaction, the products have more potential energy than the reactants, as the system absorbs energy (**Figure 6(b)**). Neither of the axes have numerical values, since you are only describing the enthalpy change, ΔH, of the reaction. CAREER LINK

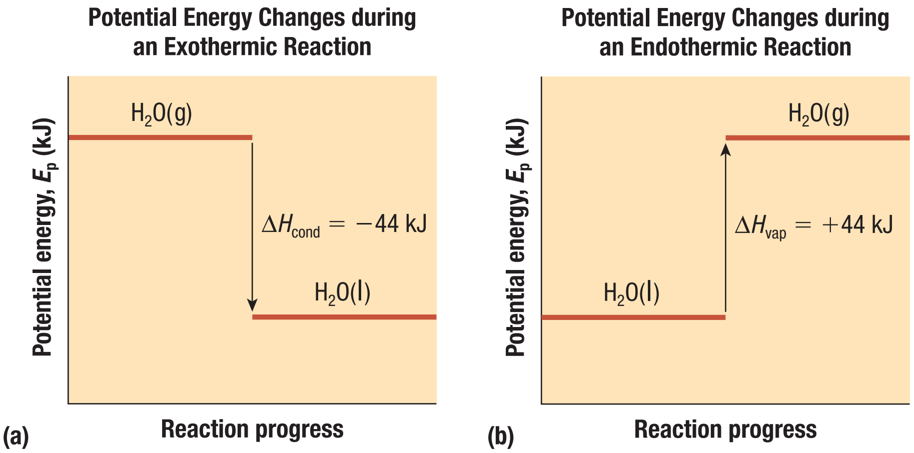


Figure 6 (a) The condensation reaction of 1 mol of water vapour is exothermic. The reactant has a higher potential energy than the product. (b) The vaporization reaction of liquid water to water vapour is endothermic. The reactant has a lower potential energy than the product.

Tutorial 3 Representing Thermochemical Enthalpy Changes

This tutorial provides an opportunity to gain experience in representing enthalpy changes in three ways: as a thermochemical equation with an energy term, as a thermochemical equation with a ΔH value, and in potential energy diagrams.

Sample Problem 1: Thermochemical Equations with Energy Terms

The combustion of methane gas, $CH_4(g)$, is an exothermic reaction. When 1 mol of methane burns, 802.3 kJ of energy is released. Write the thermochemical equation both by representing the energy change as a ΔH value, and by representing the energy change as an energy term in the equation.

Solution

Step 1. Write the balanced chemical equation without the energy term.

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

Step 2. To write the thermochemical equation with the energy included, decide whether the energy term should be on the reactant or product side. Since an exothermic reaction releases energy, place the energy term on the right, or product, side of the equation.

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) + 802.3\ kJ$

Notice that in this type of equation, you do not change the sign of the thermal energy term.

Step 3. To write the thermochemical equation with the ΔH to the side, determine the sign of the enthalpy change.

Since combustion reactions are exothermic, the enthalpy change has a negative value.

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \quad \Delta H_c = -802.3\ kJ$

Sample Problem 2: Drawing Potential Energy Diagrams

Draw potential energy diagrams for the following reactions:

(a) $CO_2(s) + 20.3\ kJ \rightarrow CO_2(g)$

(b) $CaCl_2(s) \rightarrow CaCl_2(aq) \quad \Delta H_{sol} = -82.8\ kJ$

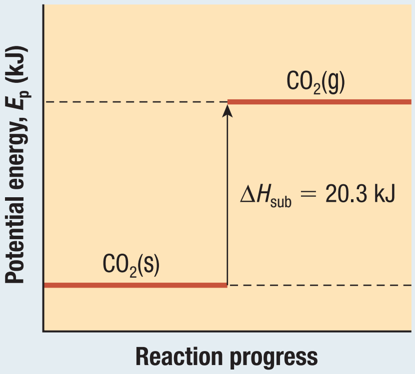
(c) $2\ Ag(s) + Cl_2(g) \rightarrow 2\ AgCl(s) + 254\ kJ$

Solution

(a) $CO_2(s) + 20.3\ kJ \rightarrow CO_2(g)$

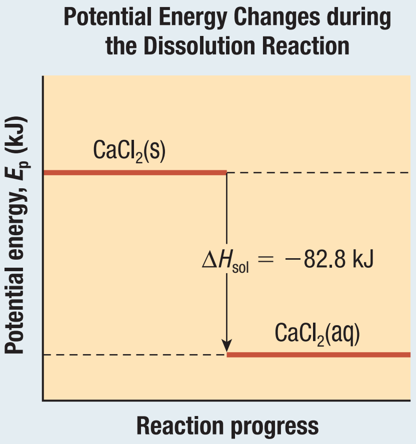
Since the energy term is on the reactant side of the equation, it is endothermic. Draw the reaction coordinates with the *x*-axis labelled "Reaction progress" and the *y*-axis labelled "Potential energy, E_p (kJ)." Since the product will have greater potential energy than the reactant, point the arrow from the reactant upward to the product. Write the reactant on the lower left-hand side of the graph and the product on the upper right-hand side of the graph. Include the ΔH of the reaction. This process is sublimation, so ΔH is ΔH_{sub}.

Potential Energy Changes during the Sublimation Reaction



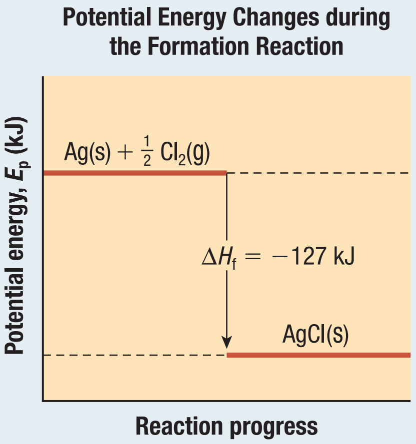
(b) $CaCl_2(s) \rightarrow CaCl_2(aq)\ \Delta H_{sol} = -82.8\text{ kJ}$

Since ΔH is negative, this reaction is exothermic. In an exothermic reaction, the reactants will have greater energy than the products, so the arrow will point downward from the reactant to the product.



(c) $2\text{ Ag}(s) + Cl_2(g) \rightarrow 2\text{ AgCl}(s) + 254\text{ kJ}$

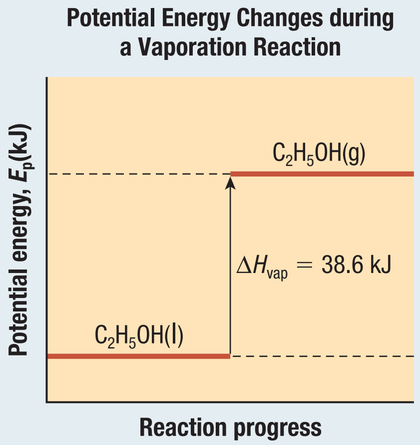
Since the energy term is on the side of the product, the reaction is exothermic. The equation is for the formation of 2 mol AgCl(s), so divide reactants, product, and enthalpy in half. Draw the potential energy diagram, per mole of AgCl(s) formed.



Practice

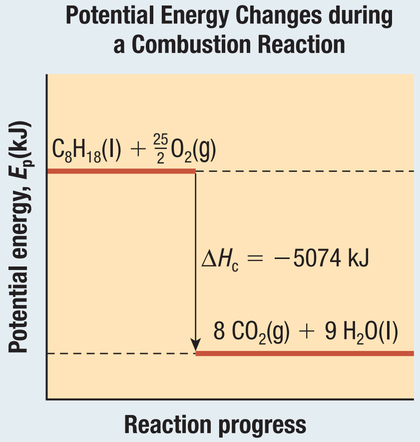
1. The molar enthalpy of combustion of ethyne, $C_2H_2(g)$, is −1300 kJ/mol. T/I C
   (a) Write a thermochemical equation for the combustion of 1 mol of ethyne.
   [ans: $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2\text{ CO}_2(g) + H_2O(g) + 1300\text{ kJ}$]
   (b) Draw a potential energy diagram for the reaction.
2. A cold pack consists of an inner pouch containing ammonium nitrate, $NH_4NO_3(s)$, and an outer pouch of water. Twisting the pack breaks the inner pouch and allows the water and ammonium nitrate to mix. As the ammonium nitrate dissolves, the temperature of the surroundings decreases. The energy change per mole of ammonium nitrate dissociated is 25.7 kJ. T/I C
   (a) Classify the reaction as endothermic or exothermic. [ans: endothermic]
   (b) Draw a potential energy diagram for the reaction. Label the change in enthalpy.
   (c) Write a thermochemical equation for this reaction.
   [ans: $NH_4NO_3(s) + 25.7\text{ kJ} \xrightarrow{H_2O} NH_4NO_3(aq)$]

3. Write out the corresponding thermochemical equation for the reaction depicted by each of the following potential energy diagrams: T/I



(a)

[ans: $C_2H_5OH(l) \rightarrow C_2H_5OH(g)\ \Delta H_{vap} = 38.6$ kJ]



(b)

[ans: $C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8\ CO_2(g) + 9\ H_2O(l)\ \ \Delta H_c = -5074$ kJ]

4. In a coffee-cup calorimeter, 50.0 mL of 0.100 mol/L $AgNO_3$(aq) and 50.0 mL of 0.100 mol/L HCl(aq) are mixed. The following equation represents the reaction that occurs:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

The two solutions were initially at 22.6 °C, and the final temperature is 23.4 °C. Calculate the thermal energy that accompanies this reaction in kJ/mol of AgCl formed. Assume that the combined solution has a mass of 100.0 g and a specific heat capacity of 4.18 J/(g · °C). K/U T/I [ans: −70 kJ]

5.2 Review

Summary

- Specific heat capacity, *c*, is the quantity of thermal energy required to raise the temperature of 1 g of a substance by 1 °C. The units for specific heat capacity are J/(g·°C).
- The quantity of thermal energy required to raise the temperature of a substance depends on the substance's mass, its specific heat capacity, and the temperature change.
- Calorimeters are devices that are used to determine the amount of thermal energy transferred during a chemical or physical change.
- Under constant pressure, the enthalpy change of a reaction, ΔH, equals the thermal energy released or absorbed by a system, q.
- The molar enthalpy of a reaction can be determined using $\Delta H = n\Delta H_r$.
- Exothermic reactions release energy and have a negative ΔH.
- Endothermic reactions absorb energy and have a positive ΔH.
- The enthalpy change of a reaction can be written as an energy term in a chemical equation or a ΔH value written after the chemical equation.

Questions

1. A potato is wrapped in aluminum foil and cooked in a campfire. The wrapped potato is then removed from the fire and allowed to cool for 1 min. The aluminum foil can be safely removed using your fingers, but touching the inside of the potato results in a serious burn. Use Table 1 on page 292 to explain these observations. (*Hint*: A potato contains a great deal of water.) K/U T/I A
2. Assuming gasoline is pure $C_8H_{18}(l)$, predict the sign of q_{system}, ΔH, and $q_{\text{surroundings}}$ for the process of burning gasoline into $CO_2(g)$ and $H_2O(g)$. K/U T/I
3. The enthalpy change for the chemical reaction represented by the chemical equation
   $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$
   is −891 kJ. K/U T/I
   (a) What is the enthalpy change for each mole of water formed?
   (b) What is the enthalpy change for each mole of carbon dioxide formed?
   (c) What is the enthalpy change for each mole of oxygen reacted?
4. The molar enthalpy of solution for ammonium chloride is +14.8 kJ/mol. What is the final temperature observed when 20.0 g of ammonium chloride is added to 125 mL water at 20.0 °C? K/U T/I
5. Draw a potential energy diagram for the reactions represented by the following equations: K/U T/I C
   (a) $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
   $\Delta H = 26\ \text{kJ}$
   (b) The combustion reaction of ethane,
   $C_2H_6(g) + \frac{7}{2}\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$
   $\Delta H_c = -1423\ \text{kJ}$
6. Rewrite each of the following using a thermochemical equation with a ΔH value: K/U T/I C
   (a) The standard molar enthalpy of combustion for propane is −2220 kJ/mol.
   (b) The molar enthalpy for the separation of the atoms in the chlorine molecule is 243 kJ /mol of chlorine.
   (c) The molar enthalpy of the formation of iron(III) oxide from its elements is −824 kJ/mol of iron(III) oxide.
   (d) The molar enthalpy for the decomposition of hydrogen chloride into its elements is +93 kJ/mol.
7. For each of the following, write a thermochemical equation that includes an energy term within the equation. K/U T/I C
   (a) The formation of 1 mol of copper(II) chloride from its elements releases 220.1 kJ of energy.
   (b) The energy absorbed when graphite is converted to diamond is 2.0 kJ/mol of graphite.
   (c) The decomposition of silver chloride into its elements requires 127.1 kJ/mol of silver chloride.

Bond Energies

5.3

Ethyne, C_2H_2, is a colourless hydrocarbon commonly known as acetylene. This compound burns readily to produce flames with temperatures greater than 3000 °C. At these temperatures, a torch burning a mixture of oxygen and acetylene can cut through steel (**Figure 1**). Oxyacetylene torches are also used for welding metals together. However, many welders today use electric welding torches.

Is it possible to predict how much energy the combustion of acetylene releases? The answer is yes; you can estimate the enthalpy change of any chemical reaction if you know the quantity of energy associated with the chemical bonds of both the reactants and products.

Figure 1 A worker in heat-resistant protective clothing uses an oxyacetylene torch to cut steel.

Measuring Bond Energies

A covalent bond between 2 atoms will break if enough energy is supplied. The quantity of energy required to break a chemical bond is its **bond dissociation energy**. Bond dissociation energies have positive values. For example, a single covalent C–H bond in a hydrocarbon (such as methane or propane) has an average bond energy of 413 kJ/mol. This means that it takes 413 kJ of energy to break 1 mol of C–H bonds into 1 mol of C atoms and 1 mol of H atoms. Conversely, when a C–H bond forms, 413 kJ of energy is released, in keeping with the law of conservation of energy. **Table 1** lists average bond energies for several covalent bonds.

bond dissociation energy the energy required to break a given chemical bond

Table 1 Average Bond Energies (kJ/mol)

Single bonds			Multiple bonds
H–H 432	N–H 391	I–I 149	C=C 614
H–F 565	N–N 160	I–Cl 208	C≡C 839
H–Cl 427	N–F 272	I–Br 175	O=O 495
H–Br 363	N–Cl 200	S–H 347	C=O* 745
H–I 295	N–Br 243	S–F 327	C≡O 1072
C–H 413	N–O 201	S–Cl 253	N=O 607
C–C 347	O–H 467	S–Br 218	N=N 418
C–N 305	O–O 146	S–S 266	N≡N 941
C–O 358	O–F 190	Si–Si 340	C≡N 891
C–F 485	O–Cl 203	Si–H 393	C=N 615
C–Cl 339	O–I 234	Si–C 360	
C–Br 276	F–F 154	Si–O 452	
C–I 240	F–Cl 253		
C–S 259	F–Br 237		
	Cl–Cl 239		
	Cl–Br 218		
	Br–Br 193		

*C=O in CO_2(g)=799

Why are bond dissociation energies reported as average bond energies? The bond dissociation energy of a given bond depends on the types of atoms and bonds in the same molecule.

For example, consider the stepwise decomposition of methane and the energy required for each step to occur:

Process	Energy Required (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	435
$CH_3(g) \rightarrow CH_2(g) + H(g)$	453
$CH_2(g) \rightarrow CH(g) + H(g)$	425
$CH(g) \rightarrow C(g) + H(g)$	339
	Total = 1652

$$\text{Average} = \frac{1652}{4} = 413$$

Although a C–H bond is broken in each step, a different amount of energy is required each time. This shows that the bond energy of a C–H bond is affected by the number of atoms and bonds around it. Therefore, 413 kJ/mol only approximates the energy associated with a C–H bond in a particular molecule. The use of an average bond energy is convenient for predicting enthalpy changes in chemical reactions.

Multiple Bonds and Bond Energies

Notice in the data given in Table 1 (page 307) that multiple bonds have larger bond energies than single bonds. For example, 839 kJ/mol of energy is required to break a triple bond between carbon atoms. Breaking a double bond between carbon atoms requires only 614 kJ/mol of energy, and it takes only 347 kJ/mol of energy to break a single C–C bond. This suggests that multiple bonds are generally stronger than single bonds.

A relationship also exists between the number of bonds between atoms (that is, number of electrons shared) and the length of a covalent bond (that is, distance between nuclei): as the number of bonds increases, the bond length shortens (**Table 2**).

Table 2 Bond Lengths of Some Common Bonds

Bond	Bond type	Bond length (pm)	Bond energy (kJ/mol)
C–C	single	154	347
C=C	double	134	614
C≡C	triple	120	839
C–O	single	143	358
C=O	double	123	745
C–N	single	143	305
C=N	double	138	615
C≡N	triple	116	891

Enthalpy and Bond Energies

Bond energy values can be used to calculate approximate enthalpy changes, ΔH, for reactions. During a chemical reaction, the bonds in the reactants must first break. For bonds to be broken, energy must be *added*—an endothermic process. Hence, energy terms associated with bond breaking have *positive* signs. Making new bonds in the products *releases* energy—an exothermic process. Therefore, energy terms associated with bond making have *negative* signs.

We can write the enthalpy change for a reaction as

$$\Delta H = \begin{array}{l}\text{sum of energies required}\\ \text{to break old bonds}\\ \text{(positive values)}\end{array} + \begin{array}{l}\text{sum of energies released in}\\ \text{the formation of new bonds}\\ \text{(negative values)}\end{array}$$

This leads to the equation

$$\Delta H = \underbrace{\Sigma n \times D \text{ (bonds broken)}}_{\text{energy required}} - \underbrace{\Sigma n \times D \text{ (bonds formed)}}_{\text{energy released}}$$

where the symbol Σ (sigma) means "the sum of," *n* is the amount (in moles) of a particular bond type, and *D* is the bond energy per mole of bonds. *D* is always a positive value. The value of *D* is obtained from reference tables, such as Table 1 (page 307).

The first step in using bond energies to predict Δ*H* for a reaction is to determine how many of each type of bond must be broken in the reactants. Next, determine the number of bonds of each type that form in the products. Finally, use bond energy data from Table 1 (page 307) to calculate the total energy required to break the reactant bonds, followed by the total energy released by the formation of product bonds. The energy change, Δ*H*, of the reaction is the difference between these two sums.

Tutorial 1 Estimating Enthalpy Change from Bond Energies

In this tutorial, you will use bond energies to calculate an approximate value of the enthalpy change, Δ*H*, for a number of different chemical reactions. (Note that in this tutorial Table 1 on page 307 is referenced often.)

Sample Problem 1: Using Bond Energies and a Balanced Chemical Equation to Estimate Δ*H*

Using the bond energies in Table 1, calculate the enthalpy change for the reaction in which hydrogen gas, $H_2(g)$, is combined with fluorine gas, $F_2(g)$, to produce 2 moles of hydrogen fluoride gas, HF(g). This reaction is represented by the balanced chemical equation:

$$H_2(g) + F_2(g) \rightarrow 2\,HF(g)$$

Given: for $H_2(g)$: $n_{H–H} = 1$ mol; $D_{H–H} = 432$ kJ/mol;
for $F_2(g)$: $n_{F–F} = 1$ mol; $D_{F–F} = 154$ kJ/mol;
for HF(g): $\mathrm{n}_{H–F} = 2$ mol; $D_{H–F} = 565$ kJ/mol

Required: Δ*H*

Analysis: $\Delta H = \Sigma n \times \mathrm{D}_{\text{bonds broken}} - \Sigma n \times D_{\text{bonds formed}}$

$$\Delta H = (n_{H-F}D_{H-F} + n_{F-F}D_{F-F}) - n_{H-F}D_{H-F}$$

Solution:

1 mol each of H–H and F–F bonds are broken. The bonds formed are 2 mol of H–F bonds. Therefore,

$$\begin{aligned}\Delta H &= (n_{H-F}D_{H-F} + n_{F-F}D_{F-F}) - n_{H-F}D_{H-F}\\ &= (1\text{ mol} \times D_{H-H} + 1\text{ mol} \times D_{F-F}) - 2\text{ mol} \times D_{H-F}\\ &= \left[\left(1\,\cancel{\text{mol}} \times \frac{432\text{ kJ}}{\cancel{\text{mol}}}\right) + \left(1\,\cancel{\text{mol}} \times \frac{154\text{ kJ}}{\cancel{\text{mol}}}\right)\right] - \left(2\,\cancel{\text{mol}} \times \frac{565\text{ kJ}}{\cancel{\text{mol}}}\right)\end{aligned}$$

$$\Delta H = -544\text{ kJ}$$

Statement: The reaction of 1 mol of hydrogen gas and 1 mol of fluorine gas to produce 2 mol of hydrogen fluoride releases 544 kJ of energy. Thus, the enthalpy change (Δ*H*) is −544 kJ.

Sample Problem 2: Using Bond Energies and Lewis Diagrams to Estimate Δ*H*

Using the bond energies in Table 1, calculate the enthalpy change for the reaction in which methane gas, $CH_4(g)$, is combined with chlorine gas and fluorine gas to produce

Freon-12 gas, $CF_2Cl_2(g)$. **Figure 2** shows the Lewis structures of methane and Freon-12. The balanced chemical equation for the formation of 1 mol of Freon-12 is

$$CH_4(g) + 2\ Cl_2(g) + 2\ F_2(g) \rightarrow CF_2Cl_2(g) + 2\ HF(g) + 2\ HCl(g)$$


methane Freon-12

Figure 2

Solution

Step 1. For each reactant and product, identify the number of moles of bonds, the amount of bonds in the reaction, and the bond energy per mole (using the data in Table 1). Organize this information in a table, similar to **Table 3.**

Table 3 Bonds and Bond Energies in Reactants and Products

	Substance	Number of bonds moles of ($n_{\text{substance}}$)	Amount of bonds in reaction	Bond energy per mole
reactants	$CH_4(g)$	4 mol C–H bonds	4 mol	413 kJ/mol
	$Cl_2(g)$	1 mol Cl–Cl bonds	2 mol	239 kJ/mol
	$F_2(g)$	1 mol F–F bonds	2 mol	154 kJ/mol
products	$CF_2Cl_2(g)$	2 mol C–F bonds 2 mol C–Cl bonds	2 mol 2 mol	485 kJ/mol 339 kJ/mol
	HF(g)	1 mol H–F bonds	2 mol	565 kJ/mol
	HCl(g)	1 mol H–Cl bonds	2 mol	427 kJ/mol

Step 2. Calculate the enthalpy change, ΔH, of the reaction.

$$\Delta H = \Sigma n \times D_{\text{bonds broken}} - \Sigma n \times D_{\text{bonds formed}}$$

$$\Delta H = (nD_{\text{C}-\text{H}} + nD_{\text{Cl}-\text{Cl}} + nD_{\text{F}-\text{F}}) - (nD_{\text{C}-\text{F}} + nD_{\text{C}-\text{Cl}} + nD_{\text{H}-\text{F}} + nD_{\text{H}-\text{Cl}})$$

For convenience, first add the total energy absorbed to break the bonds in the reactants:

$$\begin{aligned}\Sigma n \times D_{\text{bonds broken}} &= (nD_{\text{C}-\text{H}} + nD_{\text{Cl}-\text{Cl}} + nD_{\text{F}-\text{F}}) \\ &= \left(4\ \cancel{\text{mol}} \times \frac{413\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(2\ \cancel{\text{mol}} \times \frac{239\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(2\ \cancel{\text{mol}} \times \frac{154\ \text{kJ}}{\cancel{\text{mol}}}\right) \\ &= 1652\ \text{kJ} + 478\ \text{kJ} + 308\ \text{kJ} \\ \Sigma n \times D_{\text{bonds broken}} &= 2438\ \text{kJ}\end{aligned}$$

This is the energy required to break the bonds in the reactants.

Now, add the total energy released when the bonds of products form.

$$\begin{aligned}\Sigma n \times D_{\text{bonds formed}} &= (nD_{\text{C}-\text{F}} + nD_{\text{C}-\text{Cl}} + nD_{\text{H}-\text{F}} + nD_{\text{H}-\text{Cl}}) \\ &= \left(2\ \cancel{\text{mol}} \times \frac{485\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(2\ \cancel{\text{mol}} \times \frac{339\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(2\ \cancel{\text{mol}} \times \frac{565\ \text{kJ}}{\cancel{\text{mol}}}\right) + \\ &\qquad \left(2\ \cancel{\text{mol}} \times \frac{427\ \text{kJ}}{\cancel{\text{mol}}}\right) \\ &= 970\ \text{kJ} + 678\ \text{kJ} + 1130\ \text{kJ} + 854\ \text{kJ} \\ \Sigma n \times D_{\text{bonds formed}} &= 3632\ \text{kJ}\end{aligned}$$

This is the energy released when the bonds are formed in the products.

Subtract the energy released when the bonds of the products form from the energy absorbed to break the bonds of the reactants.

$$\Delta H = \Sigma n \times D_{\text{bonds broken}} - \Sigma n \times D_{\text{bonds formed}}$$

$$= 2438 \text{ kJ} - 3632 \text{ kJ}$$

$$\Delta H = -1194 \text{ kJ}$$

The sign of the enthalpy change in the formation Freon-12 gas is negative. This is an exothermic reaction and energy is released.

Statement: When 1 mol of Freon-12 gas is formed by reacting gaseous methane, chlorine, and fluorine, 1194 kJ of energy is released. Thus, the enthalpy change (ΔH) is −1194 kJ.

Sample Problem 3: Using Bond Energies and Chemical Structures to Estimate ΔH

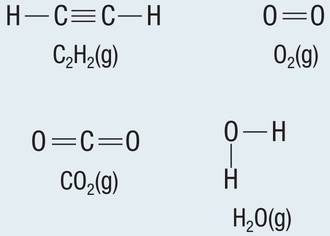
Using bond energies from Table 1, determine whether the complete combustion of ethyne gas (acetylene), $C_2H_2(g)$, to carbon dioxide gas and liquid water is exothermic or endothermic.

Solution

Step 1. Write the balanced chemical equation for the combustion of 1 mol of ethyne:

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2\ CO_2(g) + H_2O(g)$$

Step 2. Determine the bonding of each substance by drawing structural formulas for each molecule in the reaction:



Step 3. Determine the number of moles of reactants and products, the number of moles of bonds broken or formed, and the molar bond energy for each. Organize this information in a table, similar to **Table 4.**

Table 4 Bonds and Bond Energies in Reactants and Products

	Substance	Number of moles of bonds ($n_{\text{substance}}$)	Amount of bonds in reaction	Bond energy per mole
reactants	$C_2H_2(g)$	2 mol C–H bonds 1 mol C≡C bonds	2 mol 1 mol	413 kJ/mol 839 kJ/mol
	$O_2(g)$	1 mol O=O bonds	$\frac{5}{2}$ mol	495 kJ/mol
products	$CO_2(g)$	2 mol C=O bonds	4 mol	799 kJ/mol
	$H_2O(g)$	2 mol H–O bonds	2 mol	467 kJ/mol

Note that in Table 1, the asterisk indicates that $CO_2(g)$ has a different ΔH than a regular C=O double bond.

Step 4. Calculate the enthalpy change, ΔH, of the reaction.

$$\Delta H = \Sigma n \times D_{\text{bonds broken}} - \Sigma n \times D_{\text{bonds formed}}$$

$$\Delta H = (n_{\text{C}-\text{H}}D_{\text{C}-\text{H}} + n_{\text{C}\equiv\text{C}}D_{\text{C}\equiv\text{C}} + n_{\text{O}=\text{O}}D_{\text{O}=\text{O}}) - (n_{\text{C}=\text{O}}D_{\text{C}=\text{O}} + n_{\text{H}-\text{O}}D_{\text{H}-\text{O}})$$

$$= \left[\left(2\ \cancel{\text{mol}} \times \frac{413\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(1\ \cancel{\text{mol}} \times \frac{839\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(\frac{5}{2}\ \cancel{\text{mol}} \times \frac{495\ \text{kJ}}{\cancel{\text{mol}}}\right)\right] - \left[\left(4\ \cancel{\text{mol}} \times \frac{799\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(2\ \cancel{\text{mol}} \times \frac{467\ \text{kJ}}{\cancel{\text{mol}}}\right)\right]$$

$$= (826\ \text{kJ} + 839\ \text{kJ} + 1237.5\ \text{kJ}) - (3196\ \text{kJ} + 934\ \text{kJ})$$

$$= 2902.5\ \text{kJ} - 4130\ \text{kJ}$$

$$\Delta H = -1228\ \text{kJ}$$

Statement: When enthalpy change has a negative value, there is more energy released by the formation of the bonds in the products than is absorbed by the breaking of the bonds in the reactants. Therefore, thermal energy is released to the surroundings, and the reaction is exothermic.

Practice

1. Use the data from Table 1 to calculate the energy to separate 1 mol of chloromethane, $CH_3Cl(g)$, into free atoms. K/U T/I [ans: 1578 kJ/mol]
2. Using bond energies, verify that the complete combustion of ethene gas, $C_2H_4(g)$ ($H_2C{=}CH_2$), to gaseous carbon dioxide and water is an exothermic reaction. K/U T/I [ans: −1313 kJ]
3. Using the data from Table 1, calculate the enthalpy change of the chemical reaction represented by the balanced equation

   $N_2H_2(g) + F_2(g) \rightarrow N_2(g) + 2\ HF(g)$

   Is the reaction endothermic or exothermic? Explain. K/U T/I [ans: −717 kJ; exothermic]
4. Propane, $C_3H_8(g)$, is a gaseous fuel that burns with oxygen. Write the balanced chemical equation for this complete combustion reaction, and use the bond energies from Table 1 to calculate the quantity of energy released. K/U T/I A [ans: −2057 kJ]

The bonds between specific atoms and the bond energies associated with these bonds are very similar, even when the bonds are located in different entities. For example, the bond energy of the C–H bond in methane is similar to the bond energies of the C–H bonds in ethane, $C_2H_6(g)$; ethyne, $C_2H_2\ (g)$; and chloromethane, CH_3Cl (g). Thus, molecules with similar bonds act in similar ways.

Since the bond energies of similar bonds are nearly the same in different molecules, you can calculate and compare the enthalpy changes of reactions by using bond energies because they provide a good approximation of the actual bond energy value. For example, in Sample Problem 3 in Tutorial 1, you calculated an enthalpy change of −1227 kJ/mol for the combustion reaction of acetylene gas. The experimental value of this reaction is −1299 kJ/mol. CAREER LINK

5.3 Review

Summary

- Bond energy is the quantity of energy required to break a chemical bond.
- As the number of bonds increases, the bond length shortens.
- More energy is needed to break multiple bonds than to break single bonds.
- Bond breaking is an endothermic process.
- Bond making is an exothermic process.
- An approximate value of the ΔH of a reaction can be calculated using the bond energies of the reactants and products.

Questions

1. Use bond energy values (Table 1, page 307) to estimate ΔH for the reactions represented by the following equations: K/U T/I
   (a) $H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$
   (b) $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$
2. Use bond energy values (Table 1, page 307) to estimate ΔH for the reactions represented by the following equations: K/U T/I
   (a) $HCN(g) + 2\,H_2(g) \rightarrow CH_3NH_2(g)$
   (b) $N_2H_4(g) + 2\,F_2(g) \rightarrow N_2(g) + 4\,HF(g)$
3. Explain why ΔH values of chemical reactions are found using bond energies that are not always equal to values found by experiment. Assume experimental error is not a factor. K/U T/I
4. Consider the reaction represented by the equation

   $$A_2 + B_2 \rightarrow 2\,AB \quad \Delta H = -549\text{ kJ}$$

   The bond energy for A_2 is one-half the AB bond energy. The bond energy of B_2 is 432 kJ/mol. Calculate the bond energy of A_2. K/U T/I
5. In which molecule, N_2, N_2H_2 or N_2O_4, would the nitrogen–nitrogen bond be the shortest, and why? Draw Lewis structures to help you decide. K/U T/I C
6. Explain why the numerical value of a carbon–carbon bond in a molecule of ethanol would differ from that in a molecule of ethane. Include Lewis structures for ethanol and ethane in your explanation. K/U T/I C
7. The bond energy of a C–O single bond is less than the bond energy of a C=O double bond. Explain why this is true. K/U T/I
8. Acetic acid is responsible for the sour taste of vinegar. Acetic acid can be manufactured using the reaction represented by the equation

   $$CH_3OH(g) + CO(g) \rightarrow CH_3COOH(l)$$

   Use bond energy values from Table 1 (page 307) to estimate the ΔH for this reaction. K/U T/I
9. Consider the reaction represented by the equation

   $$C_2H_4(g) + F_2(g) \rightarrow C_2H_4F_2(g)\ \Delta H = -549\text{ kJ}$$

   Estimate the carbon–fluorine bond energy, given that the C–C bond energy is 347 kJ/mol, the C=C bond energy is 614 kJ/mol, and the F–F bond energy is 154 kJ/mol. K/U T/I
10. In photosynthesis, a plant converts carbon dioxide and water to glucose, $C_6H_{12}O_6(s)$, and oxygen. Use bond energy values from Table 1 (page 307) to estimate the amount of energy the Sun provides to produce 1 mol of glucose. Assume the straight-chain version of glucose (p. 101). K/U T/I
11. Carbon monoxide, CO(g), can react with oxygen, $O_2(g)$, to produce carbon dioxide, $CO_2(g)$. Use bond energy values from Table 1 (page 307) to determine if this reaction is exothermic or endothermic. K/U T/I
12. Carbon dioxide, $CO_2(g)$, can react with water, $H_2O(l)$, to produce carbonic acid, $H_2CO_3(aq)$, a component of acid rain. K/U T/I C
    (a) Write a balanced equation for this reaction.
    (b) Use Lewis structures to illustrate this reaction.
    (c) Determine the energy required to convert 1 mol of carbon dioxide to 1 mol of carbonic acid.
13. Many barbecues are fuelled by propane, $C_3H_8(g)$. Other barbecues are fuelled by natural gas, which is mostly methane, $CH_4(g)$. K/U T/I
    (a) Use bond energy values to estimate the amount of heat produced by the complete combustion of 1 mol of propane, and of 1 mol of methane.
    (b) How many moles of natural gas are needed to produce the same amount of energy as 1.0 mol of propane?

5.4 Hess's Law

Imagine you and some friends are hiking up a mountain trail. You come to a fork in the trail and decide to break into two groups. One group follows a short, steep path while the other takes a set of stairs with a gradual slope. Eventually, both groups reach the top of the trail and are rewarded by a beautiful view. Although the two groups took different routes, everyone reached the same place. We can think of the process of a chemical reaction as behaving in a similar way to these mountain climbers. There is more than one possible route to get from reactants to products.

Enthalpy Change and Hess's Law

From experimental evidence, chemists have found that the change in enthalpy in a chemical process is independent of the path taken. This means that in going from an initial set of reactants to a final set of products, the change in enthalpy is the same regardless of whether the conversion happens in one step or in a series of steps. To illustrate this concept, consider the analogy of going from the bottom floor to the top floor of a building. The net vertical distance you travel is the same regardless of whether you take the stairs or the elevator. Similarly, the change in enthalpy of converting one chemical to another is the same whether the conversion happens in one reaction or in more than one.

Figure 1 Hess's work is one of the earliest examples of the field of theoretical chemistry.

Germain Henri Hess, a professor at the University of St. Petersburg, Russia, (**Figure 1**) was interested in whether the number of steps involved in a chemical process affected the enthalpy change of a reaction. At a time when most chemists were identifying new chemical substances, Hess was interested in why atoms are attracted to one another. He determined that the change in enthalpy would always be the same no matter how many steps it took to get the desired product.

Consider the reaction in which gaseous nitrogen and oxygen combine to form nitrogen dioxide gas. There are at least two ways we might get from reactants to products. The overall reaction could occur in a single step. The thermochemical equation for this single-step reaction is

$$N_2(g) + 2\,O_2(g) \rightarrow 2\,NO_2(g) \quad \Delta H = 68\ \text{kJ}$$

However, nitrogen dioxide can also be made using a two-step process. The thermochemical equations for the two steps are

$$N_2(g) + O_2(g) \rightarrow 2\,NO(g) \quad \Delta H = 180\ \text{kJ}$$

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g) \quad \Delta H = -112\ \text{kJ}$$

If you add these two equations, you get the equation for the overall (net) reaction for the formation of nitrogen dioxide gas. Similarly, the sum of the enthalpy changes of the reactions represented by these equations is equal to the enthalpy change for the net reaction for the formation of nitrogen dioxide gas.

$$\begin{array}{ll} N_2(g) + O_2(g) \rightarrow 2\,\cancel{NO}(g) & \Delta H = 180\ \text{kJ} \\ 2\,\cancel{NO}(g) + O_2(g) \rightarrow 2\,NO_2(g) & \Delta H = -112\ \text{kJ} \\ \hline N_2(g) + 2\,O_2(g) \rightarrow 2\,NO_2(g) & \Delta H = 68\ \text{kJ} \end{array}$$

This example illustrates that when a reaction proceeds from reactants to products, the change in enthalpy is the same whether the reaction occurs in one step or several. This generalization is now called Hess's law.

Hess's law
The enthalpy change for the conversion of reactants to products is the same whether the conversion occurs in one step or several steps.

Hess's law is very useful for studying energy changes in chemical reactions that cannot be analyzed using calorimetry. Some reactions, such as the reaction of glycerine, $C_3H_5(OH)_3(l)$, with potassium permanganate, $KMnO_4(s)$, are too fast or dangerous (**Figure 2**). Other reactions, such as the synthesis of nitrogen dioxide from its elements, occur too slowly. **Figure 3** illustrates the application of Hess's law to this chemical reaction. The two-step process is shown in blue. The first step involves a large positive enthalpy change ($\Delta H = 180$ kJ), but the second step involves a negative enthalpy change ($\Delta H = -112$ kJ). The sum of these two enthalpy changes is equal to the enthalpy change of the one-step process (shown in red).

Figure 2 The reaction of potassium permanganate with glycerine. Potassium permanganate reacts so vigorously with most organic compounds, it must be stored separately.

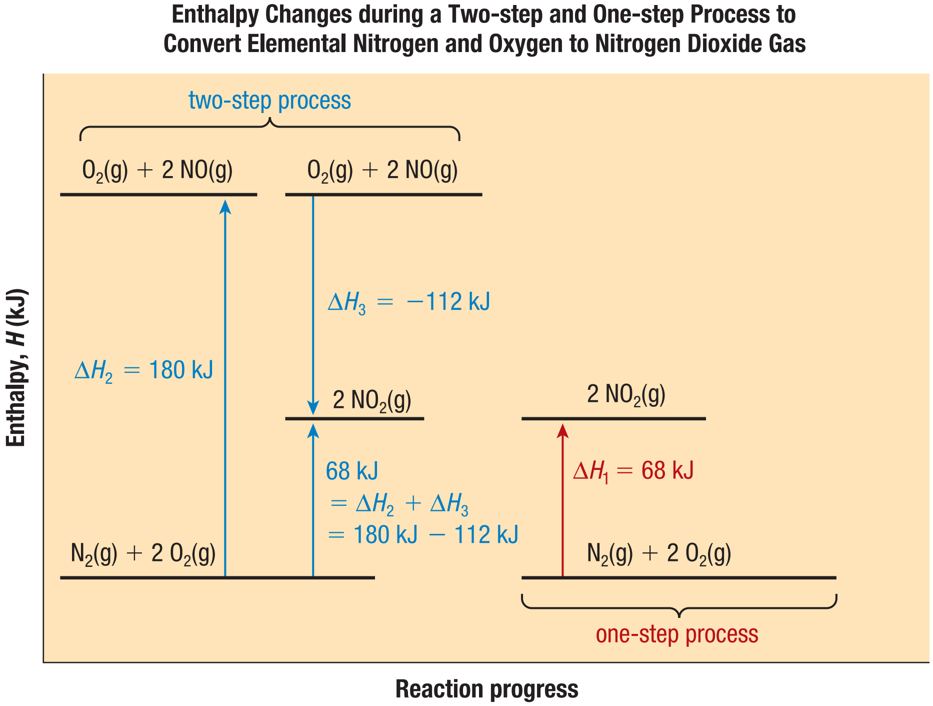


Figure 3 Enthalpy change diagram for the formation of nitrogen dioxide gas from gaseous nitrogen and oxygen. The net enthalpy change is the same whether the process occurs in one step or two.

Rules for Enthalpy Changes

To use Hess's law to calculate enthalpy changes for chemical reactions, you must apply the following two rules:

1. If you reverse a chemical reaction, you must also reverse the sign of ΔH.
2. The magnitude of ΔH is directly proportional to the number of moles of reactants and products in a reaction. If the coefficients in a balanced equation are multiplied by a factor, the value of ΔH is multiplied by the same factor.

To understand the first rule, recall that the sign of ΔH indicates the direction of the thermal energy flow. If the direction of the reaction is reversed, the direction of the thermal energy flow will also be reversed. Consider the preparation of xenon tetrafluoride, $XeF_4(s)$. The thermochemical equation for this reaction is

$$Xe(g) + 2\ F_2(g) \rightarrow XeF_4(s) \quad \Delta H = -251 \text{ kJ}$$

The forward reaction is exothermic, so 251 kJ of thermal energy flows from the chemical system to the surroundings. In the reverse reaction, solid xenon tetrafluoride decomposes to gaseous xenon, $Xe(g)$, and fluorine, $F_2(g)$, and thermal energy flows from the surroundings to the chemical system.

$$XeF_4(s) \rightarrow Xe(g) + 2\ F_2(g) \quad \Delta H = 251 \text{ kJ}$$

In the reverse reaction, the sign of ΔH is positive. Therefore, the reverse reaction is endothermic.

The second rule tells you that the value of ΔH depends on the amounts of the substances reacting. For example, 251 kJ of thermal energy is released during the reaction of 1 mol of xenon gas and 2 mol of fluorine gas. However, when the amounts of these reactants are doubled, twice as much thermal energy is released 502 kJ.

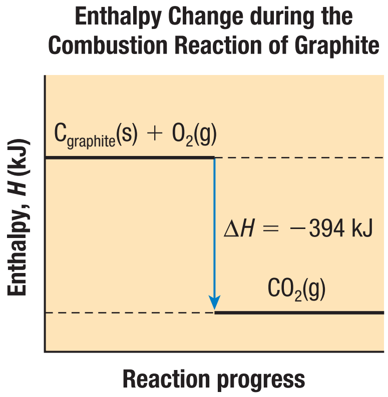


Figure 4 Enthalpy change diagram for the combustion of graphite

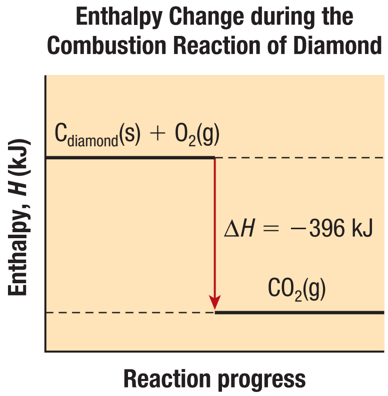


Figure 5 Enthalpy change diagram for the combustion of diamond

Tutorial 1 Calculating ΔH Using Hess's Law

In this tutorial, you will use Hess's law to calculate the enthalpy change of a reaction by algebraically manipulating two or more other reaction equations.

Sample Problem 1: Calculate ΔH Using Enthalpy Change Diagrams

Graphite and diamond are two forms of solid carbon. Graphite is a soft, black, slippery material that is the substance in pencils that makes marks. Diamond is a hard, crystalline substance used in making jewellery. Use the data in **Figure 4** and **Figure 5** to calculate the enthalpy change for the conversion of graphite to diamond.

$$C_{graphite}(s) \rightarrow C_{diamond}(s)$$

Solution

Step 1. Use the data in Figure 4 and Figure 5 to write balanced thermochemical equations for the combustion reactions.

$$(1)\ C_{graphite}(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -394\text{ kJ}$$

$$(2)\ C_{diamond}(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -396\text{ kJ}$$

Step 2. Rearrange the equations as needed to get the required reactants and products.

In the conversion reaction, graphite is a reactant and diamond is a product. Therefore, reverse the second equation and change the sign of its ΔH.

$$(3)\ CO_2(g) \rightarrow C_{diamond}(s) + O_2(g) \qquad \Delta H = +396\text{ kJ}$$

Step 3. Add equations (1) and (3) and their respective enthalpy values to obtain the conversion reaction equation and ΔH value.

$$\begin{array}{ll} C_{graphite}(s) + \cancel{O_2(g)} \rightarrow \cancel{CO_2(g)} & \Delta H = -394\text{ kJ} \\ \underline{\cancel{CO_2(g)} \rightarrow C_{diamond}(s) + \cancel{O_2(g)}} & \underline{\Delta H = +396\text{ kJ}} \\ C_{graphite}(s) \rightarrow C_{diamond}(s) & \Delta H = \quad +2\text{ kJ} \end{array}$$

Statement: The enthalpy change during the conversion of graphite to diamond is 2 kJ/mol.

Sample Problem 2: Calculate ΔH for the Production of Ethene Using Hess's Law

Ethene gas, $C_2H_4(g)$, is the raw material for the synthesis of the plastic polyethylene. Engineers designing a process to make ethene from ethane gas, $C_2H_6(g)$, need to know the change in enthalpy of the desired reaction represented by the following balanced chemical equation:

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

The engineers have the following thermochemical equations:

$$(1)\ \ C_2H_6(g) + 3.5\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l) \qquad \Delta H = -1559\text{ kJ}$$

$$(2)\ \ C_2H_4(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 2\ H_2O(l) \qquad \Delta H = -1411\text{ kJ}$$

$$(3)\ \ 2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) \qquad \Delta H = -572\text{ kJ}$$

Solution

Step 1. Identify the equations that have reactants or products on the same side of the arrow as in the desired equation.

Equation (1) contains 1 mol of $C_2H_6(g)$, so use it as written:

(1) $C_2H_6(g) + 3.5\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l) \qquad \Delta H = -1559\ kJ$

Step 2. Reverse (2) and (3) so that reactants and products are on the same side as in the desired equation. Reverse the sign of ΔH. This gives you equations (4) and (5), in which ethene gas and hydrogen gas are on the products side.

(4) $2\ CO_2(g) + 2\ H_2O(l) \rightarrow C_2H_4(g) + 3\ O_2(g) \qquad \Delta H = 1411\ kJ$

(5) $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g) \qquad \Delta H = 572\ kJ$

Step 3. Check the coefficients of all entities in the equations to see if any must be adjusted by a factor so as to be equal to the coefficients in the desired equation. If so, then multiply each ΔH by the same factor.

Equation (5) has 2 mol of hydrogen gas on the product side, while the desired equation has only 1 mol. Multiply equation (5) and its ΔH by the factor 0.5:

(6) $H_2O(l) \rightarrow H_2(g) + 0.5\ O_2(g) \qquad \Delta H = 286\ kJ$

The coefficient of oxygen is now 0.5, which represents 0.5 mol of oxygen gas (not 0.5 molecules).

Step 4. Add equations (1), (4), and (6), and their changes in enthalpies.

$$\begin{array}{lllllr}
(1) & C_2H_6(g) + \cancel{3.5\ O_2(g)} & \rightarrow \cancel{2\ CO_2(g)} & + \cancel{3\ H_2O(l)} & \Delta H = & -1559\ kJ \\
(4) & \cancel{2\ CO_2(g)} + \cancel{2\ H_2O(l)} & \rightarrow C_2H_4(g) & + \cancel{3\ O_2(g)} & \Delta H = & 1411\ kJ \\
(6) & \cancel{H_2O(l)} & \rightarrow H_2(g) & + \cancel{0.5\ O_2(g)} & \Delta H = & 286\ kJ \\
\hline
 & C_2H_6(g) & \rightarrow H_2(g) & + C_2H_4(g) & \Delta H = & 138\ kJ
\end{array}$$

Statement: The enthalpy change for the production of ethene gas from ethane gas is 138 kJ per mole of ethane.

Investigation 5.4.1

Hess's Law (page 334)
Now that you have learned how Hess's law is used to determine the enthalpy of a reaction, you will use calorimetry to get an experimental value for two reactions to determine the enthalpy of combustion.

Practice

1. Consider the following thermochemical equations:

$NH_3(g) \rightarrow \frac{1}{2}\ N_2(g) + \frac{3}{2}\ H_2(g) \quad \Delta H = 46\ kJ$

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g) \quad \Delta H = -484\ kJ$

(a) Calculate ΔH for the reaction represented by the following equation:
$2\ N_2(g) + 6\ H_2O(g) \rightarrow 3\ O_2(g) + 4\ NH_3(g)$ [ans: 1268 kJ]

(b) Draw an enthalpy diagram of the reaction. T/I C

2. Consider the following thermochemical equations:

$2\ ClF(g) + O_2(g) \rightarrow Cl_2O(g) + F_2O(g) \qquad \Delta H = 167.4\ kJ$
$2\ ClF_3(g) + 2\ O_2(g) \rightarrow Cl_2O(g) + 3\ F_2O(g) \qquad \Delta H = 341.4\ kJ$
$2\ F_2(g) + O_2(g) \rightarrow 2\ F_2O(g) \qquad \Delta H = -43.4\ kJ$

(a) Calculate ΔH for the reaction represented by the following equation:
$ClF(g) + F_2(g) \rightarrow ClF_3(g)$ [ans: −108.7 kJ]

(b) Draw an enthalpy diagram of the reaction. T/I C

3. If iron(III) oxide is heated with carbon monoxide, carbon dioxide and metallic iron are produced according to the equation

$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

Determine the enthalpy of this reaction given the reactions

$C(graphite) + \frac{1}{2}\ O_2 \rightarrow CO \qquad \Delta H = -110.5\ kJ$
$C(graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5\ kJ$
$2Fe(s) + 3/2\ O_2(g) \rightarrow Fe_2O_3(s) \qquad \Delta H = -824.2\ kJ$ T/I

[ans: $\Delta H = -24.8\ kJ$]

5.4 Review

Summary

- Hess's law states that the enthalpy change of a process is the same whether the process takes place in one step or in a series of steps.
- By applying Hess's law, we can manipulate and combine different chemical equations to determine the enthalpy change of a reaction of interest.

Questions

1. (a) State Hess's law in your own words.
   (b) In a correct equation for a reverse reaction, what happens to the sign and magnitude of ΔH?
   (c) When you multiply the coefficients of a balanced equation by a constant, what changes must you make to the sign and magnitude of ΔH? K/U
2. Explain how Hess's law is consistent with the law of conservation of energy. K/U
3. What characteristic of enthalpy change is the basis of Hess's law? K/U
4. Phosphorus burns spontaneously in air to produce tetraphosphorus decaoxide, $P_4O_{10}(s)$:

   $4\ P(s) + 5\ O_2(g) \rightarrow P_4O_{10}(s)$

   Using the following thermochemical equations, determine:
   (a) the enthalpy of combustion for phosphorus
   (b) the molar enthalpy of combustion for phosphorus, expressed in kJ/mol K/U T/I

   $4\ P(s) + 3\ O_2(g) \rightarrow P_4O_6(s) \quad \Delta H = -1640\text{ kJ}$
   $P_4O_6(s) + 2\ O_2(g) \rightarrow P_4O_{10}(s) \quad \Delta H = -1344\text{ kJ}$

5. Nitric oxide gas, $NO(g)$, can be oxidized in air to produce nitrogen dioxide gas, $NO_2(g)$:

   $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

   Determine the enthalpy change for this reaction using any of these thermochemical equations: K/U T/I

   $O_2(g) \rightarrow 2\ O(g) \quad \Delta H = +495\text{ kJ}$
   $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \quad \Delta H = -199\text{ kJ}$
   $2\ O_3(g) \rightarrow 3\ O_2(g) \quad \Delta H = -427\text{kJ}$

6. Liquid hydrazine, $N_2H_4(l)$, is a rocket fuel. It combusts in oxygen gas to form nitrogen gas and liquid water:

   $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(l)$

   Use the following thermochemical equations to calculate the enthalpy change for the combustion of liquid hydrazine: K/U T/I

   $2\ NH_3(g) + 3\ N_2O(g) \rightarrow 4\ N_2(g) + 3\ H_2O(l) \quad \Delta H = -1010\text{ kJ}$
   $N_2O(g) + 3\ H_2(g) \rightarrow N_2H_4(l) + H_2O(l) \quad \Delta H = -317\text{ kJ}$
   $2\ NH_3(g) + \frac{1}{2}\ O_2(g) \rightarrow N_2H_4(l) + H_2O(l) \quad \Delta H = -143\text{ kJ}$
   $H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286\text{ kJ}$

7. Solid calcium carbide, $CaC_2(s)$, reacts with liquid water to produce ethyne, $C_2H_2(g)$ (acetylene):

   $CaC_2(s) + 2\ H_2O(l) \rightarrow Ca(OH)_2(aq) + C_2H_2(g)$

   Using the following thermochemical equations, calculate the enthalpy change for this reaction: K/U T/I

   $Ca(s) + 2\ C_{graphite}(s) \rightarrow CaC_2(s) \quad \Delta H = -62.8\text{kJ}$
   $Ca(s) + \frac{1}{2}\ O_2(g) \rightarrow CaO(s) \quad \Delta H = -635.5\text{ kJ}$
   $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) \quad \Delta H = -653.1\text{ kJ}$
   $C_2H_2(g) + \frac{5}{2}\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(l) \quad \Delta H = -1300.\text{ kJ}$
   $C_{graphite}(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5\text{ kJ}$

8. The neutralization reaction between lithium hydroxide solution, $LiOH(aq)$, and hydrochloric acid, $HCl(aq)$, will produce water and aqueous lithium chloride, $LiCl(aq)$. Using the following thermochemical equations, determine the enthalpy of neutralization for 1 mol of aqueous lithium hydroxide: K/U T/I

   $\frac{1}{2}\ H_2(g) + \frac{1}{2}\ Cl_2(g) \rightarrow HCl(g) \quad \Delta H = -92.3\text{ kJ}$
   $H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l) \quad \Delta H = -285.8\text{ kJ}$
   $Li(s) + \frac{1}{2}\ Cl_2(g) \rightarrow LiCl(s) \quad \Delta H = -815.0\text{ kJ}$
   $Li(s) + \frac{1}{2}\ O_2(g) + \frac{1}{2}\ H_2(g) \rightarrow LiOH(s) \quad \Delta H = -487.0\text{ kJ}$
   $LiOH(s) \rightarrow LiOH(aq) \quad \Delta H = -19.2\text{ kJ}$
   $HCl(g) \rightarrow HCl(aq) \quad \Delta H = -77.0\text{ kJ}$
   $LiCl(s) \rightarrow LiCl(aq) \quad \Delta H = -36.0\text{ kJ}$

Standard Enthalpies of Formation

5.5

Sulfur dioxide gas, $SO_2(g)$, is a colourless, odourless air pollutant. The majority of atmospheric sulfur dioxide gas comes from the combustion of fossil fuels containing sulfur impurities, such as those produced in coal-burning power plants (**Figure 1**). Once in the atmosphere, sulfur dioxide undergoes further chemical reactions to form acid precipitation, which can cause significant damage to aquatic ecosystems, in addition to having other negative effects on the environment. CAREER LINK

Figure 1 Coal-burning power plants are a major artificial source of sulfur dioxide emissions.

An important step in the production of acid precipitation is the reaction of sulfur dioxide with oxygen to produce sulfur trioxide. The balanced chemical equation for the formation of 1 mol of sulfur trioxide gas is

$$SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$$

Measuring the enthalpy change of this reaction in the laboratory is difficult because the sulfur compounds are toxic. However, the enthalpy change can be calculated using Hess's law and the following thermochemical equations:

$$(1)\ S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g) \quad \Delta H = -441.0\ kJ$$

$$(2)\ S(s) + \frac{1}{2}O_2(g) \rightarrow SO_2(g) \quad \Delta H = -296.8\ kJ$$

Applying Hess's law, equation (1) remains unchanged because sulfur trioxide gas is on the product side. Equation (2) is reversed so that sulfur dioxide gas is on the reactant side, resulting in equation (3).

$$\begin{array}{lll}
(1) & \cancel{S(s)} + \frac{\overset{1}{\cancel{3}}}{2}O_2(g) \rightarrow SO_3(g) & \Delta H = -441.0\ kJ \\
(3) & SO_2(g) \rightarrow \cancel{S(s)} + \cancel{O_2(g)} & \Delta H = +296.8\ kJ \\
\hline
 & SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g) & \Delta H_r = -144.2\ kJ
\end{array}$$

Therefore, the enthalpy change for the production of sulfur trioxide gas is −144.2 kJ. Equations (1) and (2) are formation equations, and represent the formation of a compound from its elements.

Standard Enthalpy of Formation

The **standard enthalpy of formation ($\Delta H_f°$)** of a compound is the change in enthalpy that occurs when 1 mol of a compound is formed from its elements, with all substances in their standard states. A substance is in a **standard state** when it is in its most stable form at SATP, (25 °C, 100 kPa). **Figure 2** shows oxygen, sodium, and mercury, each in their standard state.

standard enthalpy of formation ($\Delta H_f°$) the change in enthalpy that accompanies the formation of 1 mol of a compound from its elements in their standard states

standard state the most stable form of a substance under standard conditions, 25 °C and 100 kPa

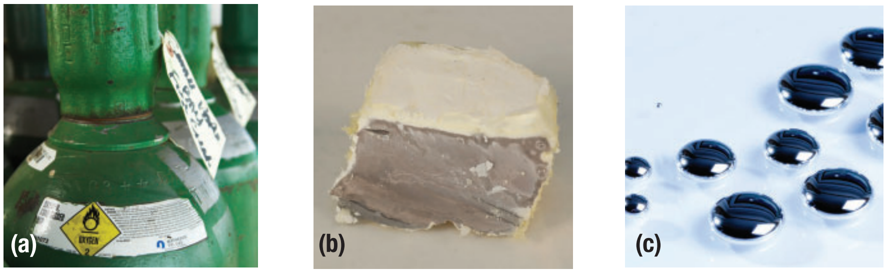


Figure 2 Three elements in their standard state: (a) oxygen gas, $O_2(g)$; (b) sodium metal, Na(s); and (c) liquid mercury, Hg(l).

Most elements are solids in their standard state. However, the standard state of the noble gases, as well as of the diatomic elements—hydrogen, oxygen, nitrogen, fluorine, and chlorine—is the gas state. The standard state of bromine and mercury is the liquid state. The standard state for a substance in solution is at a concentration of 1 mol/L. The degree sign on the symbol ΔH_f° indicates that the process takes place under standard conditions (25 °C, 100 kPa). The standard enthalpy of formation, ΔH_f°, of an element in its standard state is zero. A value of zero is assigned since an element is in its most fundamental form at standard conditions. Thus, the standard enthalpies of formation of oxygen gas, solid sodium metal, and liquid mercury metal, for example, are zero.

Table 1 Standard Enthalpies of Formation for Several Compounds

Compound	ΔH_f° (kJ/mol)
$AlCl_3(s)$	−704.2
$Al_2O_3(s)$	−1675.7
$CaSO_4(s)$	−1434.1
$Ca_3(PO_4)_2(s)$	−4120.8
$CH_3OH(l)$	−239.1
$CH_4(g)$	−74.4
$C_2H_2(g)$	+228.2
$C_2H_5OH(l)$	−235.2
$C_2H_6(g)$	−83.8
$C_3H_8(g)$	−104.7
$C_6H_{12}O_6(s)$	−1273.1
$C_8H_{18}(l)$	−250.1
$C_{12}H_{22}O_{11}(s)$	−2225.5
$CO(g)$	−110.5
$CO_2(g)$	−393.5
$Fe_2O_3(s)$	−824.2
$HCN(g)$	+135.1
$HCl(g)$	−92.3
$HF(g)$	−273.3
$H_2O(g)$	−241.8
$H_2O(l)$	−285.8
$H_2SO_4(l)$	−814.0
$H_3PO_4(l)$	−1271.7
$MgO(s)$	−601.6
$Mg(OH)_2(s)$	−924.5
$NH_3(g)$	−45.9
$NH_4Cl(s)$	−314.4
$NH_4ClO_4(s)$	−295.8
$NO(g)$	+90.2
$NO_2(g)$	+33.2
$SiCl_4(l)$	−687.0
$SiO_2(s)$	−910.7

Consider the thermochemical equation for the formation of nitrogen dioxide gas from its elements in their standard states:

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \quad \Delta H_f^\circ = 33.2 \text{ kJ/mol}$$

Like all standard enthalpy of formation equations, this standard enthalpy of formation equation shows the formation of 1 mol of the product. The formation of nitrogen dioxide gas from its elements is endothermic, absorbing 33.2 kJ/mol from its surroundings. Enthalpies of formation may be either exothermic or endothermic (**Table 1**).

Using Standard Enthalpies of Formation to Calculate Enthalpy Change

Since references such as Table 1 (left) provide the standard enthalpies of formation, ΔH_f°, for many pure substances, you can use these values to calculate the standard enthalpy of reaction, ΔH_r°, for many chemical reactions. Consider the combustion of methane gas, $CH_4(g)$, represented by the balanced equation.

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$$

Figure 3 illustrates one possible pathway for the combustion of methane.

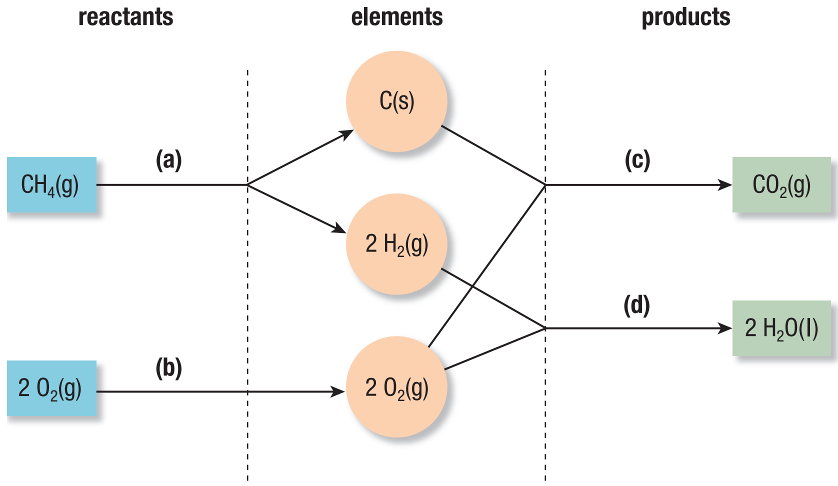


Figure 3 In this pathway for the combustion of methane, the reactants are broken down into their constituent elements in reactions (a) and (b). The elements are then used to synthesize the products in reactions (c) and (d).

In reactions (a) and (b) of the pathway shown in Figure 3, the reactants are decomposed into their elements. In reaction (a), methane is broken down into elemental carbon and hydrogen gas. The balanced chemical equation for the reaction is

$$CH_4(g) \rightarrow C(s) + 2\,H_2(g)$$

The equation above is the reverse of the formation equation for methane

$$C(s) + 2\,H_2(g) \rightarrow CH_4(g) \quad \Delta H_f^\circ = -74.4 \text{ kJ}$$

From Table 1 (left), you know that ΔH_f° for the formation of methane is –74.4 kJ/mol. Since you change the sign of ΔH whenever you reverse a reaction, ΔH° for the decomposition of methane into its elements is +74.4 kJ.

Oxygen gas exists in its elemental state, $O_2(g)$. It cannot be broken down further; no energy change occurs, so $\Delta H°_{(b)}$ is 0 kJ:

$$2\ O_2(g) \rightarrow 2\ O_2(g)\quad \text{(no change)}$$

In reactions (c) and (d) of the pathway shown in Figure 3, the elements from the decomposition of the reactants combine to form the final products, $CO_2(g)$ and $H_2O(l)$. The balanced chemical equations are

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_f° = \Delta H°_{(c)} = -393.5\ \text{kJ/mol}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_f° = -285.8\ \text{kJ/mol}$$

Since 2 mol of water is formed in the combustion of methane, the $\Delta H_f°$ of $H_2O(l)$ must be multiplied by 2, as follows:

$$2[H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)] \quad \Delta H_f° = 2(-285.8\ \text{kJ/mol})$$

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) \quad \Delta H°_{(d)} = -571.6\ \text{kJ/mol}$$

The change in enthalpy for the reaction is the sum of the $\Delta H°$ values:

$$\Delta H_r° = 74.4\ \text{kJ} + 0\ \text{kJ} + (-393.5\ \text{kJ}) + (-571.6\ \text{kJ})$$
$$\Delta H_r° = -890.7\ \text{kJ}$$

The use of $\Delta H_f°$ values to determine the enthalpy of combustion of methane is summarized in **Figure 4**. The decomposition of methane gas into its elements is an endothermic reaction; however, when elements combine to form products, a large quantity of energy is released.

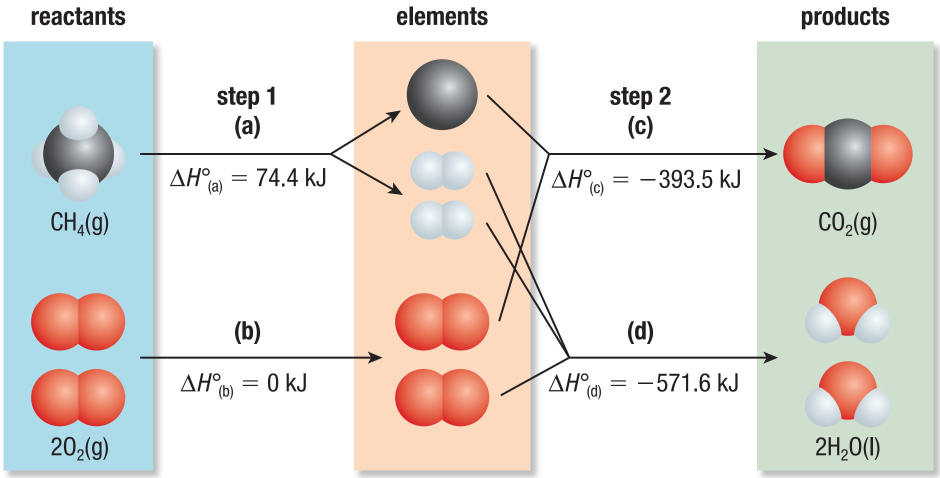


Figure 4 A schematic diagram of the energy changes for the reaction represented by the equation $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

Since only $\Delta H_f°$ values were used in this example, we can state the following simplification: the enthalpy change for any reaction can be calculated by subtracting the sum of the enthalpies of formation of the reactants from the sum of the enthalpies of formation of the products. The enthalpies of formation are multiplied, as dictated by the balanced equation. That is,

$$\Delta H_r° = \Sigma n_{\text{products}} \Delta H°_{\text{products}} - \Sigma n_{\text{reactants}} \Delta H°_{\text{reactants}}$$

where Σ represents the sum of terms, and n_{products} and $n_{\text{reactants}}$ represent the amount in moles of each product or reactant, respectively.

Investigation **5.5.1**

Calorimetry versus Enthalpies of Formation (page 335)

Now that you have learned how standard enthalpies of formation are used to estimate the enthalpy change of a reaction, you will compare experimental results from calorimetry to enthalpies of formation.

Using this equation, the change in enthalpy for the combustion of methane gas is −890.7 kJ, which agrees with the value we obtained previously:

$$\begin{aligned}\Delta H_r^\circ &= [\Delta H^\circ_{(c)} + \Delta H^\circ_{(d)}] - [\Delta H^\circ_{(a)} + \Delta H^\circ_{(b)}]\\ &= [-393.5\text{ kJ} + 2(-285.8\text{ kJ})] - (-74.4\text{ kJ} + 0\text{ kJ})\\ &= -965.1\text{ kJ} + 74.4\text{ kJ}\\ \Delta H_r^\circ &= -890.7\text{ kJ}\end{aligned}$$

Tutorial 1 *ΔH* and Standard Enthalpies of Formation

In this tutorial, you will calculate the enthalpy change of a reaction, ΔH, using standard enthalpy of formation values and Table 1 (page 320).

Sample Problem 1: Calculating *ΔH* from Standard Enthalpies of Formation

Using standard enthalpies of formation in Table 1, calculate the standard change in enthalpy for the thermite reaction represented by the balanced equation

$$2\text{ Al(s)} + \text{Fe}_2\text{O}_3\text{(s)} \rightarrow \text{Al}_2\text{O}_3\text{(s)} + 2\text{ Fe(s)}$$

Given: from Table 1, $\Delta H_f{^\circ}_{\text{Fe}_2\text{O}_3\text{(s)}} = -824.2$ kJ/mol; $\Delta H_f{^\circ}_{\text{Al}_2\text{O}_3\text{(s)}} = -1675.7$ kJ/mol; $\Delta H_f{^\circ}_{\text{Al(s)}} = 0$ kJ/mol; $\Delta H_f{^\circ}_{\text{Fe(s)}} = 0$ kJ/mol

Required: ΔH°_r for the thermite reaction

Analysis: $\Delta H^\circ_r = \Sigma n_{\text{products}}\Delta H^\circ_{\text{products}} - \Sigma n_{\text{reactants}}\Delta H^\circ_{\text{reactants}}$

Solution: Since Fe(s) and Al(s) are in their standard states, you can rewrite this equation as

$$\begin{aligned}\Delta H^\circ_r &= n_{\text{Al}_2\text{O}_3\text{(s)}}\,\Delta H_f{^\circ}_{\text{Al}_2\text{O}_3\text{(s)}} - n_{\text{Fe}_2\text{O}_3\text{(s)}}\,\Delta H_f{^\circ}_{\text{Fe}_2\text{O}_3\text{(s)}}\\ &= -1675.7\text{ kJ} - (-824.2\text{ kJ})\\ \Delta H^\circ_r &= -851.5\text{ kJ}\end{aligned}$$

Statement: The standard enthalpy change for the thermite reaction is −851.5 kJ.

Sample Problem 2: Comparing Combustion Reactions

Until recently, liquid methanol was used to fuel high-performance engines in race cars. Gasoline is a mixture of hydrocarbons, but assume for this problem that gasoline is pure liquid octane, $\text{C}_8\text{H}_{18}\text{(l)}$. Using the data in Table 1, determine the standard enthalpy of combustion per gram of (a) methanol and (b) octane. Then (c) determine which fuel has the greater standard enthalpy per gram. The balanced chemical equation for the combustion of methanol is

$$2\text{ CH}_3\text{OH(l)} + 3\text{ O}_2\text{(g)} \rightarrow 2\text{ CO}_2\text{(g)} + 4\text{ H}_2\text{O(l)}$$

The balanced chemical equation for the combustion of octane is

$$2\text{ C}_8\text{H}_{18}\text{(l)} + 25\text{ O}_2\text{(g)} \rightarrow 16\text{ CO}_2\text{(g)} + 18\text{ H}_2\text{O(l)}$$

(a) **Given:** From Table 1: $\Delta H_f{^\circ}_{\text{CH}_3\text{OH(l)}} = -239.1$ kJ/mol; $\Delta H_f{^\circ}_{\text{O}_2\text{(g)}} = 0$ kJ/mol; $\Delta H_f{^\circ}_{\text{CO}_2\text{(g)}} = -393.5$ kJ/mol; $\Delta H_f{^\circ}_{\text{H}_2\text{O(l)}} = -285.8$ kJ/mol; $M_{\text{CH}_3\text{OH}} = 32.05$ g/mol

Required: $\Delta H^\circ_{\text{per gram CH}_3\text{OH}}$ for the combustion of methanol

Analysis: $\Delta H^\circ_r = \Sigma n_{\text{products}}\,\Delta H^\circ_{\text{products}} - \Sigma n_{\text{reactants}}\Delta H^\circ_{\text{reactants}}$

Since $\text{O}_2\text{(g)}$ is in its standard state, you can write this equation as

$$\Delta H^\circ_r = [n_{\text{CO}_2\text{(g)}}\,\Delta H_f{^\circ}_{\text{CO}_2\text{(g)}} + n_{\text{H}_2\text{O(l)}}\,\Delta H_f{^\circ}_{\text{H}_2\text{O(l)}}] - n_{\text{CH}_3\text{ OH(l)}}\,\Delta H_f{^\circ}_{\text{CH}_3\text{OH(l)}}$$

Solution:

Step 1. Rewrite the equation for the combustion of methanol so that methanol has a coefficient of 1:

$$\text{CH}_3\text{OH(l)} + \tfrac{3}{2}\text{ O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{ H}_2\text{O(l)}$$

Step 2. Insert the appropriate values into the equation for standard enthalpy of formation and solve:

$$\begin{aligned}\Delta H^\circ_{\text{r}} &= [n_{\text{CO}_2\text{(g)}}\Delta H^\circ_{\text{f CO}_2\text{(g)}} + n_{\text{H}_2\text{O(l)}}\Delta H^\circ_{\text{f H}_2\text{O(l)}}] - n_{\text{CH}_3\text{OH(l)}}\Delta H^\circ_{\text{f CH}_3\text{OH(l)}}\\ &= [-393.5\text{ kJ} + 2(-285.8\text{ kJ})] - (-239.1\text{ kJ})\\ &= -965.1\text{ kJ} + 239.1\text{ kJ}\\ \Delta H^\circ_{\text{r}} &= -726.0\text{ kJ}\end{aligned}$$

Step 3. Convert to enthalpy per gram of liquid methanol:

$$\Delta H^\circ_{\text{per gram CH}_3\text{OH}} = \left(\frac{-726.0\text{ kJ}}{1\ \cancel{\text{mol}}}\right)\left(\frac{1\ \cancel{\text{mol}}}{32.05\text{ g}}\right)$$

$$\Delta H^\circ_{\text{per gram CH}_3\text{OH}} = -22.65\text{ kJ}$$

Statement: The combustion reaction of methanol releases 22.65 kJ/g methanol.

(b) **Given:** From Table 1: $\Delta H_{\text{f}}^\circ{}_{\text{C}_8\text{H}_{18}\text{(l)}} = -250.1$ kJ/mol; $\Delta H_{\text{f}}^\circ{}_{\text{O}_2\text{(g)}} = 0$ kJ/mol;
$\Delta H_{\text{f}}^\circ{}_{\text{CO}_2\text{(g)}} = -393.5$ kJ/mol; $\Delta H_{\text{f}}^\circ{}_{\text{H}_2\text{O(l)}} = -285.8$ kJ/mol;
$M_{\text{C}_8\text{H}_{18}} = 114.26$ g/mol

Required: $\Delta H^\circ_{\text{per gram C}_8\text{H}_{18}}$ for the combustion of octane

Analysis:

$$\Delta H^\circ_{\text{r}} = [n_{\text{CO}_2\text{(g)}}\Delta H^\circ_{\text{f CO}_2\text{(g)}} + n_{\text{H}_2\text{O(l)}}\Delta H^\circ_{\text{f H}_2\text{O(l)}}] - n_{\text{C}_8\text{H}_{18}\text{(l)}}\Delta H^\circ_{\text{f C}_8\text{H}_{18}\text{(l)}}$$

Solution:

Step 1. Rewrite the equation for the combustion of octane so that octane has a coefficient of 1:

$$\text{C}_8\text{H}_{18}\text{(l)} + \tfrac{25}{2}\ \text{O}_2\text{(g)} \rightarrow 8\ \text{CO}_2\text{(g)} + 9\ \text{H}_2\text{O(l)}$$

Step 2. Insert the appropriate values into the equation for standard enthalpy of formation and solve:

$$\begin{aligned}\Delta H^\circ_{\text{r}} &= [n_{\text{CO}_2\text{(g)}}\Delta H^\circ_{\text{f CO}_2\text{(g)}} + n_{\text{H}_2\text{O(l)}}\Delta H^\circ_{\text{f H}_2\text{O(l)}}] - n_{\text{C}_8\text{H}_{18}\text{(l)}}\Delta H^\circ_{\text{f C}_8\text{H}_{18}\text{(l)}}\\ &= [8(-393.5\text{ kJ}) + 9(-285.8\text{ kJ})] - (-250.1\text{ kJ})\\ &= (-3148\text{ kJ} - 2572.2\text{ kJ}) + 250.1\text{ kJ}\\ \Delta H^\circ_{\text{r}} &= -5470.1\text{ kJ/mol} \quad\text{or}\quad -5.4701\times 10^3\text{ kJ/mol}\end{aligned}$$

Step 3. Convert to enthalpy per gram of C_8H_{18}:

$$\Delta H^\circ_{\text{per gram C}_8\text{H}_{18}} = \left(\frac{-5.4701\times 10^3\text{ kJ}}{1\ \cancel{\text{mol}}}\right)\left(\frac{1\ \cancel{\text{mol}}}{114.22\text{ g/}\cancel{\text{mol}}}\right)$$

$$\Delta H^\circ_{\text{per gram C}_8\text{H}_{18}} = -47.891\text{ kJ/g}$$

Statement: The combustion reaction of octane releases −47.891 kJ of energy per gram of octane.

(c) **Solution:** The enthalpy of combustion per gram of octane is more than twice that per gram of methanol.

Practice

1. Calculate the enthalpy of combustion for acetylene gas, $\text{C}_2\text{H}_2\text{(g)}$, using standard enthalpies of formation values. T/I [ans: −1301.0 kJ/mol]
2. Compare the enthalpy of combustion for 1.00 g of acetylene gas to that of 1.00 g of propane gas, $\text{C}_3\text{H}_8\text{(g)}$, using standard enthalpies of formation values. T/I
[ans: $\Delta H_{\text{c}}^\circ{}_{\text{acetylene}} = -50.0$ kJ/g, $\Delta H_{\text{c}}^\circ{}_{\text{propane}} = -50.3$ kJ/g]

5.5 Review

Summary

- The standard enthalpy of formation, $\Delta H_f°$, of a compound is the change in enthalpy that accompanies the formation of 1 mol of a compound from its elements, with all elements in their standard states.
- The standard state of an element is the state of matter in which the element exists under SATP conditions (25 °C, 100 kPa).
- The enthalpy of formation of any element in its standard state is equal to zero.
- The enthalpy change for a reaction is determined by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products:
  $\Delta H^{\circ}_{\text{reaction}} = \Sigma n_{\text{products}} \Delta H^{\circ}_{\text{products}} - \Sigma n_{\text{reactants}} \Delta H^{\circ}_{\text{reactants}}$

Questions

1. Which of the following elements is in its standard state? K/U T/I
   (a) $Hg(g)$
   (b) $Mg(s)$
   (c) $O_2(l)$
   (d) $Br_2(l)$
2. Calculate $\Delta H°$ for the reactions represented by the following equations: K/U T/I
   (a) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$
   (b) $C(s) + O_2(g) \rightarrow CO_2(g)$
   (c) $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$
   (d) $C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$
3. The combustion reaction of octane is represented by the equation
   $$2\ C_8H_{18}(l) + 25\ O_2(g) \rightarrow 16\ CO_2(g) + 18\ H_2O(l) \qquad \Delta H_r = -1.09 \times 10^4\ \text{kJ}$$
   What is the $\Delta H°$ for the reaction given by the following equation?
   $$8\ CO_2(g) + 9\ H_2O(l) \rightarrow C_8H_{18}(l) + \tfrac{25}{2}\ O_2(g)$$ K/U T/I
4. The fuel used in reusable booster rockets consists of a mixture of aluminum and ammonium perchlorate. The following equation represents a possible reaction of this mixture:
   $$3\ Al(s) + 3\ NH_4ClO_4(s) \rightarrow Al_2O_3(s) + AlCl_3(s) + 3\ NO(g) + 6\ H_2O(g)$$
   Using enthalpies of formation, calculate $\Delta H°$ for this reaction. K/U T/I
5. Consider the reaction between chlorine trifluoride gas, $ClF_3(g)$, and ammonia gas, $NH_3(g)$, represented by the equation
   $$2\ ClF_3(g) + 2\ NH_3(g) \rightarrow N_2(g) + 6\ HF(g) + Cl_2(g) \qquad \Delta H° = -1196\ \text{kJ}$$
   Calculate $\Delta H_f°$ for $ClF_3(g)$. K/U T/I
6. The oxidation of methylhydrazine, $N_2H_3CH_3(l)$, by dinitrogen tetroxide, $N_2O_4(l)$, was used for propulsion in the Space Shuttle orbiter. This reaction is represented by the equation
   $$4\ N_2H_3CH_3(l) + 5\ N_2O_4(l) \rightarrow 12\ H_2O(g) + 9\ N_2(g) + 4\ CO_2(g)$$
   The enthalpy of formation for liquid methylhydrazine is +53 kJ/mol and the enthalpy of formation for liquid dinitrogen tetroxide is −20 kJ/mol. Calculate $\Delta H°$ for this reaction. K/U T/I
7. The standard enthalpy of combustion of ethene gas, $C_2H_4(g)$, is −1411.1 kJ/mol at SATP. Calculate $\Delta H_f°$ for ethene gas. K/U T/I
8. Liquid ethanol, $C_2H_5OH(l)$, has been proposed as an alternative fuel. Calculate the standard enthalpy of combustion per gram of liquid ethanol. K/U T/I
9. Methanol, $CH_3OH(l)$, has been proposed as an alternative fuel. K/U T/I A
   (a) Calculate the standard enthalpy of combustion per gram of liquid methanol.
   (b) Compare the standard enthalpy of combustion per gram of methanol to that of ethanol in Question 8.
   (c) Based on your answer in (b), which fuel would be the most convenient source of energy for a vehicle? Explain why.
10. The melting point of the element gallium, $Ga(s)$, is so low that gallium will melt in your hand. The quantity of thermal energy required to melt gallium is 5.59 kJ/mol. K/U T/I
    (a) Write a thermochemical equation for the melting of gallium.
    (b) What are the enthalpies of formation of solid and liquid gallium at SATP? Why are they not equal?

Present and Future Energy Sources

5.6

How we supply our energy needs now and how we will supply them in the future are among the most complex and challenging issues of our time. Every energy source and energy technology—both conventional and alternative—has costs and benefits related to its availability, its sustainability, and its impact on ecosystems, the climate, economics, and politics.

Conventional Fuels

Conventional fuels are fuels that are commonly used today. These include organic fuels, such as wood or straw; fossil fuels, such as coal, petroleum, and natural gas; and nuclear fuels, such as uranium. Conventional fuels have been in use for a long enough period that we have systems in place to find, process, and deliver these fuels where they are needed. For example, petroleum may be pumped from beneath Earth's surface on an oil platform (**Figure 1**). It is then carried by pipelines or ships to a refining plant, where it is processed into useful petroleum products for everyday use.

Wood is perhaps the most widely used conventional fuel. Wood is a renewable fuel source, since we can replant trees to replace those we burn or use to produce charcoal, a wood-derived fuel. Unfortunately, the rate at which we use wood is often much faster than the rate at which some species of trees renew their populations. Carbon dioxide is a natural product of wood and charcoal combustion, and its effects as a greenhouse gas must be considered.

Figure 1 Oil platforms, such as this one off the coast of Brazil, function as small cities devoted to extracting oil from beneath the ocean floor.

Fossil Fuels

The most widely used class of fuel today is fossil fuels—petroleum (crude oil), coal, and natural gas. The energy stored in fossil fuels originated in the Sun. Through the process of photosynthesis, captured solar energy is converted to chemical energy by plants. Fossil fuels form from the decaying remains of plants and animals, which are then subjected to high temperatures and pressures beneath Earth's surface for thousands of years.

Petroleum is a thick, dark liquid that is a mixture of hydrocarbons. Crude petroleum is not used as a fuel directly; it is first refined. Refining petroleum is achieved by fractional distillation. This process takes advantage of the differences in boiling points among the different hydrocarbons in crude petroleum. The composition of crude petroleum varies, but it consists mostly of straight-chain hydrocarbons between 5 and 25 carbon atoms in length. When petroleum is heated, the smaller molecules enter the vapour state first, while the larger molecules remain in liquid form. The smaller molecules have lower boiling points than the larger molecules because they have relatively weaker intermolecular forces. The different hydrocarbons are then collected into fractions by selective condensation at different temperatures. Each fraction contains hydrocarbons with a specific range of chain lengths. **Table 1** shows some common uses for different petroleum fractions. Hydrocarbons have many uses other than as fuels, such as in the manufacture of pharmaceuticals and plastics.

Table 1 Uses of Various Petroleum Fractions

Range of carbon atoms in fraction	Uses
C_5–C_{10}	gasoline
C_{10}–C_{18}	kerosene, jet fuel
C_{15}–C_{25}	diesel fuel, heating oil, lubricating oil
$> C_{25}$	asphalt

Table 1 shows that gasoline includes only the C_5–C_{10} fraction of petroleum hydrocarbons. To meet the world's growing demand for gasoline, scientists developed a method for converting long-chain hydrocarbons into short-chain hydrocarbons, a process called cracking. Pyrolytic cracking and catalytic cracking are two types of cracking commonly used. In pyrolytic cracking, heavier molecules of the petroleum mixture are heated to about 700 °C, causing them to break into the smaller-chain hydrocarbons that comprise gasoline. In catalytic cracking, a catalyst drives the process of breaking the long-chain hydrocarbons into smaller hydrocarbons.

Natural gas is another type of fossil fuel. It is usually found with, or near, petroleum deposits. Natural gas is mostly methane gas, $CH_4(g)$, but it also contains significant quantities of other hydrocarbon gases such as ethane, propane, and butane. Natural gas is primarily used for heating buildings.

Coal is a fossil fuel formed from decaying plant matter that has been buried for millions of years. Plant material is composed primarily of cellulose, a carbohydrate. Deep beneath Earth's surface, plant matter is subjected to high pressure and temperatures. Over time, these conditions cause chemical changes in the cellulose, removing a large proportion of the oxygen and hydrogen atoms and leaving mostly atoms of carbon. There are four types of coal, which are classified based on their carbon content. From lowest to highest carbon content, these are lignite, sub-bituminous, bituminous, and anthracite. Anthracite is the most valuable type of coal because, due to its high carbon content, it releases more energy per unit mass during combustion. In Canada, coal is used primarily to produce electricity. Worldwide, more electrical power plants generate electricity by burning coal than by any other method. In 2008, 88 % of the coal used in Canada was used for electricity production.

In the past 200 years, Canada and most other countries have become highly dependent on fossil fuels. Fossil fuels form at a far slower rate than we consume them, so fossil fuels are not renewable. Fossil fuel deposits are limited in supply, and many, such as Alberta's oil sands, are difficult to process. Combustion of fossil fuels has damaging environmental consequences. Therefore, scientists, engineers, and entrepreneurs are working to find new sources of energy.

COSTS OF FOSSIL FUEL USE

The combustion of all fossil fuels produces carbon dioxide gas and water vapour, which are released into the atmosphere where they contribute to global warming and climate change. Climate change leads to loss of species due to changes to habitats and can also cause more floods, droughts, fires, and disease. CAREER LINK

Other pollutants are also released when we burn fossil fuels. For example, the combustion of coal that contains high quantities of sulfur releases sulfur dioxide gas, $SO_2(g)$. When sulfur dioxide gas combines with water in the atmosphere, sulfurous acid is formed, which falls as acid rain.

Extracting and transporting fossil fuels can be dangerous. For example, in 2010, a deep-water oil well exploded in the Gulf of Mexico and leaked oil into the ocean for almost three months before the well was successfully capped. The environmental, social, and economic damage was extensive (**Figure 2**).

Figure 2 The *Deepwater Horizon* oil leak in the Gulf of Mexico released a large amount of oil into the ocean and made many people more aware of the potential costs of using fossil fuels.

Nuclear Energy

Nuclear energy is a conventional energy source that is not subject to most of the disadvantages of fossil fuels. Nuclear energy is not a limited resource, and it does not involve the release of greenhouse gases. There are two types of nuclear reactions by which nuclear energy may be released: fusion and fission. Fusion is not currently used to generate energy on Earth. Nuclear generating plants instead use fission, which releases extremely large quantities of energy compared with chemical reactions and physical processes. Uranium-235, the primary source of nuclear energy used in fission, is also relatively inexpensive. Nuclear power plants produce substantially less air pollution than electrical generating plants fuelled by the combustion of coal.

Nevertheless, there are serious disadvantages to nuclear power generation. Nuclear power stations are expensive to build and maintain. The used (spent) fuel rods, although no longer useful in a power plant, are still highly radioactive. This nuclear waste must be properly stored to prevent radioactive radiation from entering the environment—but a safe, long-term storage solution has yet to be found. During the transformation of nuclear energy into electrical energy, vast quantities of water are used to keep the nuclear fuel rods from overheating. This is why nuclear power plants are built close to a water source (**Figure 3**). Much of the thermal energy absorbed by the water from the fuel rods enters the environment when the water is returned to its source. This can increase the water temperature sufficiently and can cause a decrease in the quantity of oxygen and other gases dissolved in the water, which can have negative consequences for aquatic life. Perhaps the greatest concern with nuclear energy generation is the potential for the accidental release of radiation. A recent reminder of these dangers occurred when an earthquake and tsunami damaged Japan's Fukushima nuclear power plant in 2011. Research continues that is aimed at improving safety, but many believe nuclear power can never be safe. WEB LINK

Figure 3 The Pickering, Ontario, nuclear power plant is built near an adequate water supply (to keep the fuel rods cool).

Alternative Energy Sources

As we deplete our fossil fuel stores and as our energy demands increase, ongoing research is focused on identifying and developing reliable new sources of energy. Some of these use renewable natural resources such as wind, solar radiation, and tides. Others involve alternative fuels such as synthetic fuels, hydrogen gas, and biofuels. A separate but related goal is to develop ways to produce energy that will be environmentally friendly. Some alternative energy sources are much more environmentally friendly than others. WEB LINK

Synthetic Coal-Based Fuels

A synthetic fuel is any fuel that is artificially formulated and manufactured. In other words, it does not appear naturally or, at least, not in usable quantities.

Coal is the starting point for two synthetic fuels. The simplest artificial fuel made from coal is **coal slurry**, which consists of pulverized coal mixed with water. Coal slurry can directly replace petroleum-based fuels in some cases. For example, coal slurry can be used directly in an oil furnace as fuel.

coal slurry a suspension of pulverized coal in water

Coal contains large hydrocarbon molecules that are either solids or thick liquids at SATP. These molecules cannot be transported through pipelines, which limits their usefulness. Chemists have developed a process called coal gasification that reduces the size of these molecules and then converts the coal to a gaseous fuel mixture. During coal gasification, coal is first mixed with oxygen gas and steam at high temperatures. This breaks many of the C–C bonds in the coal. Then, new C–H and C–O bonds form when the smaller molecules react further with the oxygen gas and water vapour. The final product is a mixture of carbon monoxide gas and hydrogen gas called synthetic gas, or **syngas**. The balanced equation for the production of syngas is

syngas a synthetic fuel produced from the gasification of coal

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

Another useful fuel, methane gas, $CH_4(g)$, is also produced during coal gasification. Since syngas is derived from coal, the environmental costs with respect to mining the coal still exist, as do the greenhouse gas concerns. On a positive note, the use of syngas as a fuel source is more energy efficient than burning coal directly.

Hydrogen Gas Fuel

Hydrogen gas can be utilized as a fuel source. Hydrogen gas has a high enthalpy of combustion, releasing about 2.5 times the quantity of energy per gram than is released by the combustion of natural gas (methane). The thermochemical equation for the combustion of 1 mol of hydrogen is

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H^\circ = -285.8 \text{ kJ}$$

The only product of hydrogen combustion is water vapour. Widespread use of hydrogen as a fuel has three main limitations: production cost, storage, and transport.

Hydrogen gas can be produced by passing an electric current through water in a process called "electrolysis." Electrolysis breaks the bonds in water molecules, forming hydrogen gas, $H_2(g)$, and oxygen gas, $O_2(g)$. The quantity of energy required to form 1 mol of hydrogen gas by electrolysis of water is −285 kJ, the same quantity released by combustion of 1 mol of hydrogen gas. Hence, with respect to sustainable energy production we are not ahead. We put in as much energy in order to produce hydrogen gas as we extract when we combust hydrogen gas. In addition, even though our oceans contain an almost endless supply of water, large-scale production of hydrogen from water is not economically feasible because the cost of electricity is too high. Hydrogen fuel is therefore far too costly to be widely used at this time.

Hydrogen gas is also difficult to store and transport. Tankers and pipelines used to transport fuels are generally constructed with metal. Molecules of hydrogen gas are able to infiltrate the metal lattice structure, making the metals brittle. Brittle metal is likely to fail, which would allow the hydrogen fuel to leak out. Since hydrogen is so flammable, a hydrogen leak could easily result in an explosion.

Biofuels

Figure 4 The sugars in corn can be fermented to produce ethanol, a biofuel.

Biofuels are fuels that are derived from living things (biomass). For example, wood can be considered a biofuel. Liquid biofuels have more applications than solid ones. The most widely known liquid biofuel is ethanol, $C_2H_5OH(l)$. A number of companies and researchers think that ethanol could supplement or even replace gasoline.

Most ethanol is produced by fermenting sugars, a process that produces liquid ethanol and carbon dioxide gas. Various sugars from different sources can be fermented to produce ethanol, but corn is the most common source of fuel-grade ethanol in North America (**Figure 4**). Corn kernels store large quantities of starch, a carbohydrate formed from long chains of glucose molecules. To make ethanol biofuel, enzymes are first added to ground corn kernels to break the starch down into sugar molecules. Yeast is then added to the sugar mixture. The yeast cells carry out fermentation to obtain energy from the sugars. The end products of fermentation are liquid ethanol and carbon dioxide gas. However, the final mixture will still contain yeast and small quantities of the reactants. The mixture is heated to kill the yeast cells, and this causes liquid ethanol to change state to ethanol vapour. The pure ethanol vapour is then captured and condensed to ethanol liquid.

A fuel can burn in an internal combustion engine only when it is in the vapour state. Ethanol is not as volatile as gasoline; that is, it does not vaporize as readily and therefore cannot be used directly as a fuel source in most automobile engines. Alternatively, *gasohol*, a solution of about 10 % ethanol in gasoline, will burn in most engines. Another ethanol-based biofuel, E85, is 85 % ethanol and 15 % gasoline. E85 can only be used in vehicles with specially designed engines. WEB LINK

Methanol, $CH_3OH(l)$, is another alcohol-based biofuel. Methanol has been used as a fuel in some race cars for many years. Research aimed at using methanol as a fuel for conventional automobiles is ongoing.

The main advantage of biofuels over fossil fuels is that they are produced from renewable sources (living plants). Biofuel production involves the use of fossil fuels—in farm machinery, transportation, and the manufacturing of the biofuels—although much less petroleum is used than in the production of gasoline. The combustion of biofuels releases the same greenhouse gases as fossil fuels, but the gases are carbon neutral, since the C is absorbed from the air. In addition, biofuel combustion releases 10–15 % fewer greenhouse gases than fossil fuels. Using plants such as corn for biofuels may also increase the cost of food and reduce our food supply at a time when Earth's population is over 7 billion. Land that was once used for producing food for humans is now being used to produce crops to be converted to biofuels. Finally, environmental costs such as soil erosion have yet to be quantified.

UNIT TASK **BOOKMARK**

As you work on your Unit Task on page 402, consider what you have read about biofuels, and ethanol in particular. Use the information in this section to help you answer the questions in the Unit Task.

Energy Efficiency

The **efficiency** of a device or system is the ratio of useful energy produced to the total amount of energy expended. Efficiency is normally calculated as a percentage. The efficiencies of various energy resources for electricity generation, industrial processes, transportation, and heating vary widely. For example, generating electricity using hydro power (hydroelectricity) is around 85 % efficient. The efficiency of electricity generation using fossil fuels, nuclear reactions, wind, and biofuels ranges from 35–45 %. Current solar methods have an efficiency of around 15 %.

efficiency the ratio of the energy output to the energy input of any system

Readily accessible non-renewable sources of energy are quickly running out. Unfortunately, our current renewable sources of energy are inadequate to satisfy the demand. Conservation is one approach to meet the demand for electrical energy. To conserve energy, newer devices are designed to use less electrical energy than older ones. For example, some appliance manufacturers claim that replacing a 20-year-old refrigerator with a modern energy-efficient unit can save over $100 each year on your electricity bill. In fact, some municipalities offer free removal services to encourage their citizens to update their appliances. We can also help meet our energy demand by improving the efficiencies of power plants.

Research This

Deep Lake Water Cooling

Skills: Researching, Analyzing, Evaluating, Communicating

SKILLS HANDBOOK **A2.1, A5.1**

In summer, air conditioners use a lot of electrical energy to provide a comfortable environment in homes, shops, and offices. Working with a company called Enwave, Toronto has found a way to reduce the load that air conditioners place on the electricity supply. Enwave's Deep Lake Water Cooling (DLWC) uses cold water from the depths of Lake Ontario to cool homes and businesses without using electrically powered air conditioners.

1. Conduct research to learn why Lake Ontario can supply large amounts of cold water.
2. Research how Deep Lake Water Cooling works, including what equipment is used and how energy is transferred during the cooling process.

A. How does DLWC affect aquatic environments? Can it be considered a green energy source? Why or why not? T/I A

B. Does DLWC take water away from Lake Ontario? Explain. T/I

C. Compare and contrast DLWC with cooling systems that use energy derived from fossil fuels. Choose an appropriate way to communicate your comparison. Be sure to include
   (a) the similarities between the energy sources
   (b) the differences between the products of each energy source
   (c) the differences between their effects on the environment T/I C

WEB LINK

5.6 Review

Summary

- The most widely used fuels today are fossil fuels, which include petroleum, coal, and natural gas. Most coal consumed in Canada is used to generate electricity. Petroleum and natural gas are primarily used for transportation and heating. Fossil fuels, however, are non-renewable energy sources, and combustion of fossil fuels releases the greenhouse gases carbon dioxide and water vapour.
- Nuclear fission, used in nuclear power plants, produces extremely large quantities of energy. However, nuclear power stations are expensive to build and operate, they have the potential for catastrophic accidents, and a long-term solution to the problem of how to safely store nuclear waste has not yet been found.
- Coal can be used to produce coal slurry and syngas, synthetic fuel that can be used in the place of other fossil fuels. These fuels can extend the limited supply of fossil fuels, but they have similar costs to conventional fossil fuels.
- Hydrogen gas can potentially be used as a fuel. A large amount of energy is released upon hydrogen combustion, but the product (water vapour) is a greenhouse gas. Hydrogen gas is currently very expensive to produce and challenging to transport and store.
- Biofuels may be a significant alternate fuel source in the future. Although biofuels are renewable, they are produced from crops such as corn. Land usage shifts from food production to energy crop production, driving up food prices.
- The efficiencies of energy resources vary widely. Much of the energy content of energy sources is lost in conversion and distribution processes, mostly as waste heat.

Questions

1. Describe each of the following possible energy sources, and suggest ways that they could replace current energy sources: K/U
   (a) nuclear fusion
   (b) ethanol
   (c) syngas from coal gasification
   (d) coal slurry
2. How do the energy changes associated with fission or fusion processes compare to the energy changes associated with chemical reactions? K/U
3. It is said that the energy we get from fossil fuels came from the Sun. Is this statement true or false? Explain your reasoning. K/U A
4. Describe the advantages and disadvantages of coal and gasoline as energy sources. Be sure to include the economic and environmental impacts. K/U A
5. The enthalpy change from burning a gram of gasoline (octane) is –47.7 kJ/g, while that from burning a gram of coal is –32.8 kJ/g. Compare coal and gasoline in terms of their efficiency as fuels. K/U A
6. The per person energy usage in Canada is one of the highest in the world. K/U A
   (a) Give two reasons for Canada's large per capita energy usage.
   (b) Identify ways Canadians could reduce their energy usage and the strengths and weaknesses of each.
7. Many people believe hydrogen cars will someday replace gasoline cars. K/U T/I A
   (a) What advantages does hydrogen have over gasoline as a fuel?
   (b) Give three reasons why hydrogen cars are not a viable option at this time.
   (c) Do you think it likely that hydrogen cars will one day replace gasoline cars? Support your answer.
8. Research the source of electrical energy that is used to generate electricity in your area. 🌐 K/U T/I A
   (a) Where does your energy come from?
   (b) How much energy does this source produce?
   (c) Investigate any alternative energy that is used in your area and determine how it is used.

5.7 Explore an Issue in Wind Technology

Is Wind Technology the Answer?

SKILLS MENU

- Defining the Issue
- Researching
- Identifying Alternatives
- Analyzing
- Defending a Decision
- Communicating
- Evaluating

On August 14, 2003, at 4:11 p.m., Ontario and much of the northeastern United States were hit by the largest blackout in North America's history. Subway trains stopped running, refrigerators and stoves were no longer functional, traffic lights did not change, and our dependence on electricity was at the forefront of everyone's thoughts. Luckily, electricity was restored within a few days. The blackout highlighted our need for a stable and reliable source of electricity. Many methods of electricity generation are available for communities and government to consider. Wind technology (**Figure 1**) is one method of electricity generation that more communities are considering as a supplement to the electricity produced by hydroelectric, thermal, and nuclear power plants. Advances in wind turbine technology have provided significant improvements in efficiency. A modern wind turbine can generate enough electricity to meet the needs of several homes. This level of efficiency has sparked a surge in the construction of wind farms (large groupings of wind turbines) across Canada. Wind farms now generate enough power to meet the electrical energy needs of over one million Canadian homes (**Figure 2**).

The use of wind to generate electricity has drawbacks. For example, wind technology is only viable in regions with strong and consistent winds. Also, wind turbines generate far less electricity than a hydroelectric or fossil fuel–burning generating plant. Hence, several wind turbines must be combined into a wind farm to make a noticeable contribution toward meeting the electricity needs of a community. This requires large tracts of land. Other drawbacks include the noise pollution wind turbines generate and the potential loss of birds and bats that collide with the turbine blades.

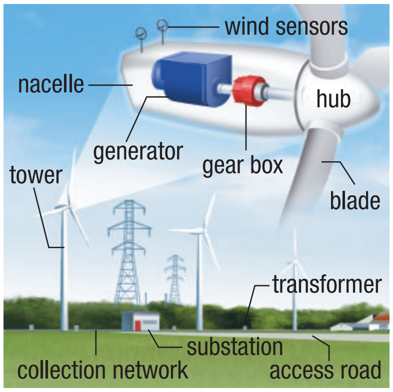


Figure 1 Main components of a typical wind farm

Figure 2 This wind farm, located on the north shore of Lake Erie, can potentially generate enough electricity for more than 20,000 homes.

The Issue

A local energy producer wishes to build a wind farm near a residential area located next to a nature reserve that includes a lake. The wind farm would generate about 15 % of the electricity used in this area. This would reduce the amount of electricity generated at a nearby coal-burning electricity generating plant, which has been supplying 100 % of the area's electricity. The wind farm has not yet been approved for construction. Concerned citizens are asking questions: Should a wind farm be built in this community? What are the environmental and economic advantages and disadvantages associated with this decision?

Goal

The local government has decided to conduct a town hall meeting to hear the views of the public on the developer's plans to build the wind farm in the area. Your group of concerned citizens is asked to make a presentation to the town hall outlining the advantages and disadvantages of a wind farm in your community, to help community members to make an informed decision about whether or not the wind farm should be built.

Research

SKILLS HANDBOOK A2, A5

Gather information that will address the following:

- the environmental and ecological advantages and disadvantages of wind farms
- the economic advantages and disadvantages of wind farms
- possible human health concerns associated with wind farms
- regulations concerning construction of wind farms in Ontario
- the process by which construction of wind farms is approved in Ontario

WEB LINK

Possible Solutions

- The environmental benefits of wind farms outweigh the disadvantages and therefore wind farms should be considered a viable source of electricity generation in the community.
- The economic costs of building and maintaining a wind farm outweigh any benefits that a wind farm will bring to the community.

Decision

In addition to describing the pros and cons of wind farms in general, the members of your group and you must decide whether you are going to support the development of the wind farm in your community or not.

Communicate

- Decide on the method you will use to communicate your decision to the citizens who attend the town hall. You may choose to include a slide presentation or a video presentation. You may also include a brochure to distribute to the town hall participants, a poster to display at the town hall, a web page, or other communication media of your choice. In your presentation, you must provide information about the advantages and disadvantages of wind generator technology.
- Present your findings to your audience. Compare your results to another group's presentation. You may be able to discover some points you omitted.

Plan for **Action**

How could you use the skills you gained from this exercise to research an issue in your own community involving a commercial enterprise that may be interfering with the local environment? Talk to several adults (parents, teachers, neighbours) to find out about issues in your local area that have led to conflict over potential damage to the environment.

1. Once you identify an issue, use your research skills to find out what you can do about it.
2. If possible, visit the site and take photos to document the issue.
3. Write a letter to the editor of your local newspaper or create another means for expressing your views publicly on the issue. Be sure to defend your position with facts that you found during your research.

WEB LINK

Investigation 5.2.1 OBSERVATIONAL STUDY

Molar Enthalpy of a Chemical Change

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

In this investigation, you will carry out a reaction in a coffee-cup calorimeter and measure the energy transfer between the chemical system and the surroundings. When aqueous sodium hydroxide, NaOH(aq), and aqueous hydrochloric acid, HCl(aq), are mixed, they undergo a neutralization reaction that forms aqueous sodium chloride, NaCl(aq), and liquid water, $H_2O(l)$. The balanced chemical equation for this reaction is

$$\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$$

Purpose

To determine the molar enthalpy of neutralization, ΔH_{neut}, for the reaction of aqueous sodium hydroxide and aqueous hydrochloric acid

Equipment and Materials

SKILLS HANDBOOK A1.2

- lab apron
- chemical safety goggles
- coffee-cup calorimeter
- two 100 mL graduated cylinders
- thermometer or temperature probe
- stirring rod
- 1.0 mol/L sodium hydroxide solution, NaOH(aq)
- 1.0 mol/L hydrochloric acid solution, HCl(aq)

Sodium hydroxide and hydrochloric acid are both corrosive. Avoid skin and eye contact. In the case of contact, wash the affected area with plenty of cool water. Inform your teacher.

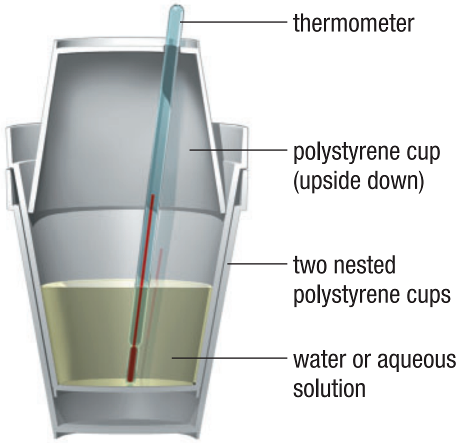


Figure 1 A coffee-cup calorimeter

Procedure

SKILLS HANDBOOK A2.3, A3

1. Put on your lab apron and safety goggles.
2. Assemble a coffee-cup calorimeter as shown in **Figure 1**.
3. Using the graduated cylinder, measure 50.0 mL of 1.0 mol/L sodium hydroxide solution and add it to the calorimeter.
4. Use the thermometer to measure and record the initial temperature of the sodium hydroxide solution. Remove and clean the thermometer under a stream of tap water. Dry it thoroughly.
5. Use the second graduated cylinder to measure 50.0 mL of 1.0 mol/L hydrochloric acid solution.
6. With the thermometer, measure and record the initial temperature of the hydrochloric acid solution. Remove and clean the thermometer under a stream of tap water.
7. Slowly pour the hydrochloric acid solution into the calorimeter. Mix the contents of the calorimeter with the stirring rod.
8. Place the thermometer in the mixture immediately. Measure and record the maximum temperature reached by the contents of the calorimeter.
9. Dispose of the chemicals according to your teacher's instructions.
10. Rinse the cups with tap water.

Analyze and Evaluate

(a) Was the reaction exothermic or endothermic? What evidence is there to support this? K/U T/I

(b) Calculate the mass of the acid solution and the base solution. Assume a density of 1.00 g/mL. K/U T/I

(c) Calculate the temperature change of the acid and base solutions. K/U T/I

(d) From the values obtained in (b) and (c), determine the thermal energy, q, released by the reaction. K/U T/I

(e) Calculate the number of moles of base in the reaction. K/U T/I

(f) Calculate the molar enthalpy of neutralization, ΔH_{neut}, of sodium hydroxide. K/U T/I

(g) Calculate the percentage difference between the value you obtained in the experiment and the accepted value for the molar enthalpy of neutralization of sodium hydroxide (−56 kJ/mol). K/U T/I

Apply and Extend

(h) What improvements would you want to make in your calorimeter design to allow you to obtain more accurate results? Explain. K/U T/I A

(i) What assumptions did you make in order to calculate the ΔH_{neut} of sodium hydroxide, NaOH(aq)? K/U T/I A

Investigation 5.4.1 OBSERVATIONAL STUDY

Hess's Law

The combustion of magnesium metal releases thermal energy and light energy. This combustion reaction is represented by the balanced equation

$Mg(s) + \frac{1}{2}\,O_2(g) \rightarrow MgO(s)$

In this investigation, you will determine the enthalpy change for this reaction using Hess's law and the following three thermochemical equations:

Reaction 1

$Mg(s) + 2\,HCl(aq) \rightarrow H_2(g) + MgCl_2(aq) \quad \Delta H_1 = ?$

Reaction 2

$MgO(s) + 2\,HCl(aq) \rightarrow H_2O(l) + MgCl_2(aq) \quad \Delta H_2 = ?$

Reaction 3

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H_3 = -286\text{ kJ}$

For the first two reactions, you will determine the enthalpy values (ΔH_1 and ΔH_2) using data collected in a coffee-cup calorimeter. The enthalpy value for the third reaction is provided.

Purpose

To determine the molar enthalpy of combustion of magnesium metal using Hess's law

Equipment and Materials

SKILLS HANDBOOK A1.2

- lab apron
- chemical safety goggles
- coffee-cup calorimeter
- 100 mL graduated cylinder
- thermometer
- steel wool
- balance and weighing boat
- stirring rod
- scoopula
- 1.0 mol/L hydrochloric acid, HCl(aq)
- 1.5 cm magnesium metal ribbon, Mg(s)
- 1 g magnesium oxide, MgO(s)

Hydrochloric acid is corrosive. Eye protection and a lab apron should be worn. In the case of contact, wash the affected area with plenty of cool water. Inform your teacher.

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Magnesium metal is flammable. Keep away from open flame.

Procedure

SKILLS HANDBOOK A2.3, A3

1. Put on your lab apron and safety goggles.
2. Obtain or assemble a coffee-cup calorimeter.

Part A: Determining the Enthalpy Change of Reaction 1

3. Use the graduated cylinder to measure 100.0 mL of 1.0 mol/L hydrochloric acid and pour it in the calorimeter.
4. With the thermometer, measure and record the initial temperature of the hydrochloric acid. Remove and clean the thermometer. Dry it thoroughly.
5. Rub a piece of the magnesium metal ribbon with steel wool. Using the balance, obtain about 0.5 g (±0.01 g) of magnesium metal. Record the actual mass.
6. Add the magnesium metal to the calorimeter. Stir the contents with the stirring rod. Ensure there are no open flames nearby.
7. Measure and record the maximum temperature reached after mixing.
8. Dispose of the calorimeter contents as directed by your teacher. Rinse and dry the calorimeter, thermometer, graduated cylinder, and stirring rod.

Part B: Measuring Enthalpy of Reaction 2

9. Repeat Steps 3 and 4.
10. Using the balance, obtain about 1.0 g (±0.01 g) of solid magnesium oxide. Record the actual mass.
11. Add the magnesium oxide to the calorimeter. Stir the contents with the stirring rod.
12. With the thermometer, measure and record the maximum temperature reached after mixing.

Analyze and Evaluate

(a) From your data, determine the thermal energy, *q*, for reaction 1 and for reaction 2. K/U T/I

(b) Determine the enthalpy of reaction per mole of magnesium (reaction 1) and the enthalpy of reaction per mole of magnesium oxide (reaction 2). K/U T/I

(c) Using Hess's law, determine the molar enthalpy of combustion of magnesium. You will need both of the values you determined experimentally and the given value for reaction 3. K/U T/I

(d) Calculate the percentage difference between the value you obtained and the accepted value for the enthalpy of magnesium combustion (−602 kJ/mol). K/U T/I

(e) Suggest at least three possible sources of error that may account for the difference you calculated. K/U T/I A

Apply and Extend

(f) Magnesium is often a component in sparklers, hand-held fireworks that emit sparks. Explain why magnesium is used in these products. K/U T/I A

Investigation 5.5.1 ACTIVITY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Calorimetry versus Enthalpies of Formation

In this activity, you will use enthalpies of formation to determine the enthalpy change of a chemical reaction. Then, you will use the enthalpy values obtained from calorimetry experiments to calculate standard enthalpies of formation. Finally, you will compare the results of the two calculations.

The calorimetry data is from an experiment involving a bomb calorimeter. During the experiment, the thermal energy released by the substance in the calorimeter is transferred directly to the calorimeter rather than to water. The quantity of energy transferred is determined using

$$q_{\text{bomb}} = c_{\text{bomb}} \times \Delta T$$

where c_{bomb} is the heat capacity of the calorimeter in J/°C.

Purpose

SKILLS HANDBOOK A2.4

To compare the experimental value of the enthalpy of combustion of ethanol with that derived from calculations based on enthalpies of formation for ethanol, water, and carbon dioxide.

Procedure

1. Determine the enthalpy of combustion per mole of ethanol using the experimental data in **Table 1**.

Table 1 Data from Combustion of Ethanol in a Bomb Calorimeter

Mass of ethanol	3.26 g
Heat capacity of calorimeter	11.7 kJ/°C
Initial temperature of calorimeter	21.5 °C
Final temperature of calorimeter	29.4 °C

2. Determine the enthalpy of combustion per mole of ethanol using the standard enthalpies of formation in **Table 2**.

Table 2 Standard Enthalpies of Formation

Substance	$\Delta H_f°$ (kJ/mol)
$H_2O(l)$	−285.8
$CO_2(g)$	−393.5
$C_2H_5OH(l)$	−235.2

Analyze and Evaluate

(a) Calculate the percent difference between the values you calculated in Steps 1 and 2. Explain any discrepancy between the two methods. K/U T/I

Apply and Extend

(b) Ethanol is commonly used as a fuel for cars and for heating homes. Based on your results, explain why ethanol makes a good fuel. K/U A

(c) Calculate the enthalpy of combustion for ethanol using bond energies and compare it with the other values. K/U T/I

CHAPTER 5 SUMMARY

Summary Questions

1. Create a study guide based on the Key Concepts on page 284. For each point, create three or four sub-points that provide further information, relevant examples, explanatory diagrams, or general equations.
2. Look back at the Starting Points questions on page 284. Answer these questions using what you have learned in this chapter. Compare your latest answers with those that you wrote at the beginning of the chapter. Note how your answers have changed.

Vocabulary

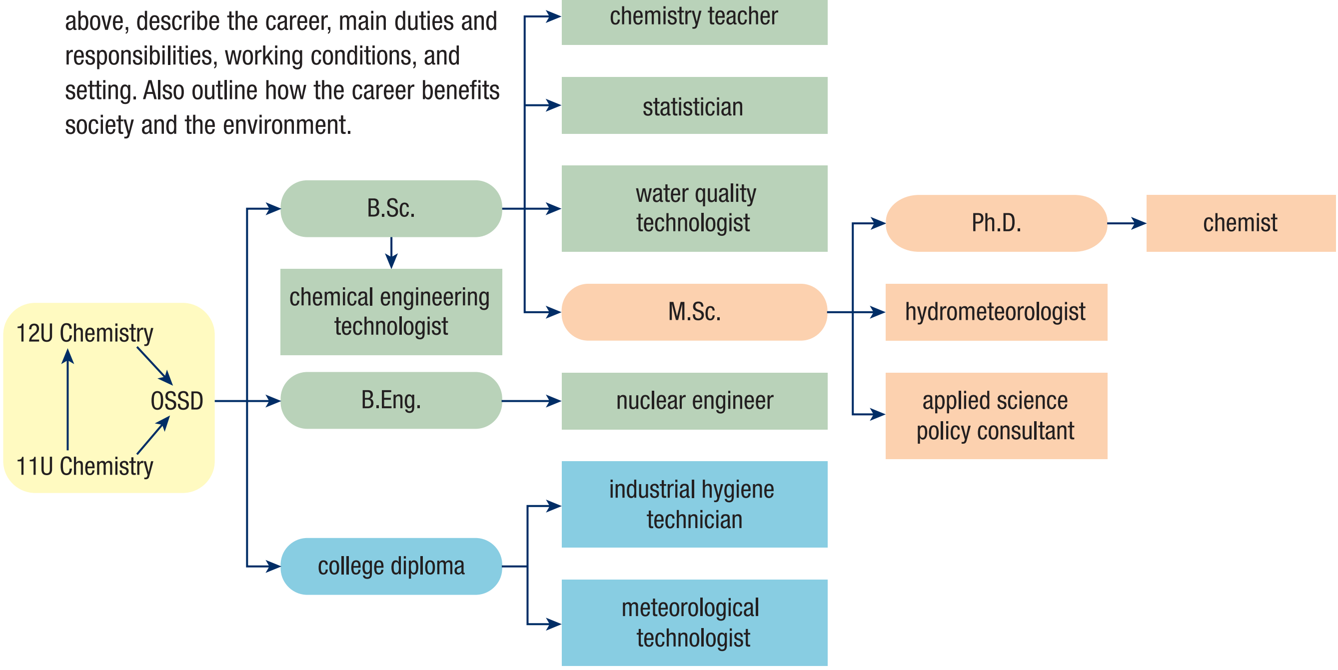
thermochemistry (p. 286)
energy (p. 286)
work (p. 286)
potential energy (p. 286)
kinetic energy (p.286)
thermal energy (p. 287)
heat (p. 287)
temperature (p. 287)
Law of Conservation of Energy (p. 287)
chemical system (p. 287)
surroundings (p. 287)
open system (p. 287)
closed system (p. 287)
isolated system (p. 287)
exothermic (p. 288)
endothermic (p. 288)
fusion (p. 289)
fission (p. 289)
specific heat capacity (*c*) (p. 292)
calorimetry (p. 293)
calorimeter (p. 293)
enthalpy (*H*) (p. 298)
enthalpy change (ΔH) (p. 298)
molar enthalpy change (ΔH_r) (p. 299)
potential energy diagram (p. 302)
bond dissociation energy (p. 307)
Hess's law (p. 314)
standard enthalpy of formation ($\Delta H_f°$) (p. 319)
standard state (p. 319)
coal slurry (p. 327)
syngas (p. 327)
efficiency (p. 329)

CAREER PATHWAYS

SKILLS HANDBOOK A7

Grade 12 Chemistry can lead to a wide range of careers. Some require a college diploma or a B.Sc. degree. Others require specialized or postgraduate degrees. This graphic organizer shows a few pathways to careers mentioned in this chapter.

1. Select two careers related to Thermochemistry that you find interesting. Research the educational pathways that you would need to follow to pursue these careers. What is involved in the required educational programs? Prepare a brief report of your findings.
2. For one of the two careers that you chose above, describe the career, main duties and responsibilities, working conditions, and setting. Also outline how the career benefits society and the environment.



CHAPTER 5 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. During a chemical reaction, which of the following statements is ALWAYS true? (5.1) K/U
   (a) A system loses energy to its surroundings.
   (b) A system gains energy from its surroundings.
   (c) The total energy of a system and its surroundings remains constant.
   (d) The kinetic energy of the system equals the potential energy of the surroundings.
2. Which of the following properties is NOT required to determine the amount of thermal energy needed to raise the temperature of a substance? (5.2) K/U
   (a) mass
   (b) volume
   (c) temperature change
   (d) specific heat capacity
3. Which of the following is true of endothermic reactions? (5.2) K/U
   (a) They have a positive *q* value.
   (b) They release energy.
   (c) They have energy terms written on the product side of the reaction.
   (d) They can be identified by an increase in temperature of the surroundings.
4. How much energy is absorbed by a 2.5 g substance that has a specific heat capacity of 0.58 J/g·°C and undergoes a temperature increase of 1.2 °C? (5.2) K/U T/I
   (a) 1.2 J
   (b) 1.7 J
   (c) 12 kJ
   (d) 17 kJ
5. Which of the following chemical bonds requires the most energy to break? (5.3) K/U
   (a) a hydrogen bond
   (b) a single bond
   (c) a double bond
   (d) a triple bond
6. Given the thermochemical equation

   $$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) + 286\ \text{kJ}$$

   what is the ΔH of the decomposition of 2 mol of $H_2O(l)$ into hydrogen gas and oxygen gas? (5.4) K/U
   (a) −286 kJ
   (b) +286 kJ
   (c) −572 kJ
   (d) +572 kJ
7. Given the formation reaction represented by

   $C(s) + 2\ H_2(g) \rightarrow CH_4(g)$

   which of the following substances in the reaction has a ΔH_f° of 0? (5.5) K/U
   (a) $C(s)$ (c) $CH_4(g)$
   (b) $H_2(g)$ (d) both (a) and (b)
8. Which of the following is NOT a fossil fuel? (5.6) K/U
   (a) uranium (c) petroleum
   (b) coal (d) natural gas

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

9. In a chemical reaction, both the reactants and the products have potential energy. (5.1) K/U
10. The ΔH of an exothermic reaction is a positive value. (5.2) K/U
11. Scientists use potential energy diagrams to describe the total energy of a system. (5.2) K/U
12. The state of the reactants and the products is not important when calculating the enthalpy of a reaction. (5.2) K/U
13. When calculating the enthalpy of a reaction, it is important that the equation you are analyzing is accurately balanced. (5.2) K/U
14. Bond energies between the same atoms are similar in different molecules. (5.3) K/U
15. Two ways to estimate the enthalpy change of a chemical reaction are by enthalpies of formation and bond energies. (5.3, 5.5) K/U
16. When you reverse a reaction, you must also reverse the enthalpy term of the initial reaction. (5.4) K/U
17. If you write a combustion reaction for each of the substances in a chemical reaction, these reactions can be used in a Hess's Law calculation to determine the enthalpy of the reaction. (5.4) K/U
18. For any reaction that can be written as a series of steps, the change of enthalpy is the same as the sum of the enthalpy changes for the steps. (5.2, 5.4) K/U
19. The enthalpy of formation of oxygen gas, $O_2(g)$, is a negative value. (5.5) K/U
20. Not all conventional fuels are non-renewable. (5.6) K/U
21. A modern wind turbine can generate enough electricity to meet the needs of several cities. (5.7) K/U

Go to Nelson Science for an online self-quiz.

WEB LINK

CHAPTER 5 REVIEW

Knowledge

For each question, select the best answer from the four alternatives.

1. The total amount of potential energy and kinetic energy of a substance is called
   (a) energy of motion
   (b) conservation of energy
   (c) energy of composition
   (d) thermal energy (5.1) K/U
2. How much energy is released when the temperature of a 21.2 kg mass of a substance decreases by 15 °C, if the substance has a specific heat of 1.6 J/g·°C? (5.2) K/U
   (a) 199 J
   (b) 509 J
   (c) 199 kJ
   (d) 509 kJ
3. Identify the statement that is true for the reaction described by the equation below. (5.2) K/U
   $H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l) + 286\ kJ$
   (a) it is exothermic
   (b) it is endothermic
   (c) it occurs most quickly at room temperature
   (d) it has a positive enthalpy value
4. If the average bond energy of an O–H bond is 467 kJ/mol, how much energy is needed to break the bonds in 2 mol of water? (5.3) K/U
   (a) 234 kJ/mol
   (b) 467 kJ/mol
   (c) 934 kJ/mol
   (d) 1868 kJ/mol
5. Reaction A has a ΔH of −65 kJ and reaction B has a ΔH of +405 kJ. Reaction C is the combination of reaction A and 2 times reaction B. What is the ΔH of reaction C? (5.4) K/U
   (a) −745 kJ
   (b) +745 kJ
   (c) −875 kJ
   (d) +875 kJ
6. For the chemical reaction represented by
   $C(s) + O_2(g) \rightarrow CO_2(g) + 394\ kJ$
   what is the ΔH for the decomposition of 2 mol of $CO_2(g)$ into its elements? (5.5) K/U
   (a) +394 kJ
   (b) −394 kJ
   (c) +788 kJ
   (d) −788 kJ
7. Which of the following is NOT characteristic of fossil fuels? (5.6) K/U
   (a) they are renewable
   (b) they emit greenhouse gases when burned
   (c) they originate from organisms that lived millions of years ago
   (d) they may be solids, liquids, or gases
8. Energy efficiency of a device or system refers to
   (a) the ratio of the energy output to the energy input
   (b) the quantity of electrical energy generated
   (c) the percentage of energy converted to thermal energy
   (d) the ratio of energy conversion to energy distribution (5.6) K/U

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

9. The law of conservation of energy states that the energy of a system is always 0. (5.1) K/U
10. A reaction that absorbs thermal energy from its surroundings is endothermic. (5.1) K/U
11. For an exothermic reaction, the change in enthalpy, ΔH, is negative. (5.2) K/U
12. The molar enthalpy change, ΔH_r, of a substance is the energy change that occurs when 1 gram of that substance undergoes a physical, chemical, or nuclear change. (5.2) K/U
13. In a potential energy diagram, the potential energy is on the vertical (y) axis and the reaction progress is on the horizontal (x) axis. (5.2) K/U
14. More energy is released when a double bond forms than when a triple bond forms. (5.3) K/U
15. Bond energies will give a very accurate value for the enthalpy of a reaction. (5.3) K/U
16. Hess's Law states that enthalpy change is dependent on the number of steps by which a reaction occurs. (5.4) K/U
17. If the forward reaction of a reversible chemical reaction has a ΔH of −62 kJ, the ΔH of the reverse reaction is −62 kJ. (5.4) K/U
18. Hess's law supports the law of conservation of energy. (5.4) K/U
19. Nuclear generating stations use fusion to release energy. (5.6) K/U
20. Pure ethanol can be used directly as a fuel source in most automobile engines. (5.6) K/U

Understanding

Write a short answer to each question.

21. Identify each of the following as an exothermic or an endothermic process: (5.1) K/U
    (a) freezing of water
    (b) combustion of acetylene gas
    (c) neutralization of a strong acid with a strong base, which increases the temperature of the solution from 20.5 °C to 26.0 °C
    (d) dissolution of a salt, which changes the temperature of the solution from 21 °C to 19 °C
22. A chemical reaction releases 54 kJ of energy. (5.1) K/U T/I
    (a) How much energy is absorbed by the surroundings?
    (b) Is the chemical reaction exothermic or endothermic?
23. Imagine you pour 250 mL of hot cocoa into an insulated Thermos and another 250 mL into a ceramic cup. Explain why the cocoa in the Thermos stays warm for hours but the cocoa in the ceramic cup gets cold quickly, referring to thermal energy transfer. (5.2) K/U A
24. Methane, gasoline, and propane are all hydrocarbons that are commonly used as fuels in the gas state. What characteristics do the bonds of these molecules have in common that make them effective fuel sources? (5.3) K/U T/I
25. Explain why we can rearrange two chemical equations and add their enthalpy change values to determine the enthalpy change of a third reaction. (5.4) K/U
26. A chemist carries out a reaction in a calorimeter and determines that the reaction releases 724 kJ of thermal energy. She then removes one-half of the product and places it in a second vessel. How much thermal energy does she need to add to the second vessel to reverse the reaction? Ignore the specific heat of the second vessel, and assume that the reverse reaction will proceed with only the addition of thermal energy. (5.4) K/U T/I
27. Write a chemical equation for the formation of each of the following substances: (5.5) K/U T/I
    (a) $NaCl(s)$
    (b) $H_2O(s)$
    (c) $PbSO_4(s)$
    (d) $C_6H_{12}O_6(s)$
28. The standard enthalpy of formation, $\Delta H_f°$, of aluminum oxide, $Al_2O_3(s)$, is -1676 kJ/mol. Write the balanced thermochemical equation for this reaction in both styles. (5.5) K/U T/I
29. (a) Summarize the strengths and weaknesses of hydrogen gas as an alternative energy.
    (b) What possible discoveries could make hydrogen a more viable alternative to fossil fuels? (5.6) K/U A
30. The enthalpy of combustion, ΔH_{comb}, for fuel A is -30 kJ/g and for fuel B is -50 kJ/g. Based on this data, which fuel would you recommend for use in an airplane? Why? (5.6) K/U A
31. (a) Give reasons why someone might choose to use electrical energy generated from a wind farm.
    (b) Give reasons why someone might choose NOT to use electrical energy generated from a wind farm. (5.7) K/U A

Analysis and Application

32. Using a graphic organizer, compare and contrast kinetic and potential energy. Include a diagram to support your comparison and provide two examples of each type of energy. (5.1) K/U C
33. A student places a pan of water on a gas stove and heats the water with the flame from the burner. As the water heats, it begins to boil. Draw a series of diagrams that illustrate what happens to the water molecules and any energy transfers that take place. Briefly describe all the changes using the terms "exothermic," "endothermic," "system," "surroundings," "potential energy" and "kinetic energy" in the discussion. (5.1) K/U C
34. The following balanced thermochemical equation represents the combustion of methanol gas:

$$2\,CH_3OH(g) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 4\,H_2O(l) + 1452\text{ kJ}$$ (5.2) K/U T/I

    (a) What quantity of thermal energy is released for each mole of water formed?
    (b) What quantity of thermal energy is released for each mole of carbon dioxide formed?
    (c) What quantity of thermal energy is released for each mole of oxygen reacted?
    (d) What is the molar enthalpy change, ΔH_{comb}, of this reaction?
35. Determine the amount of energy absorbed by 1.00 g of each of the following substances when its temperature is raised 10.5 °C: (5.2) K/U T/I
    (a) silicon dioxide, $SiO_2(s)$
    (b) water $H_2O(l)$

36. A 100.0 mL volume of 1.0 mol/L hydrochloric acid was mixed with 100.0 mL of 1.0 mol/L sodium hydroxide at 23.5 °C in a coffee-cup calorimeter. After the reactants mix, the temperature increases to 30.6 °C. The specific heat capacity of water is 4.18 J/g·°C. (5.2) K/U T/I
   (a) How much energy is released in this reaction?
   (b) How much energy per mole of hydrochloric acid is released in the reaction?

37. The reaction by which mercury(II) oxide, HgO(s), decomposes to mercury and oxygen absorbs 90.7 kJ/moL, and is represented by the equation

   $HgO(s) \rightarrow Hg(l) + \frac{1}{2} O_2(g)$ (5.2) K/U T/I C

   (a) Write the thermochemical equation for this reaction with the thermal energy term separate from the reaction.
   (b) Write the chemical equation with the thermal energy term embedded in the reaction.
   (c) Draw the potential energy diagram for this reaction.

38. In a coffee-cup calorimeter, a student mixes 1.60 g ammonium nitrate, NH_4NO_3, with 75.0 g water at an initial temperature of 25.00 °C. After dissolution of the salt, the final temperature of the calorimeter contents is 23.34 °C. Assuming the solution has the same heat capacity and density as liquid water, calculate the enthalpy change for the dissolution of ammonium nitrate. (5.2) K/U T/I

39. How much thermal energy is released when 60.0 g of potassium metal reacts according to the following equation?

   $2\ K(s) + 2\ H_2O(l) \rightarrow H_2(g) + 2\ KOH(aq) + 160\ kJ$

   (5.2) K/U T/I

40. For 1 mol of ethanol, the enthalpy of vaporization, ΔH_{vap}, is −38.6 kJ/mol and the enthalpy of fusion, ΔH_{fus}, is −26.1 kJ/mol. (5.2) K/U T/I
   (a) Describe what happens to the energy of the molecules as the ethanol changes state from a solid to a liquid and then to a vapour.
   (b) Calculate the energy required to vaporize 2.0 mol of ethanol.
   (c) Calculate the energy required to melt 0.5 mol of solid ethanol.

41. A student carried out two different reactions in a coffee-cup calorimeter:
   (1) $CaCO_3(s) + 2\ HCl(aq) \rightarrow CO_2(g) + H_2O(l) + CaCl_2(aq)$
   (2) $CaO(s) + 2\ HCl(aq) \rightarrow H_2O(l) + CaCl_2(aq)$

   Table 1 shows the data she collected. (5.2) K/U T/I

Table 1

Data	Experiment 1 ($CaCO_3$ + HCl)	Experiment 2 (CaO + HCl)
mass of reactant	4.2 g	4.7 g
mass of acid	170.2 g	155.5 g
initial temperature	24.0 °C	23.8 °C
final temperature	26.0 °C	30.8 °C

   Assuming the specific heat capacity, *c*, of the solution is 4.18 J/g·°C and its density is 1.00 g/mL, calculate the enthalpy change of
   (a) reactions 1 and 2
   (b) the reaction given by the equation
   $CaCO_3(s) \rightarrow CO_2(g) + CaO(s)$

42. Liquid cyclohexane, $C_6H_{12}(l)$, is a 6-carbon ring with a standard enthalpy of formation of −156 kJ/mol. Liquid 1-hexene has the same molecular formula, $C_6H_{12}(l)$, but is a linear molecule with a double bond. The standard enthalpy of formation of liquid 1-hexene is −74.2 kJ/mol. (5.2, 5.3) K/U T/I A
   (a) Write the formation reactions for cyclohexane and 1-hexene. Include an energy term.
   (b) Use the enthalpy of formation to calculate the enthalpy change for the combustion of liquid cyclohexane and liquid 1-hexene.
   (c) Compare the effect of the ring structure with the double bond on the enthalpy of combustion.

43. Using bond energy values estimate the energy required to decompose these molecules into their atoms: (5.3) K/U T/I
   (a) CH_2Cl_2
   (b) CH_3Br
   (c) C_2H_2
   (d) $CH_2{=}CH_2$

44. (a) Using bond energies, verify that the combustion reaction of acetylene, $C_2H_2(g)$, is an exothermic reaction.
   (b) Briefly outline how you determined your answer to (a). (5.3) K/U T/I

45. Use bond energies to predict the enthalpy change for the following reactions. State whether the reaction is exothermic or endothermic. (5.3) K/U T/I
   (a) $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$
   (b) $H_2S(g) + 3\ F_2(g) \rightarrow SF_4(g) + 2\ HF(g)$
   (c) synthesis of 2 mol of ammonia from nitrogen and hydrogen gas
   (d) complete combustion of 1 mol of propene gas, $H_2C{=}CHCH_3(g)$.

46. The major industrial source of hydrogen gas is from the reaction represented by the following equation:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3\ H_2(g)$$

Use bond energies to predict the enthalpy change for this reaction. (5.3) K/U T/I

47. Much of the gasoline sold in Canada is a mixture of 10 % ethanol and 90 % gasoline. Gasohol is a mixture consisting of about 10 % ethanol and 90 % gasoline. The enthalpy of combustion per gram of gasoline is −47.8 kJ/g. (5.3) K/U A

   (a) Using bond energies, estimate the enthalpy of combustion per gram of ethanol. Assume that ethanol is in the gaseous state.

   $$C_2H_5OH(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(g)$$

   (b) Compare the enthalpy of the combustion reaction of ethanol to that of octane, one of the most common alkanes in gasoline. Discuss the implications of these enthalpies for a car's driver.

48. Determine the enthalpy for the reaction represented by the equation

$$SO_2(g) + \tfrac{1}{2}\ O_2(g) \rightarrow SO_3(g)$$

Use Hess's law along with the following equations:

$S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H = -296.8\ kJ$

$2\ S(s) + 3\ O_2(g) \rightarrow 2\ SO_3(g) \qquad \Delta H = -795.45\ kJ$

(5.4) K/U T/I

49. Alumina, $Al_2O_3(s)$, is a common component in sunscreens, and is produced by the reaction shown in the equation

$$Fe_2O_3(s) + 2\ Al(s) \rightarrow Al_2O_3(s) + 2\ Fe(s)$$

Determine the enthalpy change of the above reaction, given the following formation reactions:

$2\ Al(s) + \tfrac{3}{2}\ O_2(g) \rightarrow Al_2O_3(s) \qquad \Delta H = -1676\ kJ$

$2\ Fe(s) + \tfrac{3}{2}\ O_2(g) \rightarrow Fe_2O_3(s) \qquad \Delta H = -824\ kJ$

(5.4) K/U T/I

50. The enthalpy of combustion of methane gas, $CH_4(g)$, to form liquid water, $H_2O(l)$, is −891 kJ/mol. The enthalpy of combustion of $CH_4(g)$ to form steam, $H_2O(g)$, is −803 kJ/mol. Use this information to determine the enthalpy of vaporization for water. (5.4) K/U T/I

51. Ethanol and carbon dioxide are products in the fermentation reaction of glucose. The enthalpies of combustion for glucose and ethanol are –2813 kJ/mol and −1369 kJ/mol, respectively. (5.4) K/U T/I A

   (a) Calculate the molar enthalpy of the fermentation reaction given by the following equation:

   $$C_6H_{12}O_6(s) \rightarrow 2\ C_2H_5OH(l) + 2\ CO_2(g)$$

   (b) Would you expect a vessel where fermentation was occurring to feel warm or cool to the touch? Explain your answer.

52. Use equations (1) to (4) to calculate the enthalpy change for the reaction represented by equation (5). (5.4) K/U T/I

(1) $Na(s) + \tfrac{1}{2}\ H_2(g) + C(s) + \tfrac{3}{2}\ O_2(g) \rightarrow NaHCO_3(s) \qquad \Delta H = -948\ kJ$

(2) $2\ Na(s) + C(s) + \tfrac{3}{2}\ O_2(g) \rightarrow Na_2CO_3(s) \qquad \Delta H = -1131\ kJ$

(3) $H_2(g) + \tfrac{1}{2}\ O_2(g) \rightarrow H_2O(g) \qquad \Delta H = -242\ kJ$

(4) $C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -394\ kJ$

(5) $2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$

53. Use equations (1) to (4) to calculate the enthalpy change for the reaction represented by equation (5). (5.4) K/U T/I

(1) $P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g) \qquad \Delta H = -1226\ kJ$

(2) $P_4(s) + 5\ O_2(g) \rightarrow P_4O_{10}(g) \qquad \Delta H = -2967\ kJ$

(3) $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g) \qquad \Delta H = -84\ kJ$

(4) $PCl_3(g) + \tfrac{1}{2}\ O_2(g) \rightarrow POCl_3(g) \qquad \Delta H = -286\ kJ$

(5) $P_4O_{10}(s) + 6\ PCl_5(g) \rightarrow 10\ POCl_3(g)$

54. Pyruvic acid, $CH_3COCOOH(aq)$, is an intermediate product of cellular respiration in living cells. The pyruvic acid is broken down into aqueous acetic acid, $CH_3COOH(aq)$, and carbon monoxide, $CO(aq)$:

$$CH_3COCOOH(aq) \rightarrow CH_3COOH(aq) + CO(aq)$$

Use the values in **Table 2** to determine the enthalpy change for this reaction. (5.4) K/U T/I

Table 2

Compound	**ΔH_{comb} (kJ/mol)**
pyruvic acid	−1275
acetic acid	−875
carbon monoxide	−283

55. (a) With a flow chart, summarize the steps you would use to calculate the enthalpy change of a reaction

      (i) from standard enthalpies of formation

      (ii) from bond energies

   (b) Compare and contrast the two methods of calculation of enthalpy change. (5.5) K/U T/I C

56. For each reaction represented by the following equations, use the values for $\Delta H_f°$ to calculate $\Delta H°$: (5.5) K/U T/I

   (a) $2\ NH_3(g) + 3\ O_2(g) + CH_4(g) \rightarrow 2\ HCN(g) + 6\ H_2O(g)$

   (b) $Ca_3(PO_4)_2(s) + 3\ H_2SO_4(l) \rightarrow 3\ CaSO_4(s) + 2\ H_3PO_4(l)$

   (c) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

   (d) $C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$

   (e) $SiCl_4(l) + 2\ H_2O(l) \rightarrow SiO_2(s) + 4\ HCl(g)$

   (f) $MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s)$

57. (a) Syngas, the fuel made from coal, can be burned directly or converted to methanol. Calculate the $\Delta H°$ for the reaction using $\Delta H_f°$:

    $CO(g) + 2\ H_2(g) \rightarrow CH_3OH(l)$

    (b) Is the reaction exothermic or endothermic? (5.5) K/U T/I

58. (a) Write the chemical equation that represents the formation reaction of acetone, $C_3H_6O(l)$.

    (b) Using the combustion equations below, calculate the enthalpy of formation for acetone:

    (1) $H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286\ kJ$

    (2) $C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -394\ kJ$

    (3) $C_3H_6O(l) + 4\ O_2(g) \rightarrow 3\ CO_2(g) + 3\ H_2O(l) \quad \Delta H = -1784\ kJ$

    (5.5) K/U T/I

59. The combustion reaction of solid benzoic acid, $C_6H_5COOH(s)$, releases 3224 kJ/mol of energy. Use the standard enthalpies of formation for water vapour and carbon dioxide gas to determine the standard enthalpy of formation for benzoic acid. (5.5) K/U T/I

60. The process of photosynthesis produces aqueous glucose and oxygen gas from liquid water and carbon dioxide gas. (5.5) K/U T/I A
    - (a) Calculate $\Delta H°$ for photosynthesis using $\Delta H_f°$ values.
    - (b) Calculate $\Delta H°$ again, but using bond energies.
    - (c) Compare your answers to (a) and (b) and account for any differences.
    - (d) Is photosynthesis exothermic or endothermic?

61. In the presence of concentrated sulfuric acid, $H_2SO_4(aq)$, the sugar sucrose, $C_{12}H_{22}O_{11}(s)$, breaks down into elemental carbon and water vapour. (5.5) K/U T/I
    - (a) Write the chemical reaction for this process. Note that sulfuric acid is only a catalyst.
    - (b) Determine the molar enthalpy change, using standard enthalpies of formation.

62. When gasoline is heated in the presence of hydrogen gas and a catalyst, the gasoline "cracks." During cracking, gasoline decomposes to 1 mol of methane, 2 mol of ethane, and 1 mol of propane for each mole of octane. (5.5) K/U T/I A
    - (a) Write the chemical reaction for this process, assuming all of the gasoline is octane, $C_8H_{18}(l)$.
    - (b) Determine the molar enthalpy change that occurs during the cracking process, using standard enthalpies of formation.

63. Using standard enthalpies of formation, verify that the combustion reaction of hydrogen gas produces approximately 2.5 times the energy per gram as the combustion of methane gas, $CH_4(g)$, the major component of natural gas. (5.5, 5.6) K/U T/I

64. The balanced chemical equation for the combustion of propane gas is

    $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l) \quad \Delta H = -2221\ kJ$

    What mass of propane must be burned to furnish 8.7×10^4 kJ of energy, assuming the energy transfer process is 60 % efficient? (5.2, 5.6) K/U T/I A

65. Using a concept map, summarize the environmental consequences of burning fossil fuels. (5.6) K/U C

66. During the process of nuclear fusion in the Sun, hydrogen atoms produce atoms of helium and release 1.7×10^9 kJ of energy per mole of helium atoms. (5.6) K/U T/I A
    - (a) How much energy is released when 500 g of helium atoms are produced by nuclear fusion?
    - (b) How does this quantity of energy compare with other fuel sources?
    - (c) Why is a similar fusion reaction not used to generate electricity?

Evaluation

67. Some automobile and bus engines are modified to burn propane gas, $C_3H_8(g)$, as fuel. (5.5, 5.6) K/U T/I A
    - (a) Compare the amount of energy per gram released by complete combustion of propane and gasoline, assuming that gasoline is pure octane, $C_8H_{18}(l)$.
    - (b) Which is the more energy-efficient fuel source? Explain.
    - (c) Do you think that gasoline should be replaced by propane gas in the trucking industry? Defend your position.

68. In the process of coal gasification, the following reactions are used:

    $C(s) + 2\ H_2(g) \rightarrow CH_4(g)$

    $C(s) + \frac{1}{2}\ O_2(g) \rightarrow CO(g)$ (5.5, 5.6) T/I A

    - (a) Determine the enthalpy change for the combustion of each of the products in the reactions, using standard enthalpies of formation.
    - (b) Based on these values, calculate the enthalpy change per gram.
    - (c) Which is the better energy source: methane or carbon monoxide? Defend your position.
    - (d) Do you think coal gasification could supply our energy needs in a sustainable way? Defend your position by considering both economic and environmental factors.

Reflect on Your Learning

69. Describe three pieces of information that you learned in this chapter that you found surprising. Why did they surprise you? K/U T/I

70. Think about what you have learned in this chapter. How can you apply the information you have learned to your everyday life? A

71. What concepts in this chapter did you find most difficult to understand? What are some ways that you can improve your understanding of these concepts? K/U T/I

72. Think about what you knew about chemical reactions and enthalpy before you studied this chapter. What were some misconceptions you had? K/U

Research

WEB LINK

73. An environmental activist tells you that we should stop building wind farms and only build solar farms. Research the costs, advantages, and disadvantages of both methods of generating electricity. Do you agree with his position? Justify your answer. (5.7) A

74. Commercial power plants use fuel from a variety of sources, converting them into energy that people can use. Research a power plant and summarize how it converts fuel into electrical energy. A
    (a) What fuel efficiency is obtained?
    (b) What is/are the chemical reaction(s) used to produce this energy?
    (c) What is the energy change in terms of kJ/g and kJ/mol for this energy source?

75. We get the energy our bodies need to perform daily activities through the food that we eat. A
    (a) Conduct research to find the relationship between joules and calories. Using this information, compare the enthalpy change from the complete combustion of two different food sources.
    (b) Compare these enthalpy values to the energy produced during the combustion of different fuels.

76. Currently, many solar panels are only about 13 % efficient in converting solar energy to electricity. A
    (a) Research the average amount of electrical energy typically used in a Canadian home.
    (b) Determine the quantity of both solar panels and solar energy needed to meet the electrical need you identified in (a).
    (c) Is the use of solar panels a feasible energy source to provide all the energy to a home where you live? Explain.

77. Conduct research to find out details on the procedures used by Germain Henri Hess to establish Hess's law. A
    (a) Outline how Hess conducted his experiments, including the equipment he used.
    (b) What were some of the limitations that Hess had to deal with in the 1800s?
    (c) Suggest ways in which the experiment might have been different if Hess were working today.

78. Many cars today use alternative energy sources. For example, hybrid cars typically combine gasoline with electrical power. A
    (a) Research the history of the hybrid car and identify other forms of transportation that use a hybrid power source.
    (b) Describe the advantages and disadvantages of hybrid cars.
    (c) Make an educated comparison to determine if a hybrid car is worth owning.

79. Research the quantity of energy per capita that Canadians use. C A
    (a) Compare this energy use to other countries and determine any trends in the data. Choose one other country and directly compare the energy usage of that country to Canada's.
    (b) List some of the factors that contribute to this energy use.
    (c) Write a letter to your Member of Parliament stating your opinion as to whether it is morally justified for Canada to continue this present level of energy consumption.

80. Many chefs keep a box of baking soda near their stoves in case a grease fire breaks out. Research the reaction that occurs when baking soda is heated, and explain how it is effective for putting out grease fires. K/U T/I

CHAPTER 6

Chemical Kinetics

KEY CONCEPTS

After completing this chapter you will be able to

- recognize that rates of chemical reactions vary, and identify factors that affect the rate of a reaction
- describe how the rate of disappearance of a reactant and appearance of a product are stoichiometrically related
- explain how the rate of a reaction is determined by the series of elementary steps that make up the reaction
- explain the concept of a reaction mechanism
- use collision theory to explain why reaction rates increase or decrease under different conditions
- explain how industry manipulates rates of reaction to increase efficiency and how improved efficiency of reactions contributes to environmental sustainability

Why Are Some Reactions with Nitroglycerine Not Explosive?

Nitroglycerine is an extremely unstable liquid—a physical shock can cause it to explode. Originally discovered in 1847, nitroglycerine was considered too dangerous to transport or use until 1867, when Alfred Nobel discovered that mixing it with silica paste to form a solid makes it more stable. Nobel's invention, dynamite, made it possible to use the explosive power of nitroglycerine more safely. When dynamite is detonated, the nitroglycerine undergoes a rapid and highly exothermic decomposition reaction, releasing an enormous amount of energy in less than a second. Dynamite was used extensively in the building of Canada's railroads; nitroglycerine in its pure form was used as well, for tunnel blasting. The use of nitroglycerine resulted in many accidents and the deaths of labourers working on the railway.

It may therefore surprise you to learn that nitroglycerine is also used as a heart medication. Doctors use nitroglycerine to treat angina, a type of chest pain associated with clogged arteries and decreased flow of blood, which reduces the supply of oxygen to the heart. Nitroglycerine can be given to patients as a tablet, spray, ointment, or patch.

When it is used as a heart medicine, nitroglycerine does not explode. Instead, it undergoes a different chemical reaction, which releases small quantities of nitric oxide, NO(g). Nitric oxide acts on the walls of blood vessels to make their diameter larger. This increases blood flow and relieves angina. The production of nitrous oxide gas occurs at a much slower rate than the decomposition reaction of dynamite. There is far less energy released, so the nitroglycerine is not harmful. Interestingly, Alfred Nobel was prescribed nitroglycerine to treat a heart condition and, in 1998, R.F. Furchgott, L.J. Ignorro, and F. Murad won the Nobel prize for discovering that nitric oxide acts as a signalling molecule in the cardiovascular system.

The majority of chemicals can enter into a number of different chemical reactions, depending on the reactants and the conditions under which they interact. These reactions can form products at very different rates.

STARTING **POINTS**

Answer the following questions using your current knowledge. You will have a chance to revisit these questions later, applying concepts and skills from the chapter.

1. Give an example of a chemical reaction that forms products quickly and one that forms products slowly.
2. Why are some chemical reactions able to form products quickly while others only form products slowly?
3. Why might a predicted chemical reaction fail to take place (for example, a match head that fails to ignite when struck)?
4. Suggest at least three ways in which the quantity of a product formed per minute in a chemical reaction could be changed.
5. Why is it important for chemists to know the quantity of a product a chemical reaction can form per unit of time (for example, per minute)?
6. Why is industry interested in manipulating the quantity of a product a chemical reaction can form per unit of time?

Mini Investigation

An Exercise in Speed

Skills: Performing, Observing, Analyzing, Communicating

SKILLS HANDBOOK **A1.1, A1.2, A2.1**

In this activity, you will observe changes in the mass of a solution undergoing a chemical reaction and relate these changes to the speed of the reaction. When solid calcium carbonate, $CaCO_3(s)$, is placed in a dilute solution of hydrochloric acid, $HCl(aq)$; carbon dioxide gas; water; and aqueous calcium chloride, $CaCl_2(aq)$, are formed. When the reaction occurs in an open container, the carbon dioxide gas will escape into the air, so the mass of the contents of the beaker will decrease. By plotting the mass of the beaker and its contents over time, you can estimate the rate of the reaction.

The balanced chemical equation for this reaction is

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Equipment and Materials: chemical safety goggles; lab apron; gloves; 100 mL graduated cylinder; 250 mL beaker; electronic balance; timer; small piece of solid calcium carbonate, $CaCO_3(s)$; 1 mol/L hydrochloric acid solution, $HCl(aq)$

Dilute hydrochloric acid is an irritant. Avoid skin and eye contact. If you spill this chemical on your skin, wash the affected area with plenty of cool water and inform your teacher immediately.

1. Put on your safety goggles, apron, and gloves.
2. Using the graduated cylinder, carefully transfer 100 mL of the hydrochloric acid solution into a 250 mL beaker.
3. Place a small piece of solid calcium carbonate on the pan of an electronic balance. Then, place the beaker containing the hydrochloric acid on the pan beside the calcium carbonate. Tare the balance.
4. Carefully place the calcium carbonate piece into the hydrochloric acid solution in the beaker on the balance. Start the timer immediately. This is time zero.
5. Record the mass of the beaker and its contents every 30 s for 10 min.

A. Calculate the decrease in mass for each minute, starting at time zero. The decrease in mass equals the mass of carbon dioxide gas produced in the reaction during each minute T/I

B. Plot a graph of mass of carbon dioxide gas formed (*y*-axis) versus time in minutes (*x*-axis). T/I C

C. Calculate the mass of carbon dioxide gas that was formed in total over the 10 min time period. T/I

D. What was the average rate of formation of carbon dioxide gas over the 10 min interval? Calculate the rate in both g/min and in mol/min. T/I

E. During what time was the rate of carbon dioxide gas formation the highest? The lowest? Mark these areas on your graph. T/I C

F. Suggest a reason why the reaction rate changed during the course of the reaction. T/I

G. How might you slow down the reaction rate? T/I

H. How might you speed up the reaction rate? T/I

6.1 Reaction Rates

chemical kinetics the area of chemistry that deals with rates of reactions

reaction rate the change in concentration of a reactant or a product of a chemical reaction per unit time

Chemical kinetics is the branch of chemistry concerned with the rates of chemical reactions. A rate is a change in a measurable quantity over time. You have already experienced how different processes can proceed at different rates. For example, during a journey by plane from Toronto to Vancouver, the speed at which you travel will be much different than if you travelled from Toronto to Montréal by train. You could calculate the average speed for both these journeys by dividing the distance by the time. Different chemical reactions also proceed from reactants to products at different rates. For example, the combustion of propane takes just a fraction of a second, while the oxidation of silver may take years. The **reaction rate** of a chemical reaction is the change in concentration of a reactant or product per unit time. How do we determine the reaction rate of a specific chemical reaction?

Measuring Reaction Rates

To determine the speed of a journey, you need to know only the distance travelled and the time it took to travel from the start to the end. This will give you the average speed during the journey. Alternatively, you could use a device such as a speedometer that records the speed you are travelling at specific moments during the journey. This latter method is more similar to how the rate of a chemical reaction is determined. For a chemical reaction, it can be difficult to know exactly when the reaction is complete. Therefore, chemists track the progress of a chemical reaction by observing the appearance of a product or disappearance of a reactant at particular time points. These observations are then used to calculate reaction rate.

We must therefore have some technique to determine the quantity of either a reactant or a product at several different times during the progress of the chemical reaction. When deciding on a method to track the progress of a reaction, chemists look for a technique that does not interfere with the reaction progress or rate, and is as simple as possible to carry out. Commonly used methods include tracking changes in gas volume, colour, mass, pH, and electrical conductivity.

For example, suppose you wanted to track the reaction of calcium metal, Ca(s), in liquid water. The balanced equation for this reaction is

$$Ca(s) + 2\ H_2O \rightarrow Ca(OH)_2(aq) + H_2(g)$$

Since this reaction forms hydrogen gas, the simplest way to track the reaction progress is to measure the quantity of hydrogen gas formed. If the reaction is carried out in a closed container, you could follow the production of hydrogen gas by measuring the changes in pressure within the reaction vessel. Using an open vessel, you could determine the volume of gas produced by forcing the gas to flow into a container filled with water, such as the tube in **Figure 1**. Gas production is then determined from the quantity of water that is displaced.

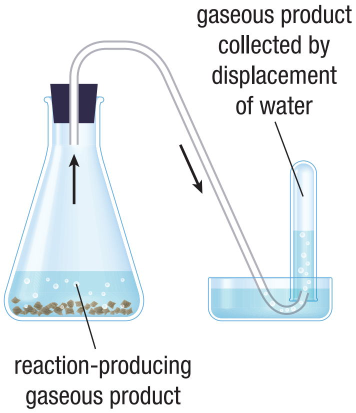


Figure 1 Some chemical reactions produce a gaseous product. For gases that are not soluble in solution, the rate of production can be measured by measuring the volume of aqueous solution displaced.

For a chemical reaction that involves a colour change, you can follow the reaction progress by measuring the change in colour intensity with a spectrophotometer. The colour of any object or substance is determined by the wavelengths of light that it absorbs. The colour you see is the remaining transmitted wavelengths. A spectrophotometer accurately detects the quantity of light absorbed at specific wavelengths. When the spectrophotometer is set up to detect changes in light absorption in the range that is absorbed by a coloured substance in a chemical reaction, the measured absorption directly correlates with changes in the quantity of that substance. For example, an aqueous solution containing only hypochlorate ions, $ClO^-(aq)$, or iodide ions, $I^-(aq)$, will be colourless. When these two solutions are combined, the hypochlorate and iodide ions react to form a coloured product, the hypoiodite ion, $IO^-(aq)$.

$$\underset{\text{colourless}}{ClO^-(aq)} + \underset{\text{colourless}}{I^-(aq)} \rightarrow \underset{\text{yellow}}{IO^-(aq)} + \underset{\text{colourless}}{Cl^-(aq)}$$

At the beginning of this reaction, there are no hypoiodite ions and the solution is clear. As the reaction progresses, the solution becomes an increasingly intense yellow colour, which directly correlates with the concentration of hypoiodite ions. By collecting spectrophotometric data at various times after the solutions are mixed, you can determine the reaction rate.

For some reactions, the reaction rate can be determined from the mass at various times during the reaction progress. This technique can be used when a gaseous substance is produced in an open vessel. As the gas escapes into the air, the mass of the vessel and its contents will decrease. Consider the reaction of solid calcium carbonate and hydrochloric acid, represented by the following equation:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CO_2(g) + H_2O(l) + CaCl_2(aq)$$

The total mass of the vessel, including the solution, reactants, and products, decreases when the carbon dioxide gas produced is allowed to escape from the vessel. By measuring the total mass at various times during the reaction, you can determine the quantity of carbon dioxide gas produced during the reaction.

UNIT TASK BOOKMARK

You can apply what you have learned about different methods of determining reaction rate to the Unit Task described on page 402.

For chemical reactions that involve a change in pH, the progress of the reaction can be observed using a pH meter, pH paper, or a pH indicator such as phenolphthalein. For example, when sulfur trioxide gas, $SO_3(g)$, is bubbled through liquid water, it forms liquid sulfuric acid, $H_2SO_4(l)$, according to the chemical equation

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

This chemical reaction contributes to acid rain, which has significant negative consequences for the environment and for some buildings and other structures. Since pH meters provide the most precise data, they are used most often for investigations of reaction rates involving pH changes. CAREER LINK

Changes in the quantities of the reactant(s) or product(s) of other chemical reactions can cause changes in conductivity (the ability to conduct an electrical current). For example, when an alkyl halide is hydrolyzed in water, the products include one or more ions. Ions are charged, so they can carry an electrical charge in solution. The following equation represents the hydrolysis of neutral molecules of 2-methyl-2-chloropropane, $(CH_3)_3CCl$, which produces hydrogen ions and chloride ions:

$$(CH_3)_3CCl(aq) + H_2O(l) \rightarrow (CH_3)_3COH(aq) + H^+(aq) + Cl^-(aq)$$

Since more ions form as the reaction progresses, the conductivity of the solution will increase over time. A conductivity meter, such as the one shown in **Figure 2**, can be used to measure the conductivity at different times.

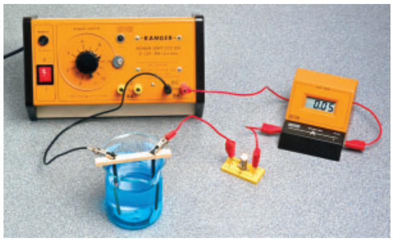


Figure 2 The rate of production of an ionic product can be measured by conductivity.

Calculating Average Reaction Rates

Collecting data on changes in the quantity of substances involved in a chemical reaction is just the first step in determining the rate of a chemical reaction. The change in concentration of a reactant or product over a specified time period is the **average reaction rate**. We can use the following equation to calculate the average rate of reaction of a reactant or product, A:

average reaction rate the change in reactant or product concentration over a given time interval

$$\text{rate}_A = \frac{\text{concentration of A at time } t_2 - \text{concentration of A at time } t_1}{t_2 - t_1}$$

In chemical notation, the symbol Δ (delta) indicates a *change* in a given quantity, and chemical symbols placed inside square brackets indicate the entity's concentration in mol/L. Using these symbols, we can rewrite the equation above as

$$\text{rate}_A = \frac{\Delta[A]}{\Delta t}$$

where [A] represents the concentration of A in mol/L, $\Delta[A]$ represents the change in the concentration of A in mol/L, and Δt represents a time interval, or change in time.

Since the concentration of a product increases with reaction progress, then Δ[A] will be positive when A is a product. However, the concentration of a reactant will decrease over time, so Δ[A] will be a negative quantity when A is a reactant. For convenience, we will always define the rate as a positive quantity, as you will see.

Consider the decomposition reaction of nitrogen dioxide, $NO_2(g)$, a brown gas that is a major contributor to smog (**Figure 3**). The following chemical equation represents the decomposition of nitrogen dioxide gas to gaseous nitric oxide, NO(g), and oxygen:

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

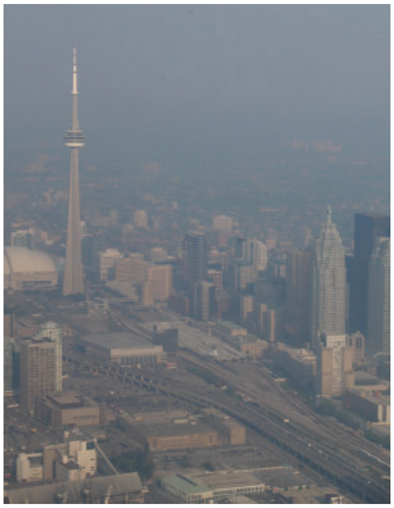


Figure 3 Nitrogen dioxide is a brown gas that can be formed from gases in tailpipe emissions. It is a major component of smog. This ground-level nitrogen dioxide gas and one of the products of its decomposition, nitric oxide gas, undergo further reactions that increase ground-level ozone, which harms humans and other living things.

Table 1 shows data collected in an investigation in which nitrogen dioxide gas was placed in a sealed flask at 300 °C. Over the 300 s time period, the concentration of the reactant, nitrogen dioxide gas, decreases with time, and the concentrations of the products, nitrogen oxide gas and oxygen gas, increase with time.

Table 1 Concentrations of Reactant and Products over Time

	Concentration (mol/L)		
Time (±1 s)	**NO_2(g)**	**NO(g)**	**O_2(g)**
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031

Let us use the data given in Table 1 to calculate the average rate at which the nitrogen dioxide gas is consumed over the first 50 s of the decomposition reaction.

$$\begin{aligned}\text{rate}_{NO_2(g)} &= \frac{\Delta[NO_2(g)]}{\Delta t} \\ &= \frac{[NO_2(g)]_{t=50\text{ s}} - [NO_2(g)]_{t=0\text{ s}}}{50\text{ s} - 0\text{ s}} \\ &= \frac{0.0079\text{ mol/L} - 0.0100\text{ mol/L}}{50\text{ s}} \\ \text{rate}_{NO_2(g)} &= -4.2 \times 10^{-5}\text{ mol/L}\cdot\text{s}\end{aligned}$$

Note that since the concentration of nitrogen dioxide gas decreases with time, $\Delta[NO_2]$ is a negative quantity. As it is customary to work with positive reaction rates, we define the rate of this particular reaction as

$$\begin{aligned}\text{rate}_{NO_2(g)} &= -\frac{\Delta[NO_2(g)]}{\Delta t} \\ &= -(-4.2 \times 10^{-5}\text{ mol/L}\cdot\text{s}) \\ &= 4.2 \times 10^{-5}\text{ mol/L}\cdot\text{s}\end{aligned}$$

Table 2 Average Rates of Disappearance of Nitrogen Dioxide Gas during Its Decomposition Reaction

Time period (±1 s)	Average reaction rate (mol/L·s)
0 to 50	4.2×10^{-5}
50 to 100	2.8×10^{-5}
100 to 150	2.0×10^{-5}
150 to 200	1.4×10^{-5}
200 to 250	1.0×10^{-5}
250 to 300	1.0×10^{-5}

The average rate for the disappearance of nitrogen dioxide gas for each 50 s interval during the decomposition reaction is given in **Table 2**. Over the same time period the rate of oxygen production is given by

$$\begin{aligned}\text{rate}_{O_2(g)} &= +\frac{\Delta[O_2(g)]}{\Delta t} \\ &= 2.2 \times 10^{-5}\text{ mol/L}\cdot\text{s}\end{aligned}$$

Note that a negative sign indicates the consumption of a reactant while a positive sign indicates the production of a product. The numerical value of the reaction rate can therefore always be a positive number.

In the chemical equation for the decomposition of nitrogen dioxide gas, both the reactant, nitrogen dioxide gas, and the product, nitric oxide gas, have the coefficient 2, so nitric oxide gas appears at the same rate that nitrogen dioxide gas is consumed. For every 2 mol of nitrogen dioxide gas that is consumed, 2 mol of nitric oxide gas appears. So, if the average rate of nitrogen dioxide gas consumption in the period 0 s to 50 s is 4.2×10^{-5} mol/L·s, then the rate of nitric oxide gas appearance over the same period must be 4.2×10^{-5} mol/L·s as well. Similarly, for every 2 mol of nitric oxide gas that appears, 1 mol of oxygen gas appears. Consequently, the rate of nitric oxide gas production will be twice that of oxygen gas. These ratios are dictated by the stoichiometry of the chemical equation.

Tutorial 1 Calculating Average Rates of Reaction

In this tutorial you will calculate average reaction rates for a specified time interval, from experimental data and stoichiometric relationships.

Sample Problem 1: Calculating Average Rate of Appearance

Using values from Table 1 calculate the average rate of appearance of nitric oxide gas over the first 50 s of the chemical reaction.

Given: From Table 1 on page 348 the measured concentrations of nitric oxide gas during the first 50 s are

Time (±1 s)	[NO(g)] (mol/L)
0	0
50	0.0021

Required: average rate of appearance of nitric oxide gas over the first 50 s

Analysis:

Since the average rate of appearance of a product will be a positive number, then

$$\text{rate}_A = \frac{\Delta[\text{A}]}{\Delta t}$$

Solution:

$$\begin{aligned}\text{rate}_\text{A} &= \frac{\Delta[\text{A}]}{\Delta t}\\ \text{rate}_{\text{NO(g)}} &= \frac{\Delta[\text{NO(g)}]}{\Delta t}\\ &= \frac{[\text{NO(g)}]_{t=50\text{ s}} - [\text{NO(g)}]_{t=0\text{ s}}}{50\text{ s} - 0\text{ s}}\\ &= \frac{0.0021\text{ mol/L} - 0\text{ mol/L}}{50\text{ s}}\\ \text{rate}_{\text{NO(g)}} &= 4.2 \times 10^{-5}\text{ mol/L·s}\end{aligned}$$

Statement: The average rate of appearance of nitric oxide gas over the first 50 s of the reaction is 4.2×10^{-5} mol/L·s.

Sample Problem 2: Calculating Average Rate of Disappearance

Using values from Table 1, calculate the average rate of disappearance of nitrogen dioxide gas over the first 100 s of the reaction.

Given: The data from Table 1 for nitric oxide gas over the first 100 s are

Time (±1 s)	[NO_2(g)] (mol/L)
0	0.0100
100	0.0065

Required: average rate of disappearance of nitrogen dioxide gas over the first 100 s

Analysis: Since the average rate of disappearance of a reactant will be a negative number, use the following equation:

$$\text{rate}_\text{A} = -\frac{\Delta[\text{A}]}{\Delta t}$$

Solution:

$$\begin{aligned}
\text{rate}_\text{A} &= -\frac{\Delta[\text{A}]}{\Delta t} \\
\text{rate}_{\text{NO}_2(\text{g})} &= -\left(\frac{\Delta[\text{NO}_2(\text{g})]}{\Delta t}\right) \\
&= -\left(\frac{[\text{NO}_2(\text{g})]_{t\,=\,100\text{ s}} - [\text{NO}_2(\text{g})]_{t\,=\,0\text{ s}}}{100\text{ s} - 0\text{ s}}\right) \\
&= -\left(\frac{0.0065\text{ mol/L} - 0.0100\text{ mol/L}}{100\text{ s}}\right) \\
&= -(-3.5 \times 10^{-5}\,\text{mol/L}\cdot\text{s}) \\
\text{rate}_{\text{NO}_2(\text{g})} &= 3.5 \times 10^{-5}\,\text{mol/L}\cdot\text{s}
\end{aligned}$$

Statement: The average rate of disappearance of nitrogen dioxide gas over the first 100 s of the reaction is 3.5×10^{-5} mol/L·s.

Practice

1. At 40 °C, hydrogen chloride gas, HCl(g), will form from the reaction of gaseous hydrogen and chlorine, according to the following balanced chemical equation:

   $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$

   Table 3 shows the data that were collected as a chemist carried out this reaction.

   Table 3 Concentrations of Reactants and Products at Specific Time Points and Average Concentrations over Specific Time Periods

	Concentration (mol/L)		
Time (s)	**$H_2(g)$**	**$Cl_2(g)$**	**HCl(g)**
0	1.000	1.000	0.000
2.16	0.500	0.500	1.000
4.32	0.250	0.250	1.500

   Using the data provided, calculate the following average rates: T/I

   (a) disappearance of hydrogen gas in the first 2.16 s of the reaction
   [ans: 0.231 mol/L·s]

   (b) appearance of hydrogen chloride gas in the first 4.32 s of the reaction
   [ans: 0.347 mol/L·s]

   (c) disappearance of chlorine gas between 2.16 s and 4.32 s
   [ans: 0.116 mol·s/]

   (d) disappearance of hydrogen gas in the first 4.32 s
   [ans: 0.174 mol/L·s]

Determining the Average Reaction Rate Using Graphical Data

Another way to determine the average rate of a reaction is by using data plotted on a graph. First, be sure you recall these math terms. A secant line is a line that intersects two points on a curve. The slope of a line is a measure of how steep the line is relative to the horizontal axis, calculated from the following expression:

$$\frac{\Delta y}{\Delta x} \text{ (rise over run)}$$

Figure 4 is a graph of the concentration of a reactant, A, versus time. The average rate of the reaction between two time points, t_1 and t_2, is equal to the slope of the secant line drawn between points t_1 and t_2 on the x-axis of the graph:

$$\text{rate}_\text{A} = -\frac{\Delta[\text{A}]}{\Delta t} \quad \text{or} \quad -\frac{\Delta y \text{ (concentration)}}{\Delta x \text{ (time)}}$$

where Δy and Δx are read from the values on the y-axis and the x-axis, respectively.

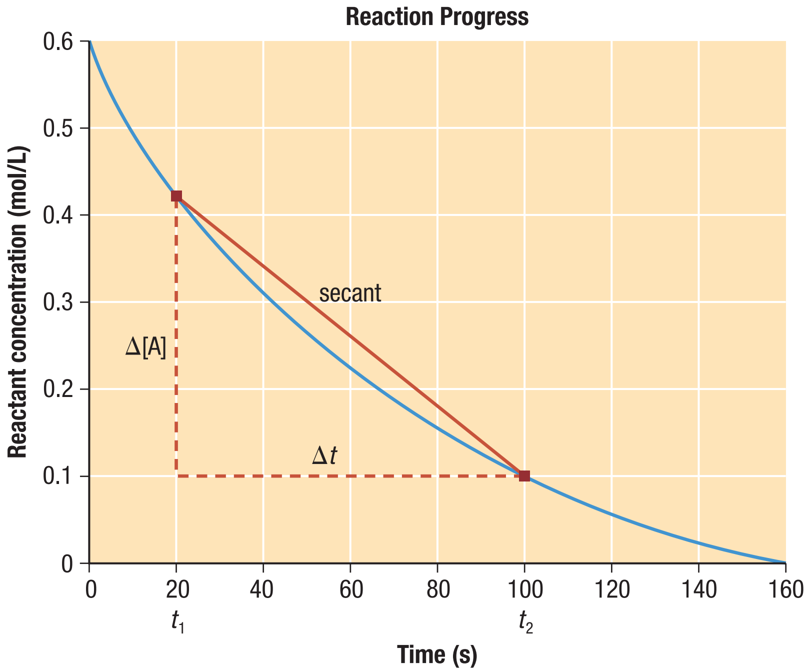


Figure 4 Concentration of a reactant, A, plotted as a function of time. The average rate of disappearance of the reactant from point t_1 to point t_2 is the slope of the secant line.

Since the reaction rate changes with time and the rate may be different depending on which reactant or product is being studied, you must be very specific when describing a rate for a chemical reaction. As you can see in **Figure 5** on the next page, plotting the concentration of a reactant—in this case, nitrogen dioxide, $NO_2(g)$—against time gives a falling curve with a steadily decreasing negative slope. If you plot data for the concentration of a product against time, the result is a rising curve with a steadily decreasing positive slope. Notice also that the curve for the concentration of the product, nitric oxide gas, NO(g), has the same shape as the curve for the concentration of nitrogen dioxide gas, except that it is inverted. Therefore, for any given time period, the slope of the secant to the curve for the concentration of nitric oxide gas will be the negative of the slope of the secant to the curve for the concentration of nitrogen dioxide gas. If you take the absolute values of these two slopes, you see that the consumption of nitrogen dioxide gas has the same average reaction rate as the formation of nitric oxide gas. You will analyze Figure 5 further in Tutorial 2.

UNIT TASK BOOKMARK

You will use your knowledge of calculating reaction rates in the Unit Task on page 402.

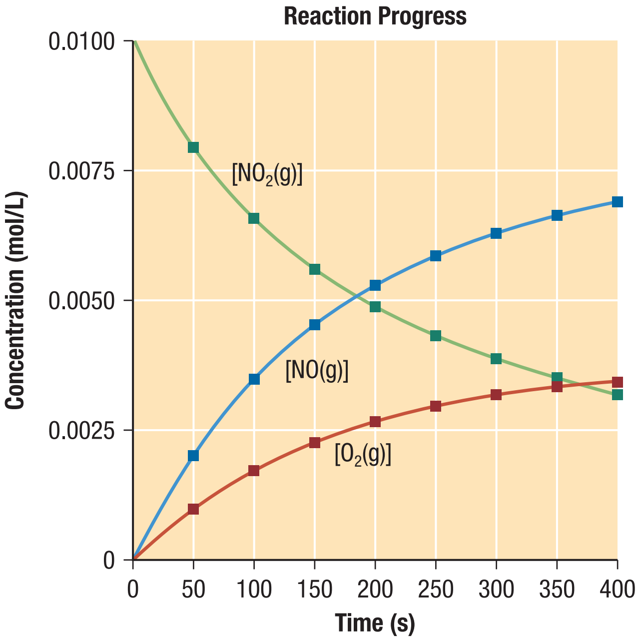


Figure 5 A sealed flask containing nitrogen dioxide gas was maintained at 300 °C. The concentrations of gaseous nitrogen dioxide, nitric oxide, and oxygen were determined every 50 s. These data were then graphed.

Tutorial 2 Determining the Average Rate of Reaction Using a Graph

In this tutorial, you will analyze the graph in Figure 5 to determine average reaction rates.

Sample Problem 1: Average Reaction Rate for the Appearance of a Product

Use Figure 5 to determine the average reaction rate for the production of oxygen gas between 180 s and 320 s.

Solution

Step 1. Since the concentrations of oxygen gas at 180 s and 320 s were not measured, they must be interpolated from the graph in Figure 5. From the graph, you may interpolate that the concentration of oxygen gas at 180 s is 0.0025 mol/L and at 320 s is 0.0031 mol/L.

Step 2. You now need to calculate the slope of the secant line, as was shown previously in Figure 4. The slope of this line is, by definition, the average rate of reaction.

$$\text{rate} = \frac{\Delta y \text{ (concentration)}}{\Delta x \text{ (time)}}$$

Therefore, the average reaction rate for the appearance of oxygen gas over the required time period is

$$\begin{aligned}\text{rate}_{O_2(g)} &= \frac{\Delta y}{\Delta x}\\ &= \frac{0.0031 \text{ mol/L} - 0.0025 \text{ mol/L}}{320 \text{ s} - 180 \text{ s}}\\ \text{rate}_{O_2(g)} &= 4.3 \times 10^{-6} \text{ mol/L·s}\end{aligned}$$

Statement: The average rate of reaction for the appearance of oxygen gas between 180 s and 320 s under the conditions of Figure 5 is 4.3×10^{-6} mol/L·s.

Practice

1. Hydrogen peroxide in aqueous solution, $H_2O_2(aq)$, will decompose to produce oxygen gas and water. Use **Figure 6** to calculate the average reaction rate for the appearance of oxygen gas between 5 s and 10 s. T/I C

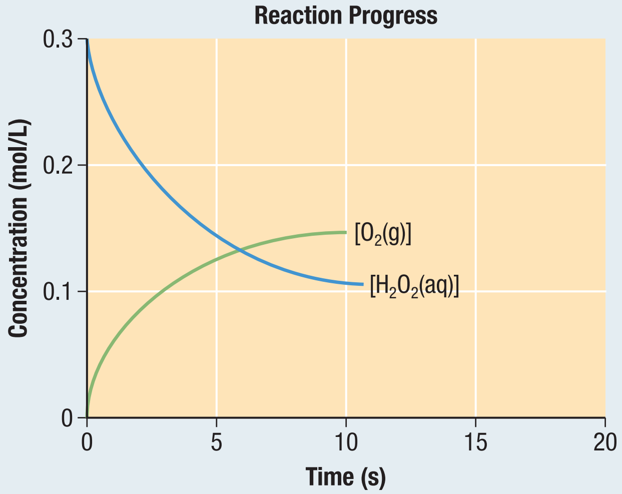


Figure 6 Change in the concentration of aqueous hydrogen peroxide and oxygen gas over time

Instantaneous Rate of Reaction

In Tutorial 2, you interpolated information from a graph of concentration versus time to determine the average rate of a reaction for a time period of interest. Alternatively, you may use such a graph to determine the rate of reaction at any single instant in time, a value known as the **instantaneous reaction rate**. Consider the graph of concentration versus time in **Figure 7**. The instantaneous rate at any time *t* is equal to the slope of the tangent to the curve at that particular instant in time. A tangent is a straight line that touches a curve at a single point and does not cross through the curve. To draw a tangent to a curve reasonably accurately, use a graphing calculator.

instantaneous reaction rate the rate of a chemical reaction at a single point in time

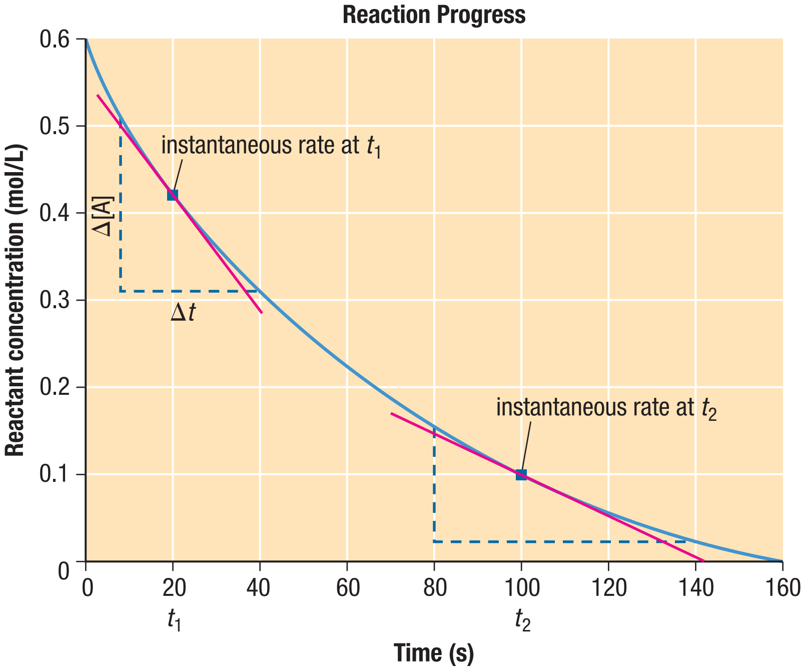


Figure 7 The instantaneous rates of reaction are given by the slopes of the tangents at the specific times of interest, in this case, t_1 and t_2.

To compare the reaction rates at the two points t_1 and t_2 in Figure 7, you can draw a line tangent to the curve at each point and calculate the slope of each tangent.

The tangent line at $t_1 = 20$ s decreases approximately 0.2 mol/L for each 32 s, so the instantaneous rate at this time is

$$\begin{aligned}
\text{rate}_{\text{instantaneous at } t_1 - 20\text{ s}} &= -\frac{\Delta y}{\Delta x} \text{ at 20 s} \\
&= -\frac{-0.2\text{mol/L}}{32\text{ s}} \\
\text{rate}_{\text{instantaneous at } t_1 = 20\text{ s}} &= 6 \times 10^{-3}\text{ mol/L} \cdot \text{s}
\end{aligned}$$

For t_2, the tangent line decreases approximately 0.15 mol/L for each 60 s, so the instantaneous rate at this time is

$$\begin{aligned}
\text{rate}_{\text{instantaneous at } t_2 = 100\text{ s}} &= -\frac{\Delta y}{\Delta x} \text{ at 100 s} \\
&= -\frac{-0.15\text{ mol/L}}{60\text{ s}} \\
\text{rate}_{\text{instantaneous at } t_2 = 100\text{ s}} &= 2.0 \times 10^{-3}\text{mol/L} \cdot \text{s}
\end{aligned}$$

The slope of the graph in Figure 7 is approximately twice as steep at t_1 as at t_2. This means that the rate of disappearance of the reactant is approximately twice as fast at t_1 as at t_2.

Investigation **6.1.1**

Reaction Rates (page 390)
Now that you have learned some methods for calculating reaction rates, you are ready to apply these skills to measure the rate of change in the concentration of a reactant over time.

Tutorial **3** Slope and Instantaneous Rate

In this tutorial, you will determine instantaneous rates of reaction from graphical data, using tangents to a curve.

Sample Problem 1: Instantaneous Rate of Appearance

Using **Figure 8**, calculate the instantaneous rate of appearance of oxygen gas at 250 s during the decomposition of nitrogen dioxide gas, $NO_2(g)$, as represented by the following balanced chemical equation:

$$2\,NO_2(g) \longrightarrow 2\,NO(g) + O_2(g)$$

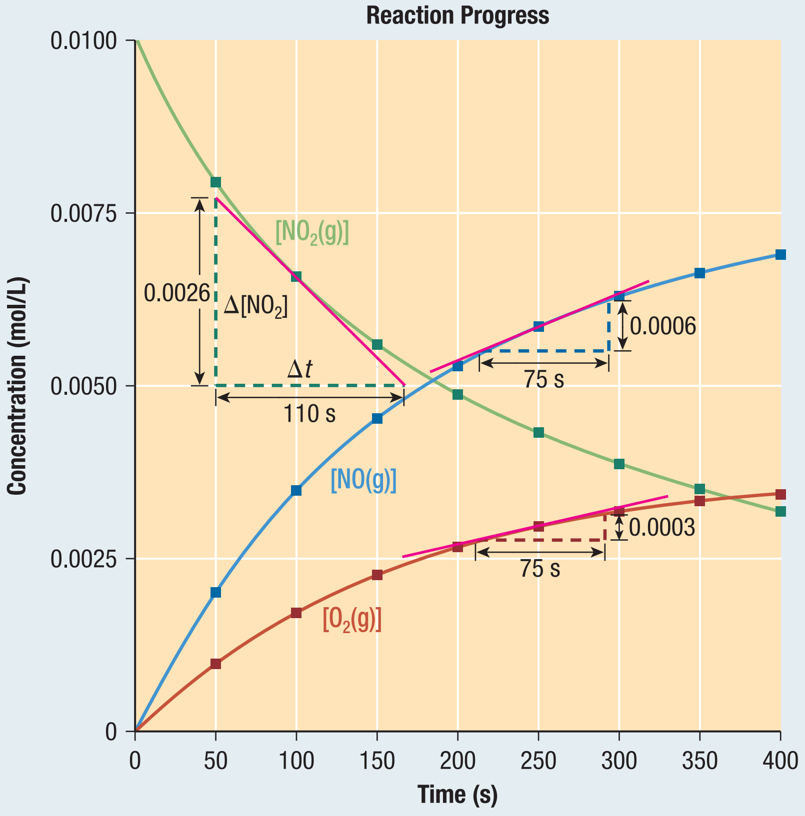


Figure 8 Concentrations of products and reactants in the decomposition reaction of nitrogen dioxide gas as a function of time

Solution

Identify the line in Figure 8 that is tangent to the oxygen gas concentration curve at 250 s. This tangent line is the hypotenuse of a right triangle; Δy is the change in concentration, $\Delta[O_2(g)]_{t\,=\,250\text{ s}}$, given as 0.0003 mol/L; and Δx is the change in time, Δt, of 75 s.

Substitute these values for Δy and Δx in the slope formula to get the instantaneous rate of appearance of oxygen gas at 250 s.

$$\begin{aligned}
\text{rate}_{\text{instantaneous at } t\,=\,250\text{ s}} &= \text{slope of the tangent line at 250 s} \\
&= \frac{\Delta y}{\Delta x} \text{ at 250 s} \\
&= \frac{\Delta[O_2(g)]_{t\,=\,250\text{ s}}}{\Delta t} \\
&= \frac{0.0003\text{ mol/L}}{75\text{ s}} \\
\text{rate}_{\text{instantaneous at } t\,=\,250\text{ s}} &= 4 \times 10^{-6}\text{ mol/L·s}
\end{aligned}$$

Statement: The instantaneous rate of appearance of oxygen gas at 250 s is 4×10^{-6} mol/L·s.

Sample Problem 2: Instantaneous Rate of Disappearance

Using Figure 8, determine the instantaneous rate of disappearance at 100 s of nitrogen dioxide gas for the chemical reaction represented by the following balanced chemical equation:

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

Solution

Identify the line in Figure 8 that is tangent to the nitrogen dioxide gas concentration curve at 100 s. This tangent line is the hypotenuse of a right triangle; Δy is the change in concentration, $\Delta[NO_2(g)]_{t\,=\,100\text{ s}}$, given as 0.0026 mol/L; and Δx is the change in time, Δt, of 110 s.

Substitute these values for Δy and Δx in the slope formula to get the instantaneous rate of disappearance of nitrogen dioxygen gas at 100 s.

$$\begin{aligned}
\text{rate}_{\text{instantaneous at } t\,=\,100\text{ s}} &= \text{slope of the tangent line at 100 s} \\
&= -\frac{\Delta y}{\Delta x} \text{ at 100 s} \\
&= -\frac{\Delta[NO_2(g)]_{t\,=\,100\text{ s}}}{\Delta t} \\
&= -\frac{-0.0026\text{ mol/L}}{110\text{ s}} \\
\text{rate}_{\text{instantaneous at } t\,=\,100\text{ s}} &= 2.4 \times 10^{-5}\text{ mol/L·s}
\end{aligned}$$

Statement: The instantaneous rate of disappearance of nitrogen dioxide gas at 100 s is 2.4×10^{-5} mol/L·s.

Sample Problem 3: Comparing Instantaneous Rates of Reaction

Using the graph of concentration versus time for the decomposition of nitrogen dioxide gas shown in **Figure 9**, determine whether the rate of appearance of nitric oxide gas is fastest at 100 s, 200 s, or 350 s. Tangent lines to the curve for nitrogen dioxide gas decomposition at these points are shown in pink.

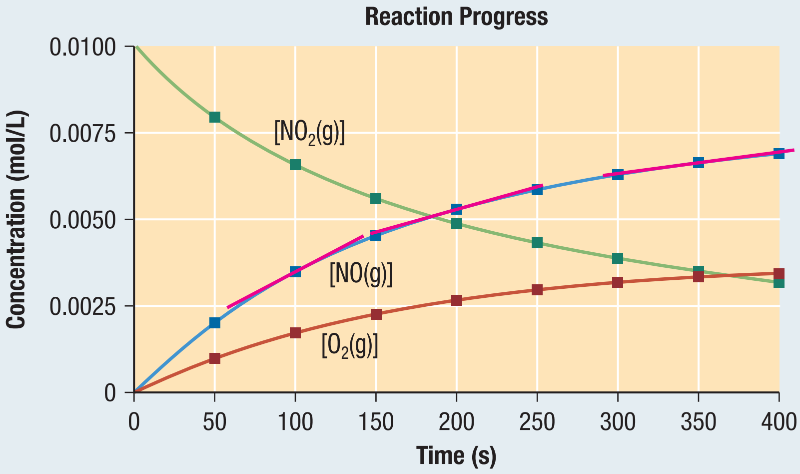


Figure 9 Concentration versus time graph for the decomposition of $NO_2(g)$

Solution

Compare the relative slopes of the tangent lines at 100 s, 200 s, and 350 s on the nitric oxide concentration curve in Figure 9. Since the slope corresponds to the rate, you know that the tangent line with the steepest slope represents the fastest instantaneous rate. Therefore, at 100 s, the instantaneous rate of appearance of nitric oxide gas is fastest, because the slope of the tangent at this point is the greatest.

Statement: For the decomposition reaction of nitrogen dioxide gas illustrated in Figure 9, the instantaneous rate of appearance of nitric oxide gas is fastest at 100 s, in comparison to the instantaneous rates at 200 s and at 350 s.

Practice

1. Using the data from **Figure 10**, calculate the instantaneous rate of appearance of oxygen gas at 4 s for the decomposition of hydrogen peroxide represented by the equation
   $2\ H_2O_2\,(aq) \rightarrow 2\ H_2O(l) + O_2(g)$ T/I C

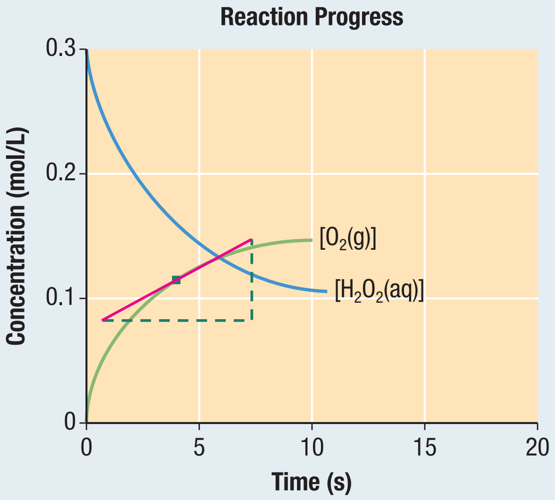


Figure 10 Concentration versus time graph for the decomposition of $H_2O_2(g)$

2. An investigation was conducted to determine the rate of reaction between 100 mL of 1.0 mol/L nitric acid, $HNO_3(aq)$, and a sample of magnesium ribbon, Mg(s), represented by this balanced chemical equation:

   $2\ HNO_3(aq) + Mg(s) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$

   The volume of hydrogen gas released was measured at 30 s intervals, and is given in **Table 4**. T/I C

   (a) Graph the volume of hydrogen gas released (*y*-axis) versus time (*x*-axis).

   (b) Calculate the instantaneous rate at 60 s, 150 s, and 210 s. [ans: 60s: 5×10^{-2} mL/s, 150 s: 0.03 mL/s, 210 s: 0 mL/s]

   (c) Is the rate of the appearance of hydrogen gas faster at 60 s or 200 s? Explain how you know, referring to your graph. [ans: 60 s]

Table 4 Volume of Hydrogen Gas Released at 30 s Intervals

Time (s)	Hydrogen gas released (mL)
0	0
30	2.0
60	3.7
90	5.2
120	6.4
150	7.3
180	8.6
210	8.6

Stoichiometric Rate Relationships

When we measure reaction rates from a graph, we often describe them using a notation that represents the negative slope of the reactant graph and the positive slope of the product graph, and allows the numerical value of the rate to be an absolute value. To do this, you use a negative (−) sign to indicate a rate of consumption of reactant and a positive (+) sign to indicate a rate of formation of product. For example, the reaction rate for the decomposition of nitrogen dioxide gas could be represented by any of these expressions:

$$-\frac{\Delta[NO_2(g)]}{\Delta t} = x\ \mathrm{mol/L{\cdot}s}$$

$$\text{or}\quad +\frac{\Delta[NO(g)]}{\Delta t} = x\ \mathrm{mol/L{\cdot}s}$$

$$\text{or}\quad +\frac{\Delta[O_2(g)]}{\Delta t} = x\ \mathrm{mol/L{\cdot}s}$$

Since nitrogen dioxide is a reactant and so is consumed, the slope of a graph of its concentration versus time will be negative.

The decomposition of nitrogen dioxide gas is represented by the following balanced chemical equation:

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

From the stoichiometry of the balanced chemical equation, the information about the rate of this reaction (the stoichiometric rate relationship) can be summarized as follows:

$$\begin{aligned}\frac{1}{2}(\text{rate of consumption } NO_2(g)) &= \frac{1}{2}(\text{rate of appearance of } NO(g))\\ &= \text{rate of appearance of } O_2(g)\end{aligned}$$

or

$$\begin{aligned}\frac{1}{2}\left(-\frac{\Delta[NO_2(g)]}{\Delta t}\right) &= \frac{1}{2}\left(\frac{\Delta[NO(g)]}{\Delta t}\right)\\ &= \frac{\Delta[O_2(g)]}{\Delta t}\end{aligned}$$

LEARNING **TIP**

Reaction Rates and Absolute Value

Note that a negative (−) sign indicates a rate of consumption of reactant and positive (+) sign indicates a rate of production of product. The numerical value *x* can therefore be an absolute value.

Notice that the coefficients of the balanced chemical equation must appear in the denominator of the coefficients of the rates to make the rates equal. These stoichiometric rate relationships apply to instantaneous reaction rates as well as to average rates of reaction. For example, in Sample Problem 1 of Tutorial 3, you calculated the instantaneous rate of oxygen gas appearance at 250 s as

$$\text{Slope of the tangent to the oxygen gas concentration curve at 250 s} = \frac{0.00030\ \text{mol/L}}{75\ \text{s}}$$
$$= 4.0 \times 10^{-6}\ \text{mol/L·s}$$

The corresponding tangent line for the nitric oxide gas concentration curve (shown in Figure 8 on page 354) indicates a change in nitric oxide gas concentration of 0.00060 mol/L at the same instant in time. The instantaneous rate for nitric oxide gas production at 250 s is therefore

$$\text{Slope of the tangent to the nitric oxide gas concentration curve at 250 s} = \frac{0.00060\ \text{mol/L}}{75\ \text{s}}$$
$$= 8.0 \times 10^{-6}\ \text{mol/L·s}$$

The slope of the tangent line at t = 250 s on the oxygen gas concentration curve is half the slope of the tangent line at t = 250 s on the nitric oxide gas concentration curve. Therefore, you can conclude that at 250 s, the rate of appearance of oxygen gas is half that of nitric oxide gas.

Tutorial 4 Calculating Rates Using Stoichiometry

In this tutorial, you will apply the stoichiometric information given in a balanced equation to calculate average and instantaneous rates of reaction.

Sample Problem 1: Writing a Stoichiometric Rate Relationship

Write the stoichiometric rate relationship between products and reactants for the decomposition of dinitrogen pentoxide gas, $N_2O_5(g)$, into gaseous nitrogen dioxide and oxygen. This reaction is represented by the following balanced chemical equation:

$$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$$

Solution

Scale the expressions for the rates of consumption of the reactant and appearance of the products by the inverse of their coefficients in the balanced chemical equation.

$$\begin{aligned}\frac{1}{2}(\text{rate of consumption of } N_2O_5(g)) &= \frac{1}{4}(\text{rate of appearance of } NO_2(g))\\ &= \text{rate of appearance of } O_2(g)\\ &= \frac{1}{2}\left(-\frac{\Delta[N_2O_5(g)]}{\Delta t}\right)\\ &= \frac{1}{4}\left(\frac{\Delta[NO_2(g)]}{\Delta t}\right)\\ &= \frac{\Delta[O_2(g)]}{\Delta t}\end{aligned}$$

Statement: The stoichiometric rate relationship between products and reactants for the decomposition of dinitrogen pentoxide gas, $N_2O_5(g)$, into gaseous nitrogen dioxide and oxygen is

$$-\frac{1}{2}\left(\frac{\Delta[N_2O_5(g)]}{\Delta t}\right) = \frac{1}{4}\left(\frac{\Delta[NO_2(g)]}{\Delta t}\right)$$

$$= \frac{\Delta[O_2(g)]}{\Delta t}.$$

Sample Problem 2: Using Stoichiometry to Calculate Instantaneous Rates

For the chemical reaction represented by the equation
$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$

(a) If the rate of disappearance of $N_2O_5(g)$ is 5.6×10^{-2} mol/L·s at 60 s, determine the rate of appearance of oxygen at this same point in time.

(b) Calculate the rate of appearance of $NO_2(g)$ at 90 s if the rate of appearance of oxygen at this time is 2.0×10^{-2} mol/L·s.

Given: (a) rate of disappearance of $N_2O_5(g)$ at 60 s,

$$\frac{\Delta[N_2O_5(g)]_{t=60\,\text{s}}}{\Delta t} = 5.6 \times 10^{-2}\ \text{mol/L}$$

(b) rate of appearance of $O_2(g)$ at 90 s,

$$\frac{\Delta[O_2(g)]_{t=90\,\text{s}}}{\Delta t} = 2.0 \times 10^{-2}\text{mol/L}$$

Required: (a) rate of appearance of $O_2(g)$ at 60 s

(b) rate of appearance of $NO_2(g)$ at 90 s

Analysis: Scale the rates by the inverse of their coefficients in the balanced chemical equation. Then, substitute the given rates and solve for the required rates.

Solution:

$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$

$$\frac{1}{2}\left(-\frac{\Delta[N_2O_5(g)]}{\Delta t}\right) = \frac{1}{4}\left(\frac{\Delta[NO_2(g)]}{\Delta t}\right)$$

$$= \frac{\Delta[O_2(g)]}{\Delta t}$$

(a) For this part, only the rate expressions for $O_2(g)$ and $N_2O_5(g)$ are needed. Substitute the rate given for $N_2O_5(g)$ and solve for the $O_2(g)$ rate.

$$\frac{\Delta[O_2(g)]}{\Delta t} = \frac{1}{2}\left(-\frac{\Delta[N_2O_5(g)]}{\Delta t}\right)$$

$$= \frac{1}{2}(5.6 \times 10^{-2}\ \text{mol/L·s})$$

$$= 2.8 \times 10^{-2}\ \text{mol/L·s}$$

(b) For the appearance of $NO_2(g)$ at time 90 s, only the $O_2(g)$ and $NO_2(g)$ rate expressions are needed. Substitute the value given for the $O_2(g)$ rate and solve for the NO_2 rate.

$$\begin{aligned}\frac{1}{4}\left(\frac{\Delta[\mathrm{NO_2(g)}]}{\Delta t}\right) &= \frac{\Delta[\mathrm{O_2(g)}]}{\Delta t}\\ \frac{\Delta[\mathrm{NO_2(g)}]}{\Delta t} &= 4\left(\frac{\Delta[\mathrm{O_2(g)}]}{\Delta t}\right)\\ &= 4(2.0 \times 10^{-2}\ \mathrm{mol/L{\cdot}s})\\ &= 8.0 \times 10^{-2}\ \mathrm{mol/L{\cdot}s}\end{aligned}$$

Statement: (a) The rate of appearance of $O_2(g)$ at 60 s is 2.8×10^{-2} mol/L·s.

(b) The rate of appearance of $NO_2(g)$ at 90 s is 8.0×10^{-2} mol/L·s.

Practice

1. The formation of ammonia gas from its elements is represented by the following balanced chemical equation:

   $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ T/I

   Determine the stoichiometric rate relationship between the rate of consumption and the rate of appearance of
   (a) hydrogen gas and ammonia gas [ans: 3:2]
   (b) nitrogen gas and hydrogen gas [ans: 1:3]
   (c) nitrogen gas and ammonia gas [ans: 1:2]

2. Ammonia gas and oxygen gas react to form nitric oxide, NO(g), and water vapour according to the following balanced chemical equation:

   $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$

   Assuming that the instantaneous rate of consumption of ammonia gas is 1.8×10^{-2} mol/L·s, determine the instantaneous rate of
   (a) oxygen gas consumption [ans: 2.2×10^{-2} mol/L·s]
   (b) water vapour appearance T/I [ans: 2.7×10^{-2} mol/L·s]

3. Consider the general chemical reaction represented by the equation $aA + bB \rightarrow cC$.

   The rate relationship formula for this reaction is

   $$\begin{aligned}\frac{1}{a}\left(-\frac{\Delta A}{\Delta t}\right) &= \frac{1}{b}\left(-\frac{\Delta B}{\Delta t}\right)\\ &= \frac{1}{c}\left(\frac{\Delta C}{\Delta t}\right)\end{aligned}$$

   where *a*, *b*, and *c*, are the coefficients from the balanced chemical equation. Use this formula to determine the values of coefficients *a*, *b*, and *c*, given the following average rate data:

   $\Delta A/\Delta t = 0.0080\ \mathrm{mol/L{\cdot}s}$; $\Delta B/\Delta t = 0.0120\ \mathrm{mol/L{\cdot}s}$; $\Delta C/\Delta t = 0.0160\ \mathrm{mol/L{\cdot}s}$.

   T/I [ans: $a = 2$, $b = 3$, $c = 4$]

6.1 Review

Summary

- To determine the rates of chemical reactions, chemists may monitor changes in pressure, volume, colour, mass, pH, or conductivity.
- Reaction rates are not constant; they change as the reaction proceeds.
- The average rate of reaction is the change in concentration of a reactant or product over a specified time period.
- The instantaneous reaction rate is the rate of a chemical reaction at one specific instant.
- By convention, reaction rates are always expressed as positive values.
- For any chemical reaction, the reaction rate can be expressed in terms of any reactant or product, and all of these rates are related by the stoichiometric relationships found in the balanced chemical equation.

Questions

1. Solid phosphorus and oxygen gas react to form solid tetraphosphorus decoxide, $P_4O_{10}(s)$. Determine the average rate of reaction for oxygen gas during the first 40 s if the concentration of oxygen changes from 0.200 mol/L to 0.000 mol/L during this time interval. T/I
2. The chemical reaction represented by the following balanced chemical equation takes place in aqueous solution:

   $$MnO_4^-(aq) + 5\ Fe^{2+}(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$$

   When the disappearance of the permanganate ion, $MnO_4^-(aq)$, is monitored, the rate of reaction for the consumption of the permanganate ion is calculated as 4.0×10^{-2} mol/L·s. Calculate the reaction rate and express it with respect to each of the other reactants and the products in the reaction. T/I
3. Gaseous ammonia and oxygen can react as shown by the following balanced chemical equation:

   $$4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$$

   The instantaneous rate of consumption of ammonia gas is 2.0×10^{-2} mol/L·s at 10 s. T/I
   (a) Determine the instantaneous rate of
      (i) consumption of oxygen gas at 10 s
      (ii) appearance of water vapour at 10 s
   (b) Explain the relationship between the instantaneous rates of ammonia gas consumption and nitrogen monoxide gas appearance in the reaction.
4. Nitric oxide gas reacts with oxygen gas to form nitrogen dioxide gas according to the following balanced chemical equation:

   $$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

   The rate of the reaction with respect to oxygen gas consumption is

   $$\text{rate} = -\frac{\Delta[O_2]}{\Delta t} = 2.0 \times 10^{-3} \text{mol/L} \cdot \text{s}$$

   (a) Express the rate of the reaction with respect to nitrogen dioxide gas formation, and then calculate the rate.
   (b) Explain why the rates have different signs. T/I
5. One mole of aqueous sulfuric acid, $H_2SO_4(aq)$, reacts with 2 mol of aqueous sodium hydrogen carbonate, $NaHCO_3(aq)$, in an acid–base reaction. T/I
   (a) Write a balanced chemical equation for this reaction.
   (b) If 0.038 mol sodium hydrogen carbonate reacts in 20 s, calculate the average reaction rate as
      (i) grams of sodium hydrogen carbonate consumed per second
      (ii) moles of sulfuric acid consumed per second
      (iii) moles of carbon dioxide gas formed per second

6.2 Factors Affecting Reaction Rates

Figure 1 Small shavings of wood ignite more easily and burn much faster than a large log with much less surface area.

In the previous section, you learned how to determine average reaction rates and instantaneous reaction rates. When chemists study reaction rates, they carefully describe the conditions under which the reaction takes place. This is because there are many factors that can affect the rate of a chemical reaction, such as the chemical and physical characteristics of the reactant(s), the concentration of the reactant(s), and the temperature at which the reaction takes place. In some cases, the presence of a substance that is not directly involved in the reaction itself can alter the rate of a chemical reaction.

You have probably observed the effect of some of these factors in your daily life. For example, you have likely started a campfire or a fire in a wood-burning stove or fireplace at some point. A wood fire is actually a series of combustion reactions occurring at once. Wood is a complex substance made up of a number of different chemicals, each of which will burn at a different rate. The reactants in a wood fire are oxygen gas and gaseous substances released from wood. It is very difficult to light a fire if you start with a large log. Instead, you usually start with small bits of wood, known as kindling, and maybe some paper. The first combustion reaction occurs when you strike a match or light a lighter. This flame is applied to the kindling, heating it. When the kindling has reached a high enough temperature, some of the chemicals on the surface of the wood enter the gas phase, mix with oxygen in the air, and then begin to burn (**Figure 1**). As more kindling begins to burn, the temperature rises, which increases the rates of the combustion reactions. At some point, the fire will be hot enough that larger pieces of wood will burn readily. You may also change the rate of the combustion reaction if you adjust the position of the logs or blow on the fire. These actions increase the concentration of oxygen that is in contact with the surface of the wood.

Chemical Nature of the Reactants

The chemical nature of a pure substance gives it its chemical properties. A chemical property relates to the behaviour of a pure substance when it undergoes a chemical change or reaction. The tendency of a substance to undergo chemical reactions, such as combustion or oxidation reactions, is an example of a chemical property. The chemical properties of a substance can profoundly affect the reaction rate, as we can see by considering oxidation reactions and the metal elements. Some metals, such as sodium and potassium, are very reactive and react with oxygen (and other substances) so quickly that they are never found naturally in their elemental state. Other metals, such as platinum, gold, and silver, are generally unreactive and so oxidation occurs very slowly (**Figure 2**). This makes these metals ideal for use in jewellery and electronics.

Figure 2 (a) Sodium reacts quickly with oxygen and must be stored covered with mineral oil to avoid exposure to the air. (b) Copper reacts slowly with atmospheric oxygen, forming a layer of brown-black copper oxide. (c) Gold does not oxidize at room temperature—it is resistant to oxidation up to its melting point of 1064 °C.

Concentration of Reactants

You may have seen signs in hospitals warning about smoking or using flames where oxygen gas is in use. Why do you think that is? Oxygen makes up about 20 % of air, but the cylinders of compressed gas used to supply oxygen to patients can be 50 % oxygen gas or higher. These higher concentrations of oxygen gas cause combustion reactions to be rapid, violent, and even explosive.

The rate of many chemical reactions increases at higher concentrations of reactants. Zinc metal will produce zinc chloride and hydrogen gas when placed in a solution of hydrochloric acid (**Figure 3**):

$$Zn(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Suppose you conducted an investigation in which you placed the same mass of zinc metal in increasingly concentrated solutions of hydrochloric acid. You would observe that the reaction rate was slow in dilute solutions of hydrochloric acid, where the concentration of this reactant was low. As the concentration of acid increased, so would the reaction rate.

Figure 3 In the reaction between zinc metal and hydrochloric acid, the rate of hydrogen gas formation will increase with the concentration of hydrochloric acid.

Surface Area

The rate of the chemical reaction between zinc metal and hydrochloric acid shown in Figure 3 could also be changed by modifying the zinc to expose more surface area. You could do this by cutting the mass into as many small pieces as possible. Similarly, 1 g of sugar will dissolve in water more quickly if added as powdered sugar than as sugar cubes. Notice that, in both of these examples, the reactants are in different states of matter (solid and liquid). For any reaction in which the reactants are in more than one state of matter, the greater the surface area of the solid, the faster the reaction rate. Since only the atoms or ions at the surface of a solid reactant can interact with other reactants, increasing the surface area of a solid reactant in effect increases its concentration. This is the main reason why kindling lights more quickly than a log. The rate of combustion of fine flour dust can be so rapid that it has caused explosions at flour mills. Workplaces that create fine particles such as flour dust are required to keep the dust under control for the safety of their workers. CAREER LINK

Investigation **6.2.1**

Factors Affecting the Rate of Chemical Reactions (page 391)

Now that you have learned about the factors that may affect the rate of a chemical reaction, you will select a reaction to investigate and then evaluate factors that may increase the reaction rate.

Temperature of the Reaction System

In general, the rate of a chemical reaction increases with the temperature at which it is carried out. Chemists have found that the rates of many reactions double for every 10 °C increase in temperature and are halved for every 10 °C decrease. If you mix a bowl of cake batter and leave it sitting on the counter at room temperature for an hour, very little will change. However, if you put the batter in the oven at 175 °C for that same period of time, chemical reactions will occur within the batter that result in a baked cake. Alternatively, you store perishable food in the refrigerator to slow down chemical reactions that will cause the food to spoil (including the chemical reactions that support the growth of micro-organisms). Many packages of medications contain directions for storage in cool places away from heat sources for the same reason.

Cold-blooded animals such as amphibians and reptiles take on the temperature of their surroundings. They are less active during cool nights than warm days because their metabolic rates, or rates at which their bodies use energy, decrease as they lose thermal energy. The infrared image in **Figure 4** shows a cold-blooded animal, a snake, that is at the same cool temperature as its surroundings. This appears as dark blue to black on the infrared image. In contrast, the warm-blooded mouse that it is eating is at much higher temperature than the surroundings, so it appears bright yellow to orange.

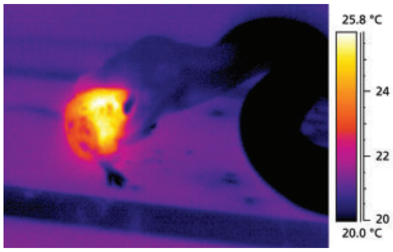


Figure 4 Notice the difference between the temperature of the mouse and the snake that is eating it. In contrast to warm-blooded animals, which maintain and regulate their own body temperature, cold-blooded animals cool down when the temperature of the surroundings drops. This lowers the rates of the chemical reactions that control muscle activity, causing the animal to become less active.

Presence of a Catalyst

catalyst a substance that alters the rate of a chemical reaction without itself being permanently changed

UNIT TASK BOOKMARK

As you work on your Unit Task on page 402, consider all the different factors that can affect reaction rate.

A **catalyst** is a substance that changes the rate of a chemical reaction but remains unchanged during the reaction. Thus, a catalyst can participate in the same reaction over and over again. Often only very small amounts of a catalyst are needed to increase the rate of a reaction.

Many industrial processes involve catalysts. For example, polyethene (also called polyethylene) is a polymer made by passing ethene gas over a metal catalyst. The metal catalyst speeds up the addition reaction that opens the double bond of ethene, allowing ethene molecules to join to make polyethene. Polyethene is used to make many things we use every day, including garbage bags, plastic wrap, squeeze bottles, and insulation for cables. Most other polymers, including synthetic rubber, nylon, polyester, PVC, and Teflon, are also made with the help of metal catalysts. Metal catalysts are used in the catalytic converters in vehicle exhaust systems that are used to reduce harmful pollution (**Figure 5**). They increase the rate at which exhaust gases react with oxygen so that more of the exhaust products will be oxidized into harmless or less harmful substances. Highly toxic carbon monoxide gas is oxidized to carbon dioxide, for example.

biological catalyst a catalyst made by a living system

Most biological reactions rely on catalysts to allow them to proceed at high rates under moderate temperature. Catalysts produced by living organisms are called **biological catalysts** or biocatalysts. Most biological catalysts are large protein molecules called enzymes.

Enzymes control most of the processes in living cells, so they are very important to health. For example, lactase is an enzyme which aids in the digestion of lactose, a sugar found in milk. Babies often have high amounts of lactase, while adults have much less. Someone with little or no lactase is lactose intolerant and has difficulty digesting milk.

Many industrial processes, including the manufacture of beer, yogurt, cheese, medicines, and enzyme-containing detergents, use biocatalysts (**Figure 6**). Most of these enzymes are produced by fermentation processes using bacteria, yeast, or moulds. Enzymes tend to be sensitive to temperature and pH, so much research has gone into finding ways to make enzymes capable of working under industrial conditions. The use of catalysts in industry can also reduce costly and environmentally harmful energy consumption by allowing reactions to proceed rapidly at relatively low temperatures.

heterogeneous catalyst a catalyst in a reaction in which the reactants and the catalyst are in different physical states

homogeneous catalyst a catalyst in a reaction in which the reactants and the catalyst are in the same physical state

Catalysts can be divided into two main types. A **heterogeneous catalyst** exists in a different state of matter from the reactants, usually as a solid. For example, in the polymer manufacturing process and the catalytic converters described previously, the metal catalyst is present in the solid phase, while the reactants are in the gas phase. A **homogeneous catalyst** is one that is in the same phase as the reactants, usually a gas or liquid phase. For example, enzymes and the reactants they catalyze are in aqueous solution, so enzymes are a type of homogenous catalyst.

Figure 5 A catalytic converter converts toxic exhaust emissions from an internal combustion engine into non-toxic substances. A thin layer of the metal catalyst is spread over a honeycomb lattice to increase the surface area of the catalyst, further increasing the reaction rate.

Figure 6 Enzymes called lipases help blue cheeses to ripen.

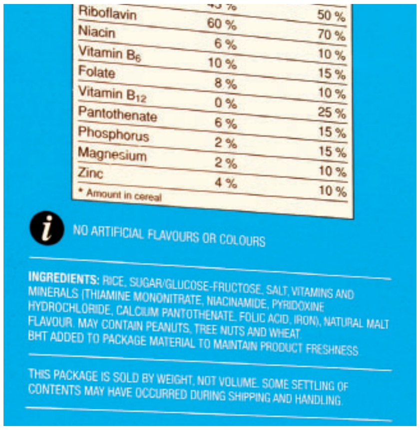
6.2 Review

Summary

- The rate of any reaction depends on the chemical nature and physical properties of the substances reacting.
- An increase in reactant concentration increases the rate of a reaction.
- When reactants are in different states of matter, an increase in reactant surface area increases the rate of a reaction.
- An increase in temperature increases the rate of a reaction.
- A catalyst increases reaction rate without being consumed in the reaction.
- Biological catalysts control most biological reactions, and most are enzymes.

Questions

1. In each example below, identify the factor that affects the reaction rate. K/U
   (a) Copper metal will turn green over time.
   (b) Milk can last several weeks when refrigerated, but will quickly sour at room temperature.
   (c) The dust in coal mines has been known to explode, whereas whole chunks of coal are difficult to ignite.
   (d) Magnesium metal is not used to make pipes.
   (e) Zeolite is added to large-chain hydrocarbons, causing them to break down into smaller, more useful molecules. The zeolite is then removed and reused.
   (f) Hydrogen peroxide (3 %) purchased in the drugstore is safe to put on open cuts. Hydrogen peroxide (30 %) purchased for the lab can cause very severe burns.
   (g) A glow stick will glow longer when placed in the freezer.
   (h) Signs warn about the dangers of having sparks or open flames near flammable fuels.
   (i) Flour mills ban smoking due to the high probability of explosions.
   (j) Phenylketonuria is a genetic disorder in which the body cannot produce the enzyme phenylalanine hydroxylase. People with this disorder cannot digest phenylalanine, a common amino acid.
2. Identify five different factors likely to affect reaction rate. Give an example of each from life outside your chemistry class that was not discussed in this section. K/U A
3. A research chemist wants to decrease the rate of a reaction by a factor of 4. How should she change the temperature to try to achieve this reduction in rate? Explain your answer. T/I
4. Digestive enzymes are present in very small quantities. Explain why they are not needed in large amounts, even though they are used by almost all biochemical processes in the body. A
5. If metal ores are mixed with carbon, they will react very slowly to produce elemental metal. What are two ways the rate of this reaction might be increased? A
6. A chemical called BHT (butylated hydroxytoluene or 2,6-di-tert-butyl-*p*-cresol) is found in many boxed foods, either in the food itself or in the packaging material (**Figure 7**).
   (a) Conduct research to find out how BHT affects chemical reaction rates. Relate this to its use in boxed foods.
   (b) Carry out a cost-benefit analysis of the use of BHT in the food industry. You may need to conduct additional research. Communicate your findings as an informative pamphlet suitable for distribution to the public. T/I C A



Riboflavin	60 %	50 %
Niacin	6 %	70 %
Vitamin B_6	10 %	10 %
Folate	8 %	15 %
Vitamin B_{12}	0 %	10 %
Pantothenate	6 %	25 %
Phosphorus	2 %	15 %
Magnesium	2 %	15 %
Zinc	4 %	10 %
* Amount in cereal		10 %

NO ARTIFICIAL FLAVOURS OR COLOURS

INGREDIENTS: RICE, SUGAR/GLUCOSE-FRUCTOSE, SALT, VITAMINS AND MINERALS (THIAMINE MONONITRATE, NIACINAMIDE, PYRIDOXINE HYDROCHLORIDE, CALCIUM PANTOTHENATE, FOLIC ACID, IRON), NATURAL MALT FLAVOUR. MAY CONTAIN PEANUTS, TREE NUTS AND WHEAT.
BHT ADDED TO PACKAGE MATERIAL TO MAINTAIN PRODUCT FRESHNESS

THIS PACKAGE IS SOLD BY WEIGHT, NOT VOLUME. SOME SETTLING OF CONTENTS MAY HAVE OCCURRED DURING SHIPPING AND HANDLING.

Figure 7 BHT is used in the packaging of this breakfast cereal.

WEB LINK

6.3 Explaining Reaction Rates

After an icy winter storm, you might sprinkle crystals of a chemical such as calcium chloride around to melt the ice (**Figure 1**). The calcium chloride dissolves in any liquid water. This chemical reaction releases thermal energy that melts the ice, which then allows more calcium chloride to go into solution and melt more ice. You may have found that the ice will melt faster if you break it up before you sprinkle the calcium chloride. You probably do not think about it, but what you are doing is increasing the surface area of the ice to increase the reaction rate! So what is happening at the level of the ions and molecules? In this section, you will explore theories that explain how surface area and other factors, including the chemical nature of the reactants, concentration of reactants, surface area, temperature, and the presence of a catalyst affect reaction rate.

Figure 1 Calcium chloride or other salts will melt ice more quickly if the ice is broken up first, exposing more surface area.

collision theory the theory that chemical reactions can occur only if reactants collide with proper orientation and with enough kinetic energy to break reactant bonds and form product bonds

Collision Theory

Collision theory states that chemical reactions can occur only if reactant atoms, molecules, or ions collide. Furthermore, the reactant entities must collide at an orientation and with enough kinetic energy that any bonds in the reactants will break and new bonds will form, making the products. The rate of a reaction depends on the frequency and the proportion of collisions that convert reactants into products. An increase in the frequency of effective collisions leads to a higher reaction rate.

Orientation

Some orientations for collisions between molecules or ions can lead to reactions while others cannot. This is sometimes called the collision geometry. As an example, think about the decomposition reaction of nitrosyl bromide gas, BrNO(g), represented by the following equation:

$$2\,\mathrm{BrNO(g)} \rightarrow 2\,\mathrm{NO(g)} + \mathrm{Br_2(g)}$$

According to collision theory, only some collisions between reactants are oriented so that a chemical reaction is possible, such as the collisions illustrated in **Figure 2(a)** and **(b)**. If the bromine atoms in the nitrosyl bromide molecules do not make direct contact, the reactants cannot form products and there will be no reaction, such as in the case shown in **Figure 2(c)**.

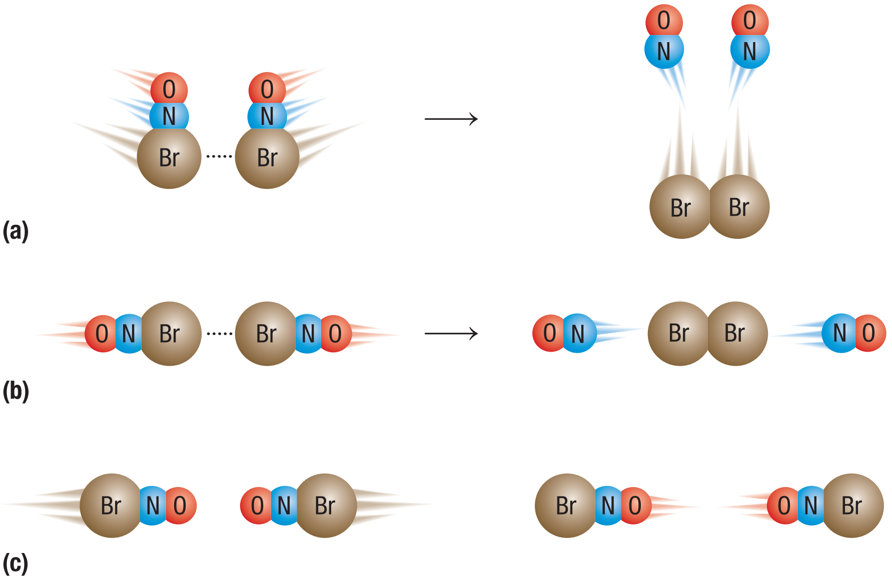


Figure 2 Several possible orientations for a collision between 2 nitrosyl bromide molecules. In (a) and (b), the orientations of the bromine atoms allow them to contact one another, so the chemical reaction can occur. In (c), the orientation of the bromine atoms prevents the bromine atoms from interacting, so the molecules move apart without reacting.

Activation Energy

The orientation of the reactant entities is only one factor in an effective collision. For a reaction to occur, the reactants must also have sufficient kinetic energy. The minimum amount of energy a reactant entity must have for a collision to be effective is called the **activation energy (E_a)**. Activation energy serves two purposes: it is used to overcome the electrostatic repulsive forces between colliding entities, and it is used to weaken the bonds of the reactants.

activation energy (E_a) the minimum energy that reactant molecules must possess for a reaction to be successful

You can think of activation energy as a potential energy hill or barrier. This concept of activation energy may be easier to understand if you think of a ball rolling (without obstacles or friction) on a smooth surface, such as the one shown in **Figure 3**. At point A, the ball has a certain quantity of potential energy. If you add kinetic energy, perhaps by pushing the ball, the ball will roll up the hill. As it rolls up the hill, the ball slows down as some of the kinetic energy is transformed into potential energy. If there is sufficient kinetic energy to reach the top of the hill (the same or more than the activation energy), the ball will roll down to the other side. In Figure 3, the ball has a higher potential energy at point B than it had at point A. If the ball had less kinetic energy at the start of its roll than the activation energy, it would have climbed only partway up the hill and then returned to point A.

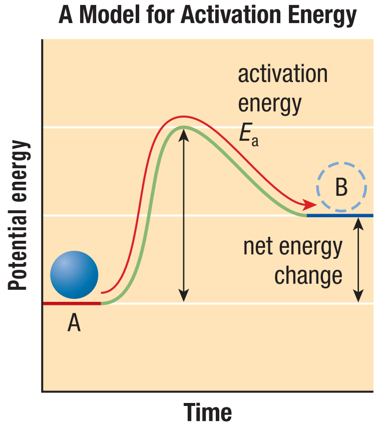


Figure 3 From point A to point B, there is a net increase in overall energy (kinetic plus potential). The ball must have a lot of energy (activation energy) to get up the hill.

In a chemical reaction, the potential energy is the energy stored in the bonds within and among the entities of the reactants, and the kinetic energy is their movement. When entities collide in an appropriate orientation, a chemical reaction can only proceed if the kinetic energy is enough to break these bonds. This quantity of energy is the activation energy (analogous to the hill in Figure 3). If the kinetic energy is sufficient, the bonds will rearrange to form the products. If the reactants do not have enough kinetic energy, the bonds of the reactants will not break and the reaction will not proceed.

For example, in the reaction represented in Figure 2, two Br–N bonds must be broken and one Br–Br bond must be formed. It takes considerable energy (243 kJ/mol) to break a Br–N bond. If 2 nitrosyl bromide molecules do not have enough kinetic energy to get over this potential energy hill, or barrier, the reaction will not take place.

The change in potential energy over the progress of this reaction between nitrosyl bromide molecules is illustrated in **Figure 4**. The unstable arrangement of atoms found at the top of the potential energy hill is called the **activated complex**, or transition state. The activation energy, E_a, represents the energy difference between reactants and the activated complex.

activated complex an unstable arrangement of atoms containing partially formed and unformed bonds that represents the maximum potential energy point in the change; also called the transition state

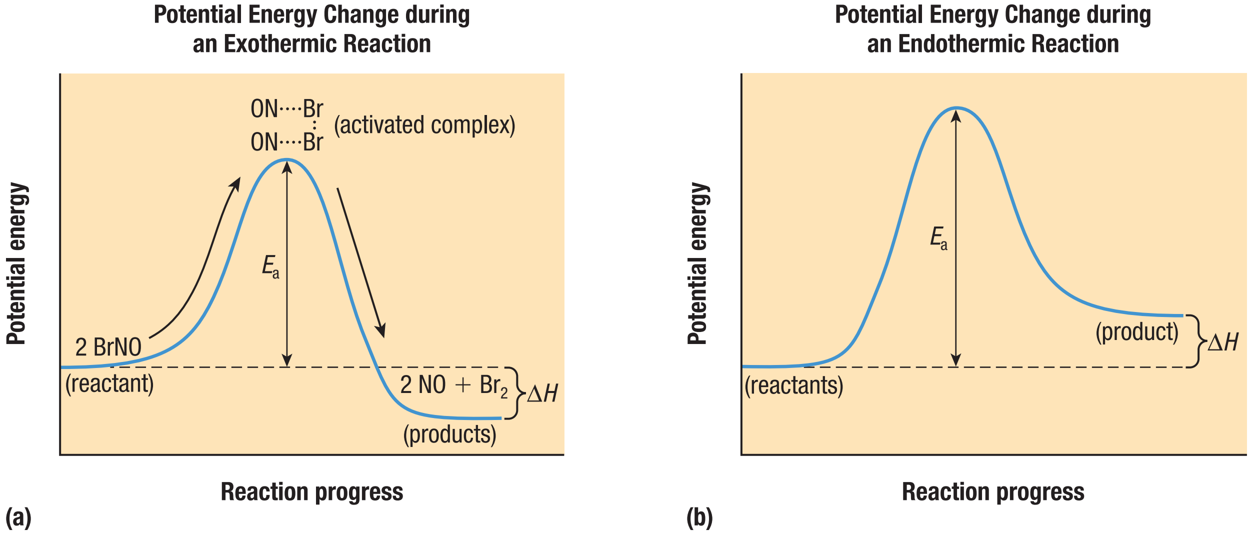


Figure 4 The change in potential energy as a function of reaction progress for (a) the reaction $2\ BrNO(g) \rightarrow 2\ NO(g) + Br_2(g)$ and (b) an endothermic reaction

Notice how, as with the ball in Figure 3, the potential energy of the products of this reaction is not the same as the potential energy of the reactants. In Section 5.3, you saw that the net change in energy between reactants and products is called the enthalpy change, ΔH. Exothermic reactions release energy and have a negative ΔH, and the reaction depicted in Figure 4(a) is an exothermic reaction. Figure 4(b) illustrates the change in potential energy during a hypothetical endothermic reaction. The potential energy gain comes from the conversion of kinetic energy. Endothermic reactions absorb energy and have a positive ΔH.

Temperature of the Reaction System

Experimental evidence shows that a relatively small increase in temperature seems to have a very large effect on reaction rate. An increase of about 10 °C will often double or triple the rate of a reaction. Temperature is considered to be a measure of the average kinetic energy of a substance. Therefore, in any sample of a substance at a given temperature, the individual entities in the sample will have different kinetic energies. Some of the entities will therefore be moving more quickly than others, so only a proportion will have a quantity of kinetic energy that equals or exceeds the activation energy. If you increase the temperature, the average kinetic energy of the entities increases. As a result, more entities in the sample will have enough kinetic energy to break the bonds of the reactants and form an activation complex. In addition, the increase in kinetic energy will also increase the rate and force of collisions between reactants, which will increase the probability that the collisions will be effective.

For a given activation energy, E_a, a much larger fraction of entities of a reactant will have the required kinetic energy at a higher temperature than at a lower temperature. A temperature rise that is a small increase in overall energy might cause a very large increase in the number of entities that have energy exceeding the activation energy. For reactants in the gas state, this relationship between the numbers of entities of a reactant and their kinetic energy is represented by a graph called the Maxwell–Boltzmann distribution (**Figure 5**).

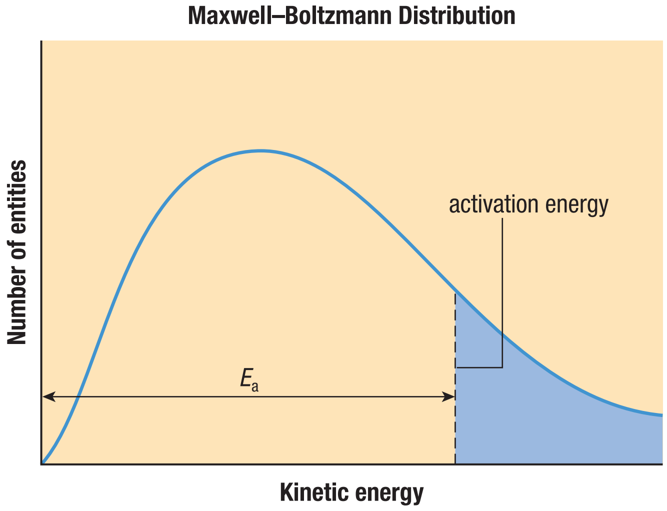


Figure 5 Only entities with kinetic energy equal to or greater than the activation energy can be involved in an effective collision. These entities are represented by the shaded area to the right of the dotted line.

At a given temperature, only a certain fraction of the reactant entities will possess enough kinetic energy to equal or exceed the activation energy, E_a. **Figure 6** on the next page shows how the Maxwell–Boltzmann distribution changes when temperature is changed. At the lower temperature, T_1, the fraction of entities that have kinetic energy equal to or greater than the activation energy is quite small. In Figure 6, this is represented by the shaded area to the right of the line that represents the activation energy and under the line for T_1. When the temperature is raised to T_2, the fraction of reactant entities with kinetic energy equal to or greater than the activation energy increases dramatically. Therefore, there are many more entities that are capable of making effective collisions at the higher temperature (provided they collide in a productive orientation). Experimental evidence shows that, for most chemical reactions, reaction rates increase exponentially with temperature. This is consistent with the theory that increases in temperature exponentially increase the probability of effective collisions.

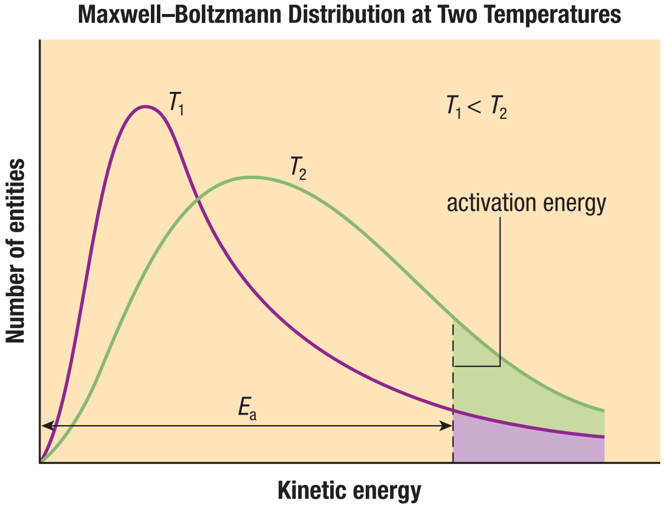


Figure 6 When the temperature of a reaction mixture is increased from T_1 to T_2, the number of entities capable of having effective collisions increases significantly.

Mini **Investigation**

Modelling Energy Distribution of Molecules

Skills: Performing, Observing, Analyzing

SKILLS HANDBOOK **A2.4**

In this activity, you will work with a group to model how temperature changes the distribution of energy among entities in a substance.

Equipment and Materials: 5 tokens per student (such as paper clips or pieces of paper)

1. Obtain 1 token, then pair up with a fellow student. Both of you should have 1 token. Each token represents an effective collision between reactants.
2. As a class, form 2 rings so that 1 ring is inside the other and each person is facing his or her partner in the other ring.
3. Play rock, paper, scissors with your partner in the other ring. Whenever one of you wins, the losing partner must pass 1 token to the winner. If there is no winner, then you both keep your tokens.
4. As a class, shift positions so that all students in the inner circle move 1 person to the right, giving everyone a new partner.
5. Repeat Steps 3 and 4 twice, then record the number of tokens held by each person in the class.
6. Repeat Steps 3 to 5 an additional three times.
7. Take note of who your current partner is. Obtain another token and return to the circle. Everyone in the class should now be in the same position but have 1 more token than at the end of Step 6. This additional token represents an increase in temperature.
8. Repeat Steps 3 to 6.

A. Do you think you could have predicted how many tokens each person would have at the end of the activity? Why or why not? T/I

B. How is obtaining an additional token in Step 7 similar to an increase in temperature? T/I

C. After each round, were the tokens distributed equally or were there many students who had many more tokens than others? How does this model the kinetic energy of entities of a substance at a given temperature? T/I

D. Relate the results of this activity to the effects of temperature on the probability of effective collisions in a reaction mixture. T/I

Chemical Nature of Reactants

For any reactant, the bond type, strength, and number determine the activation energy required for a successful collision. Reactions involving the breaking of fewer bonds per reactant proceed faster than those involving the breaking of a larger number of bonds per reactant. Weaker bonds are broken at a faster rate than stronger bonds. For example, it takes less energy to break a single C–C bond than a double C=C bond. Reactions between molecules are usually slower than reactions between ions. This is because, in molecules, covalent bonds have to be broken and new bonds re-formed. This slows down reaction rates.

The size and shape of a molecule or ion can also affect reaction rate. Some reactions involve complicated molecular substances or complex ions. These are often less reactive than smaller, less complex entities. This is in part because more bonds must be broken. However, it is also less likely that complex molecules or ions will collide in an orientation relative to each other that will be effective in allowing a reaction to occur.

Concentration and Surface Area

You are more likely to bump into another passenger while travelling on a public bus during rush hour than on a less crowded bus in the middle of the day. Similarly, if you increase the concentration of a reactant, the probability of collisions between reactant molecules increases and, hence, a greater number of effective collisions is likely to occur. Therefore, the reaction rate will be expected to increase. **Figure 7** represents two reactions occurring in aqueous solution, with two different concentrations of reactants A and B. Which reaction rate do you predict will be higher?

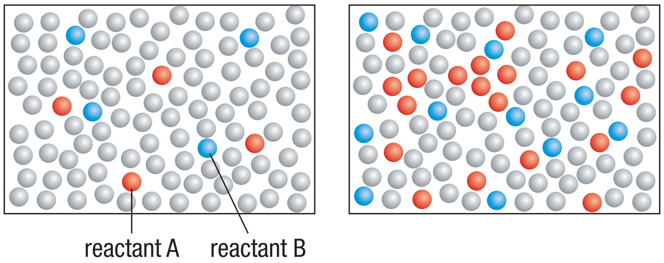


Figure 7 Two reactions occurring in aqueous solution, one with lower concentrations of the reactants and the other with higher concentrations. Identify the number of reactant A–reactant B collisions in each sample.

In a reaction involving reactants in more than one state, such as a solid reactant and a liquid reactant, increasing the surface area of the solid reactant increases the reaction rate. Imagine that you are holding a cube of some substance. Its surface area is the area of the 6 faces of the cube. If you were to cut the cube into many smaller cubes, the total surface area would increase. If you ground the cube into a powder, the surface area would be maximized. This is why many solids are powdered using a mortar and pestle before being used in a reaction.

Chemical entities that are not bound within a crystalline structure are available to react with other entities. Only the atoms, ions, or molecules at the surface of the solid reactant can collide with entities of the other reactant(s). Therefore, increasing the surface area of a solid reactant increases the probability of effective collisions in a similar manner to increases in concentration. In a reaction between a solid and a reactant in the liquid or gas phase, or in aqueous solution, increasing the surface area of the reactant in the solid phase increases the number of collisions per unit time and therefore increases the reaction rate (**Figure 8**).

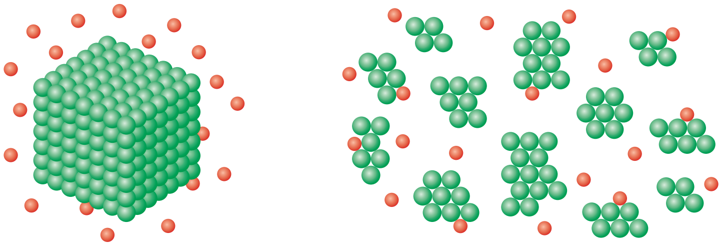


Figure 8 The entities in a solid structure have fewer potential collision sites than the same number of entities split into smaller bits, increasing the total surface area.

Catalyst Theory

For any reaction to occur, the kinetic energy of colliding reactant entities must be equal to or greater than the activation energy. However, catalysts do not increase the number of collisions between reactant entities, nor do they increase the kinetic energy of the entities of reactant(s). Instead, a catalyst provides an alternative pathway for the reaction, which has a lower activation energy. Thus, at any given temperature, a larger fraction of the entities of the reactant(s) will have kinetic energy equal to or greater than this lower activation energy. There is a greater number of effective collisions, and so the reaction rate is increased (**Figure 9**).

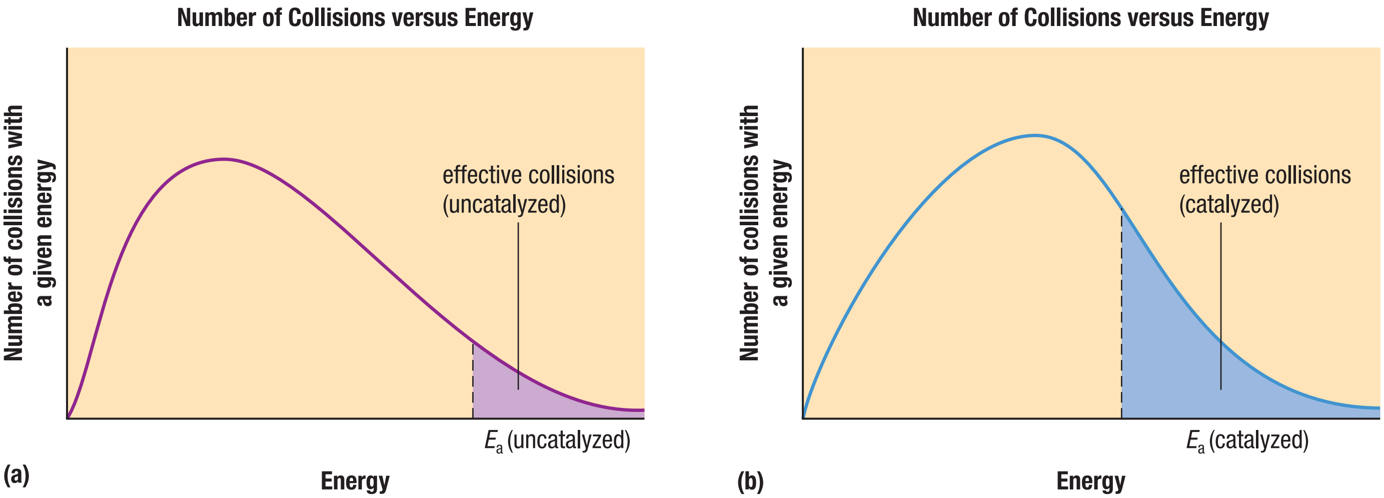


Figure 9 The effect of a catalyst on the number of reaction-producing collisions. Since a catalyst provides a reaction pathway with a lower activation energy, a much greater fraction of the collisions are successful for the catalyzed pathway (b) than for the uncatalyzed pathway (a) (at a given temperature). This allows reactants to become products at a much higher rate, even if the temperature is not increased.

A catalyst is thought to allow a reaction to occur along a different pathway of steps that results in the same overall products. However, as shown in **Figure 10**, although a catalyst lowers the activation energy, E_a, for a reaction, it does not affect the energy difference between products and reactants.

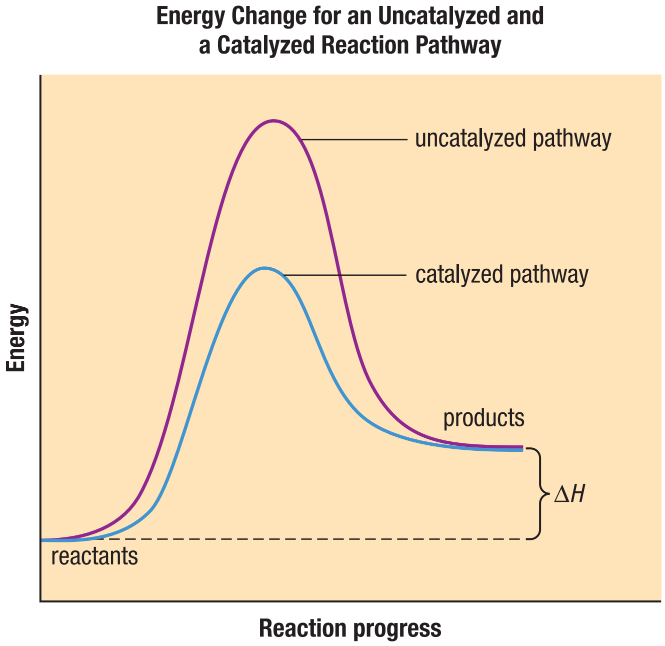


Figure 10 Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction

UNIT TASK BOOKMARK

How can you apply catalyst theory to the Unit Task on page 402?

6.3 Review

Summary

- Collision theory states that, for a chemical reaction to occur: a collision must occur between 2 or more reactant entities; the entities must collide with the correct orientation; and the entities must have a certain minimum energy.
- An effective collision is one in which reactant(s) is converted to product.
- Activation energy, E_a, is the minimum energy required for an effective collision.
- Chemical properties of the reactants determine the activation energy required for an effective collision.
- An activated complex (transition state) is an unstable arrangement of atoms at the maximum potential energy point in the change from reactant(s) to product(s).
- Increasing the surface area and the concentration of a reactant(s) increases the total number of collisions and so the number of effective collisions.
- Increasing the temperature will increase the average kinetic energy of the entities of reactant(s). This will result in more entities having a quantity of kinetic energy the same as or greater than the activation energy and will increase the number of collisions.
- A catalyst provides a reaction pathway with a lower activation energy.

Questions

1. A reaction will occur between zinc and hydrochloric acid. Describe what will happen to the reaction rate under the conditions described below. K/U
   (a) The acid is cooled to 1 °C.
   (b) The reaction mixture is stirred.
   (c) A concentration of 5.0 mol/L hydrochloric acid is used instead of 1.0 mol/L.
   (d) Powdered zinc is used instead of chunks of zinc.
   (e) The reaction is carried out in a darkened room.
2. (a) State the collision theory in your own words.
   (b) Explain why not every collision that occurs results in the formation of a product.
   (c) Explain why increasing the temperature can affect the number of collisions as well as the percentage of effective collisions. K/U
3. Think of an everyday activity, such as a handshake, that requires you to come in contact with something, to be lined up correctly, and to have a certain minimum amount of energy. Describe the activity and explain what would happen if any one of these criteria were not met. A
4. Draw and label two potential energy diagrams, one for an endothermic reaction and one for an exothermic reaction. Show ΔH and E_a. T/I C
5. A common catalyst that is used to speed up the rate of the decomposition of hydrogen peroxide is powdered manganese dioxide. K/U T/I
   (a) Describe what a catalyst is.
   (b) Explain how it affects the rate of a reaction.
   (c) Is manganese dioxide a heterogeneous or homogeneous catalyst?
   (d) Design an experiment to prove that manganese dioxide is a catalyst for this reaction. Include a list of all materials that are required.
6. (a) Write the balanced equation for the reaction between ethylene, C_2H_4 and hydrogen chloride, HCl.
   (b) Represent the reaction using Lewis structures.
   (c) Based on your Lewis structures, suggest an orientation that would result in an effective collision.
   (d) Suggest an orientation that would result in an ineffective collision. K/U T/I C

6.4 Explore an Application of Chemical Kinetics

Biocatalysts and the Environment

SKILLS MENU

- Researching
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating
- Identifying Alternatives

Enzymes are found in living organisms throughout nature. They allow for countless reactions to occur within the temperature range that supports life as we know it. Enzymes are biocatalysts—catalysts that are made by living systems or that are themselves living systems. For example, ribulose-1,5-bisphosphate carboxylase oxygenase, or Rubisco, is an enzyme produced by plant cells that catalyzes the first step in the conversion of carbon dioxide gas to glucose during photosynthesis. Alternatively, yeast cells added to bread dough to catalyze the fermentation of sugar are an example of a biocatalyst that is a living system (**Figure 1**). Like all catalysts, biocatalysts are thought to act by providing an alternative pathway for a chemical reaction that has a lower activation energy than the uncatalyzed reaction.

Biocatalysis is any method that uses biocatalysts to increase reaction rate. As we learn more about it, people working in an increasingly wide range of fields are becoming interested in using biocatalysis. For example, new pharmaceuticals are increasingly complex, which makes them very expensive to synthesize by traditional chemical methods. Researchers are exploring ways to use biocatalysis instead, as a way to reduce costs. Biocatalysis may also play a key role in improving and protecting our environment. Traditional chemical manufacturing processes often produce toxic by-products. These by-products are costly, since they must be either stored or converted to non-toxic substances and also have a risk of accidental release into the environment. Biocatalysis has the potential to reduce or eliminate such by-products. In addition, since biocatalysis can be more efficient than traditional chemical synthesis processes, it may also reduce energy and raw material use.

Figure 1 Yeast cells, when used to make bread dough rise, are an example of a biocatalyst that is a living organism.

The Application

The industrial preparation of paper is an example of a process that may benefit from the application of biocatalysis. The predominant paper pulping method used by the paper industry is the kraft process. Wood is composed of a number of substances. The most abundant and desirable is cellulose, which forms long fibres that give wood its strength. In a living tree, the cellulose fibres are associated with a group of compounds known as lignin. Although important biologically, the presence of lignin lowers the quality of paper. The kraft process removes lignin from cellulose by heating chipped wood in a solution of sodium hydroxide, NaOH(aq), and sodium sulfide, $Na_2S(aq)$. This uses a lot of energy and also produces large volumes of pollutants. Even with restricted emissions, pulp and paper manufacturers that use the kraft process often can be identified by a strong, offensive smell. The kraft process generates hydrogen sulfide gas, $H_2S(g)$, and other sulfur gas compounds as a by-product. To produce white paper, paper manufacturers have traditionally used chlorine bleach. However, using chlorine to bleach wood pulp has been shown to produce dioxins, substances that cause cancer in humans and other organisms.

Biocatalysts that are proving to be very useful in these applications include the following:

- Laccases: This class of enzymes can remove lignin from cellulose in wood without the need for harsh chemicals. These enzymes break down the lignin, leaving the cellulose intact.
- Xylanase: Treatment with this enzyme (**Figure 2**) enables manufacturers to reduce chlorine consumption by 15 to 25 %. This enzyme is used in bleaching procedures in which chlorine is completely replaced with chlorine dioxide or non-chlorine chemicals.

Figure 2 If xylanase is used for bleaching pulp, the need for chlorine in the bleaching process is reduced or eliminated.

Your Goal

To determine the pros and cons of funding for biocatalyst research for the pulp and paper industry; also to determine whether there are social costs associated with the environmental benefits, and, if so, how they are balanced

Research

SKILLS HANDBOOK A4, A5.1

Gather information about the use of traditional processes used in enzymes as catalysts in the pulp and paper industry. Here are some suggestions to help guide your research:

- What are the environmental impacts of traditional processes used in the pulp and paper industry?
- How are biocatalysts currently used in the pulp and paper industry?
- What is the focus of the pulp and paper industry's current research into the use of biocatalysts?
- What are the environmental benefits of using biocatalysts in the industry?
- What are the economic impacts of the use of biocatalysts for the pulp and paper industry?
- What percentage of pulp and paper mills currently use biocatalysts?
- What are some of the drawbacks of using biocatalysts?
- How is the paper used at your school manufactured? WEB LINK

UNIT TASK **BOOKMARK**

You might apply what you learn about the advantages and disadvantages of using biocatylysis for paper production to the Unit Task on page 402.

Summarize

SKILLS HANDBOOK A5.2

Prepare a one- to two-page point-form summary of your research. Decide whether you think biocatalyst technology is an economically and environmentally viable tool for use in the pulp and paper industry. Organize the report into pros and cons of funding biocatalyst research in the pulp and paper industry.

Communicate

SKILLS HANDBOOK A6.5

Prepare a visual presentation (PowerPoint, bristol board, tri-fold poster, or other format) of your research findings. Use diagrams where necessary.

Plan for **Action**

Biocatalysis is a useful tool for scientists working in the field of green chemistry. Green chemistry follows 12 tenets that aim to make chemical processes more sustainable and less damaging to the environment. Tenet 9 states, "Catalytic reagents (as selective as possible) are superior to stoichiometric reagents."

Create a plan to help the people in your community become better informed about the benefits of catalysts as supported by green chemistry. In creating your plan, consider the following questions. You may have to conduct additional research to complete your plan.

- How will you communicate how catalysts work to a person with little chemical knowledge?
- Are there any Canadian success stories using biocatalysis in a process that meets the standards of green chemistry?
- Are there any costs to using catalysts in a manufacturing process?
- What is the most interesting manner in which you could communicate this to your community?

WEB LINK

Rate Law

6.5

Industries continually search for ways to increase efficiency. Their aim is to maximize output while minimizing costs of production. Achieving this balance requires finding an optimal rate of production.

One strategy industries use to change their production rate is to vary the concentrations of reactants. This strategy requires much experimental work, because chemists cannot predict the effect of changing reactant concentrations on the rate of a reaction simply by looking at a balanced chemical equation. They can only determine rates of reaction from data obtained during experimental testing (**Figure 1**). One goal of this testing is to create a chemical rate law for the reaction. A chemical **rate law** is an equation that connects the rate of a reaction with the concentrations of its reactants at a given temperature and pressure.

Figure 1 To determine how the concentration of a reactant may affect the rate of a reaction, chemists carry out several runs using different initial concentrations, and determine the initial rate resulting from each run. They then compare the results to observe how the initial rate depends on the initial concentrations.

rate law the mathematical expression that allows calculation of reaction rate as a function of reactant concentration

Determining a Rate Law Equation

The concentration of a reactant may affect the rate of a reaction. In most reactions, the concentrations of the reactants and the temperature inside the reaction vessel change as soon as the reaction begins. Therefore, in gathering data to determine a rate law for a reaction, chemists look at the initial concentrations of the reactants at a specified temperature.

Consider the following equation for a chemical reaction:

$$aA + bB \rightarrow \text{products}$$

A and B represent the reactants, and *a* and *b* are the coefficients used to balance the equation. Experimental evidence has shown that the rate of a reaction is proportional to the product of the initial concentrations of the reactants, where each concentration is raised to some exponential value. This can be expressed as

$$\text{rate} \propto [A]^m[B]^n$$

This expression relates the reaction rate to the initial concentrations of reactants using exponents *m* and *n*. Note that exponents in a rate law cannot be obtained from the balanced equation; they can only be determined experimentally. The values of the exponents can be any real number. For the relatively simple reactions we will consider here, however, all exponents will be positive integers or 0.

Instead of using a proportionality sign, we can write the relationship between reactant concentrations and reaction rate as an equation:

$$\text{rate} = k[A]^m[B]^n$$

This equation is called the **rate law equation**. Notice that this equation includes a constant, *k*, known as the **rate constant**. The rate constant is unique for each reaction, and must be determined experimentally. For any reaction, *k* varies with temperature, so the temperature must be kept constant in all runs of an investigation of a chemical reaction carried out to determine the rate law for that reaction.

Each exponent in the rate law equation is called an **order of reaction** with respect to the particular reactant with which it is associated. For example, if the exponent of [A] is 1, then the reaction is *first order* with respect to A. If the exponent of [A] is 2, the reaction is *second order* with respect to A, and so on. The **total order of reaction** is the sum of the individual orders of reaction for each reactant. The orders of reaction can be used to predict reaction rates. Suppose you are given this equation,

$$2A + 2B + 3C \rightarrow \text{products}$$

and are told that the experimental evidence gives the following rate law equation:

$$\text{rate} = k[A]^1[B]^2[C]^0$$

This equation tells us that the rate of the reaction is proportional to each of the initial concentrations of the reactants raised to a given power:

$$\text{rate} \propto [A]^1 \quad \text{rate} \propto [B]^2 \quad \text{rate} \propto [C]^0$$

rate law equation the relationship among rate, the rate constant, the initial concentrations of reactants, and the orders of reaction with respect to the reactants

rate constant determined empirically and is unique for a single reaction at a specified temperature

order of reaction the exponent used to describe the relationship between the initial concentration of a particular reactant and the rate of the reaction

total order of reaction the sum of the exponents in the rate law equation

The rate of the reaction is proportional to [A] raised to the power 1. If the exponent of the concentration of a reactant is 1, when we multiply the initial concentration by 2, the rate will be multiplied by 2^1. When we multiply the initial concentration by 3, the rate will be multiplied by 3^1. Since a number raised to the power 1 is the number itself, when we double the initial concentration, the rate will double; when we triple the initial concentration, the rate will triple; and so on.

The rate of the reaction is proportional to [B] raised to the power 2. A number raised to the power 2 is the number squared. So, if the exponent of the concentration of a reactant is 2, when we double the initial concentration, the rate will be multiplied by 2^2, or 4. When we multiply the initial concentration by 3, the rate will be multiplied by 3^2, or 9, and so on.

The rate of the reaction is proportional to [C] raised to the power 0. Any non-zero number raised to the power 0 is 1. So, if the exponent of the concentration of a reactant is 0, this means that the concentration of that reactant does not affect the rate of reaction. If we double the concentration of the reactant, the rate will be multiplied by $2^0 = 1$. In other words, the rate will not change. Similarly, if we triple the initial concentration of the reactant, the rate will still not change, because the rate will be multiplied by $3^0 = 1$. Since in this reaction the rate does not depend on the initial concentration of (C), we would write the rate law equation as

$$\text{rate} = k[\text{A}]^1[\text{B}]^2$$

We can use graphs to help us recognize the order of reaction with respect to a particular reactant. Plotting experimental data as shown in **Figure 2** and looking for a straight line (indicating a direct relationship) will determine the value of *n*.

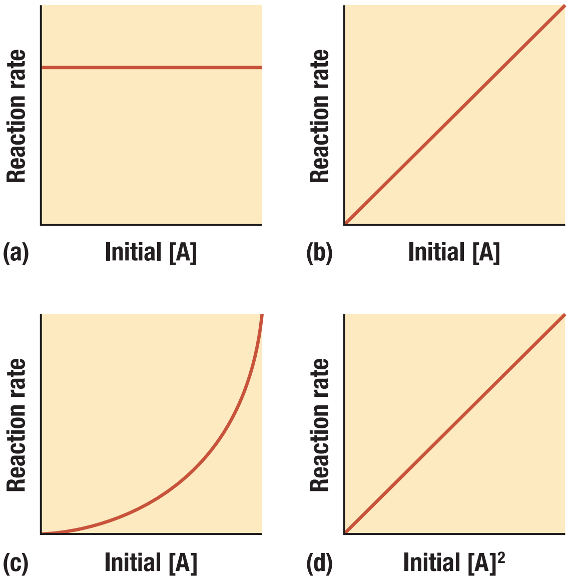


Figure 2 When a series of kinetics experiments is performed on a given system, the rates of reaction are measured for different initial concentrations of a reactant. When the evidence is graphed, you may see one or more of these results.

(a) In this plot, $r \propto [A]^0$. The reaction is zero order with respect to [A].
(b) In this plot, $r \propto [A]^1$. The reaction is first order with respect to [A].
(c) In this plot, $r \propto [A]^n$, where *n* is greater than 1.
(d) In this plot, $r \propto [A]^2$. The reaction is second order with respect to [A].

Chemists commonly use the method of initial rates to determine the rate law equation for a reaction. The **initial rate** of a reaction is the instantaneous rate determined just after the reaction begins (just after $t = 0$ s).

initial rate the rate determined just after the reaction begins (just after $t = 0$ s)

The steps in the method of initial rates are as follows:

1. Measure the instantaneous rate of reaction before there are any significant changes in concentration of the reactants.
2. Carry out several runs using different initial concentrations, determining the initial rate resulting from each run.
3. Compare these results to observe how the initial rate depends on the initial concentrations.

Note that the concentrations of the products are not expressed in the rate law equation. Since we deal with the initial instantaneous rate, we do not worry about the products, because at this stage none or close to none have been formed.

A rate law equation establishes the specific mathematical relationship between the reaction rate for a given reaction and the concentrations of reactants at the start of the reaction. We can use experimentally determined reaction rates to illustrate this. Consider the following chemical equation, which summarizes the reaction between nitric oxide, $NO(g)$, and hydrogen gas, $H_2(g)$:

$$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$$

Table 1 shows several experimentally determined rates for our sample reaction under various initial concentrations of each reactant. In order to determine the value of an exponent of the rate law equation and therefore the effect of the concentration of that reactant on the reaction rate, it is necessary to keep all other variables constant. Therefore, in runs 1 and 2 the concentration of nitric oxide gas was kept constant to see if changes in the concentration of hydrogen gas have an effect on the reaction rate. Likewise, in runs 2 and 3 the concentration of hydrogen gas was kept constant to see if changes in the concentration of nitric oxide gas have an effect on the rate.

Table 1 Initial Rates from Three Investigations for the Reaction at 800 °C Represented by $2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$

Run	Initial [NO(g)] (mol/L)	Initial [H_2(g)] (mol/L)	Initial rate (mol/L·s)
1	0.400	0.100	1.10×10^{-5}
2	0.400	0.200	2.20×10^{-5}
3	0.800	0.200	8.80×10^{-5}

Compare the data shown in the first two runs in Table 1. The nitric oxide gas concentration is identical in both cases; only the hydrogen gas concentration has been changed. Notice what happens to the rate of the reaction when the concentration of nitric oxide gas is kept constant and the concentration of hydrogen gas is doubled—the rate of the reaction doubled from 1.10×10^{-5} to 2.20×10^{-5} mol/L·s. As the concentration of hydrogen gas doubles, the rate doubles, so the reaction rate in runs 1 and 2 is directly proportional to the concentration of hydrogen gas, that is, proportional to the hydrogen gas concentration raised to the power 1:

$$\text{rate} \propto [H_2(g)]^1 \quad \text{or} \quad \text{rate} = k[H_2(g)]^1$$

Next, compare the data shown in runs 2 and 3 in Table 1. In these runs, the hydrogen gas concentration is constant and the nitric oxide gas concentration has been doubled. This time, the reaction rate went up fourfold, from 2.20×10^{-5} to 8.80×10^{-5} mol/L·s. As the concentration of nitrogen monoxide gas doubles, the rate goes up four times. The rate of the reaction in runs 2 and 3 is proportional to the square of the concentration of nitrous oxide gas:

$$\text{rate} \propto [\text{NO(g)}]^2 \quad \text{or} \quad \text{rate} = k[\text{NO(g)}]^2$$

Therefore, the rate law equation for this reaction is

$$\text{rate} = k[\text{NO(g)}]^2[\text{H}_2\text{(g)}]^1$$

The reaction is second order with respect to nitric oxide gas and first order with respect to hydrogen gas. Notice that the exponent for hydrogen gas does not match the coefficient for this reactant in the balanced equation.

Note that the rate constant, *k*, is not a true constant. It varies if you change the temperature of the reaction, add a catalyst, or change the catalyst.

In Tutorial 1. you will use experimental data to analyze a sample reaction. You will write the complete rate law equation for the sample reaction, including the rate constant, *k*, and the order with respect to each reactant.

Tutorial 1 Using Experimental Data to Formulate the Rate Law

In this tutorial, you will use experimental data to determine the rate law equation for a reaction.

Sample Problem 1: Predicting a Rate and Finding the Rate Constant

An investigation indicates that the initial rate of the reaction represented by the equation

$$\text{BrO}_3^-\text{(aq)} + 5\,\text{Br}^-\text{(aq)} + 6\,\text{H}^+\text{(aq)} \rightarrow 3\,\text{Br}_2\text{(l)} + 3\,\text{H}_2\text{O(l)}$$

at 25 °C is 3.2×10^{-3} mol/(L·s) when the initial concentration of bromate, BrO_3^-(aq), is 0.10 mol/L; the initial concentration of bromide, Br^-(aq), is 0.10 mol/L; and the initial concentration of hydrogen ion, H^+(aq), is 0.20 mol/L. The reaction is first order with respect to bromate, first order with respect to bromide, and second order with respect to hydrogen ion. Determine the initial rate of reaction if the initial concentration of hydrogen ion is doubled with no change in the bromate or bromide concentrations, and find the rate constant, *k*.

Given: $[\text{BrO}_3^-\text{(aq)}]_\text{initial} = 0.10$ mol/L; $[\text{Br}^-\text{(aq)}]_\text{initial} = 0.10$ mol/L; $[\text{H}^+\text{(aq)}]_\text{initial} = 0.20$ mol/L; $\text{rate}_\text{initial} = 3.2 \times 10^{-3}$ mol/(L·s); orders of reactions

Required: initial rate if $[\text{H}^+\text{(aq)}]_\text{initial}$ is doubled, and the rate constant, *k*

Solution:

Step 1. The rate law for the reaction is

$$\text{rate} = k[\text{BrO}_3^-\text{(aq)}]^1[\text{Br}^-\text{(aq)}]^1[\text{H}^+\text{(aq)}]^2$$

Since the rate is second order with respect to hydrogen ion, if the initial concentration of hydrogen ion is doubled (multiplied by 2), the initial rate will be multiplied by 2^2, or 4. The new rate is

$$4 \times (3.2 \times 10^{-3}\ \text{mol/(L·s)}) = 1.3 \times 10^{-2}\ \text{mol/(L·s)}$$

Step 2. To find *k*, rearrange the rate law equation to solve for *k* and enter the values provided:

$$k = \frac{\text{rate}}{[\text{BrO}_3^-\text{(aq)}]^1[\text{Br}^-\text{(aq)}]^1[\text{H}^+\text{(aq)}]^2}$$

$$= \frac{3.2 \times 10^{-3} \dfrac{\cancel{\text{mol}}}{\cancel{\text{L}}\cdot\text{s}}}{\left(0.10\,\dfrac{\cancel{\text{mol}}}{\cancel{\text{L}}}\right)\left(0.10\,\dfrac{\text{mol}}{\text{L}}\right)\left(0.20\,\dfrac{\text{mol}}{\text{L}}\right)^2}$$

$$k = 8.0\ \text{L}^3/(\text{mol}^3\cdot\text{s})$$

Statement: If the initial concentration of hydrogen ion is doubled, the initial rate of reaction will be 1.3×10^{-2} mol/(L·s). The rate constant, *k*, is 8.0 $\text{L}^3/(\text{mol}^3\cdot\text{s})$.

Sample Problem 2: Determining the Rate Law Equation

Under acidic conditions, hydrogen peroxide, $H_2O_2(aq)$, oxidizes iodide ions, $I^-(aq)$, to triiodide ions, $I_3^-(aq)$. The balanced equation describing this reaction is

$$H_2O_2(aq) + 3\,I^-(aq) + 2\,H^+(aq) \rightarrow I_3^-(aq) + 2\,H_2O(l)$$

A chemist runs a series of reactions using the method of initial rates. She varies the initial concentrations of the 3 reactants as shown in **Table 2**. Using these data, determine the reaction orders with respect to $H_2O_2(aq)$, $I^-(aq)$, and $H^+(aq)$. State the rate law equation for the reaction.

Table 2 Initial Data from Runs at 25 °C of the Reaction Represented by $H_2O_2(aq) + 3\,I^-(aq) + 2\,H^+(aq) \rightarrow I_3^-(aq) + 2\,H_2O(l)$

Run	Initial $[H_2O_2(aq)]$ (mol/L)	Initial $[I^-(aq)]$ (mol/L)	Initial $[H^+(aq)]$ (mol/L)	Initial rate (mol/(L·s))
1	0.100	0.100	0.00030	1.5×10^{-5}
2	0.200	0.100	0.00030	3.0×10^{-5}
3	0.100	0.200	0.00030	3.0×10^{-5}
4	0.100	0.100	0.00060	1.5×10^{-5}

Given: experimental data provided in Table 2

Required: the order of reaction with respect to each reactant and the rate law equation

Analysis: Use the general form of the rate law equation to begin writing the rate law for this reaction:

$$\text{rate} = k[H_2O_2(aq)]^m[I^-(aq)]^n[H^+(aq)]^p$$

To determine the orders of reaction, look for pairs of data in which the initial concentration of only 1 reactant changes. Then, insert values for m, n, and p into the rate equation along with 1 set of data from the table.

Solution:

Step 1. Find m.

Look at the data from runs 1 and 2, because the initial concentration of hydrogen peroxide changed while the concentrations of iodide and hydrogen remained constant. When the initial concentration of hydrogen peroxide doubled, the rate of reaction doubled. Thus, the rate of reaction and the initial concentration are directly proportional. The exponent m in the rate law equation is therefore 1, and the order of reaction with respect to $H_2O_2(aq)$ is 1.

Step 2. Find n.

Look at the data from runs 1 and 3, because the initial concentration of iodide changed while the concentrations of hydrogen peroxide and hydrogen remained constant. When the initial concentration of iodide doubled, the rate of reaction doubled. The exponent n in the rate law equation is therefore 1, and the order of reaction with respect to $I^-(aq)$ is 1.

Step 3. Find p.

Look at the data from runs 1 and 4, because the initial concentration of hydrogen changed while the concentrations of hydrogen peroxide and iodide remained constant. When the initial concentration of hydrogen doubled, the rate of reaction remained unchanged. The exponent p in the rate law equation is therefore 0, and the order of reaction with respect to $H^+(aq)$ is 0.

Step 4. Therefore, for this reaction,

$$\text{rate} = k[\text{H}_2\text{O}_2(\text{aq})]^1[\text{I}^-(\text{aq})]^1[\text{H}^+(\text{aq})]^0$$

The total order of this reaction is

$$m + n + p = 1 + 1 + 0$$
$$= 2$$

You do not need to include the exponent when it is 1. Since the exponent of $[\text{H}^+(\text{aq})]$ is 0, the rate does not depend on the initial concentration of hydrogen, so you do not include it in the rate law equation. The rate law equation is

$$\text{rate} = k[\text{H}_2\text{O}_2(\text{aq})][\text{I}^-(\text{aq})]$$

Statement: The rate law equation is rate $= k[\text{H}_2\text{O}_2(\text{aq})][\text{I}^-(\text{aq})]$. The total order of the reaction is 2.

Investigation 6.5.1

The Iodine Clock Reaction System (page 392)
Now that you have learned about the rate law equation, you will run experiments to collect the data needed to determine the order of reaction with respect to one of the reactants involved in the reaction of iodate ions and bisulfite ions.

Practice

1. A series of investigations is performed for the theoretical reaction $2\text{A} + 3\text{B} + \text{C} \rightarrow \text{D} + 2\text{E}$.

   When the initial concentration of A is doubled, the rate increases by a factor of 4.

   When the initial concentration of B is doubled, the rate is doubled.

   When the initial concentration of C is doubled, there is no effect on rate. T/I

   (a) What is the order of reaction with respect to each of the reactants? [ans: A = 2, B = 1, C = 0]

   (b) Write the rate law equation for the reaction. [ans: rate = $k[\text{A}]^2[\text{B}]^1$]

2. The reaction represented by the balanced chemical equation

   $\text{CO(g)} + \text{NO}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + \text{NO(g)}$

   is first order with respect to carbon monoxide and first order with respect to nitrogen dioxide. The initial rate of the reaction at 175 °C is 2.5 mol/(L·s) when the concentration of carbon monoxide is 0.025 mol/L and the concentration of nitrogen dioxide is 0.055 mol/L. T/I

   (a) Determine the rate of reaction if the carbon monoxide concentration is doubled with no change in the nitrogen dioxide concentration. [ans: 5.0 mol/(L·s)]

   (b) Determine the rate if the nitrogen dioxide concentration is tripled with no change in carbon monoxide concentration. [ans: 7.5 mol/(L·s)]

   (c) Determine the rate if the carbon monoxide concentration is doubled and the nitrogen dioxide concentration is tripled. [ans: 15 mol/(L·s)]

3. The reaction represented by the balanced chemical equation

   $2\ \text{NO(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\ \text{NOCl(g)}$

   was studied at –10 °C. The initial rate of reaction was determined by measuring the rates of change in the concentrations of NO(g) and Cl_2(g) near the beginning of the reaction **(Table 3)**. T/I

   Table 3 Initial Data from Runs at 25 °C of the Reaction Represented by $2\ \text{NO(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\ \text{NOCl(g)}$

Run	Initial [NO(g)] (mol/L)	Initial [Cl_2(g)] (mol/L)	Initial rate (mol/(L·s))
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.44

(a) What is the rate law equation? [ans: rate = $k[\text{NO(g)}]^2[\text{Cl}_2\text{(g)}]$]
(b) What is the value of the rate constant? [ans: 1.8×10^2 $\text{L}^2/\text{mol}^2{\cdot}\text{s}$]

4. The reaction represented by the balanced chemical equation

$$2\,\text{I}^-(\text{aq}) + \text{S}_2\text{O}_8^{\,2-}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\,\text{SO}_4^{\,2-}(\text{aq})$$

was studied at 25 °C. The initial rate of reaction was determined by measuring the rates of change in the concentrations of I^-(aq) and $\text{S}_2\text{O}_8^{\,2-}$(aq) near the beginning of the reaction **(Table 4)**. T/I

Table 4 Initial Rates from Runs at 25 °C of the Reaction Represented by $2\,\text{I}^-(\text{aq}) + \text{S}_2\text{O}_8^{\,2-}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\,\text{SO}_4^{\,2-}(\text{aq})$

Run	Initial $[\text{I}^-(\text{aq})]$ (mol/L)	Initial $[\text{S}_2\text{O}_8^{\,2-}(\text{aq})]$ (mol/L)	Initial rate (mol/(L·s))
1	0.080	0.040	12.5×10^{-6}
2	0.040	0.040	6.25×10^{-6}
3	0.080	0.020	6.25×10^{-6}
4	0.032	0.040	5.00×10^{-6}
5	0.060	0.030	7.00×10^{-6}

(a) Determine the rate law equation. [ans: rate = $k[\text{I}^-(\text{aq})][\text{S}_2\text{O}_8^{\,2-}(\text{aq})]$]
(b) Calculate a value for the rate constant for each investigation and an average value for the initial rate constant. Include units. [ans: average $k = 3.9 \times 10^{-3}$ L/mol·s]

5. The experimental observations in **Table 5** were obtained for the reaction represented by the following balanced chemical equation:
$2\,\text{A} + \text{B} + 2\,\text{C} \rightarrow 3\,\text{D}$ T/I
(a) What is the order of reaction with respect to each of the reactants? [ans: A = 2, B = 0, C = 1]
(b) Write the rate law equation for the reaction. [ans: rate = $k[\text{A}]^2[\text{C}]$]
(c) Calculate a value for the rate constant, including units. [ans: 0.30 $\text{L}^2/\text{mol}^2{\cdot}\text{s}$]
(d) Calculate the rate of production of D when [A] = [B] = [C] = 0.40 mol/L. [ans: 1.9×10^2 mol/L·s]

Table 5 Initial Rates from Four Runs at 25 °C of the Reaction Represented by $2\,\text{A} + \text{B} \rightarrow 3\,\text{D}$

Run	1	2	3	4
Initial [A] (mol/L)	0.10	0.20	0.10	0.10
Initial [B] (mol/L)	0.10	0.10	0.30	0.10
Initial [C] (mol/L)	0.10	0.10	0.10	0.20
D formation rate (mol/(L·s))	3.0×10^{-4}	1.2×10^{-3}	3.0×10^{-4}	6.0×10^{-3}

Units for *k*

The order of a reaction can be determined from the units of the rate constant, *k*. Rate is always measured in mol/(L·s). Therefore, a first-order reaction has the unit s^{-1} because

$$\text{rate} = k[\text{A}]$$

Inserting units for rate into this expression gives

$$\frac{\text{mol}}{\text{L}{\cdot}\text{s}} = k \times \frac{\text{mol}}{\text{L}}$$

Dividing both sides of this equation by (mol/L) gives

$$\frac{\dfrac{\cancel{\text{mol}}}{\cancel{\text{L}}{\cdot}\text{s}}}{\dfrac{\cancel{\text{mol}}}{\cancel{\text{L}}}} = \frac{k \times \dfrac{\cancel{\text{mol}}}{\cancel{\text{L}}}}{\dfrac{\cancel{\text{mol}}}{\cancel{\text{L}}}}$$

Simplifying,

$$\frac{1}{\text{s}} = k$$

Therefore, *k* for a first-order reaction has units of s^{-1}.

Table 6 contains a summary of the units for *k*. These units vary depending on the total order of reaction. It is useful to go through the same process shown above to check the units for *k* that correspond to each reaction order.

Table 6 Units of *k* by Total Reaction Order

Total reaction order	Units of *k*
0	mol/(L·s)
1	1/s or s^{-1}
2	L/(mol·s)
3	$\text{L}^2/(\text{mol}^2{\cdot}\text{s})$

6.5 Review

Summary

- A rate law equation describes the relationship between the rate of a reaction and reactant concentrations. It follows the general format rate $= k[\text{A}]^m[\text{B}]^n$, where [A] and [B] are the concentrations of reactants, *m* and *n* are the orders of reaction, and *k* is the rate constant. Values of *m*, *n*, and *k* must be determined by experimentation.
- If the exponent of [A] is 1, then the reaction is first order with respect to A. If the exponent of [A] is 2, then the reaction is second order with respect to A, and so on.
- The total order of a reaction can be determined from the rate constant units.

Questions

1. The gas-phase decomposition of dinitrogen pentoxide, represented by the following balanced chemical equation, was studied:

   $2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$

   The initial rate of reaction was determined by measuring the rate of change in the concentration of dinitrogen pentoxide gas, $N_2O_5(g)$, at constant temperature near the beginning of the reaction (**Table 7**).

   Write the rate law equation for the reaction, and calculate the value of the rate constant. K/U T/I

Table 7 Initial Data from Constant Temperature Runs

Run	Initial $[N_2O_5(g)]$ (mol/L)	Initial rate (mol/(L·s))
1	0.0750	8.90×10^{-4}
2	0.190	2.26×10^{-3}
3	0.275	3.26×10^{-3}
4	0.410	4.85×10^{-3}

2. The decomposition of nitrosyl chloride, NOCl(g), represented by the following balanced chemical equation, was studied:

   $2\ NOCl(g) \rightarrow 2\ NO(g) + Cl_2(g)$

   The initial rate of reaction was determined by measuring the rate of change in the concentration of nitrosyl chloride gas at constant temperature near the beginning of the reaction (**Table 8**). K/U T/I

Table 8 Initial Data from Constant-Temperature Runs

Run	Initial [NOCl(g)] (mol/L)	Initial rate (mol/(L·s))
1	3.0×10^{-1}	5.98×10^{4}
2	2.0×10^{-1}	2.66×10^{4}
3	1.0×10^{-1}	6.64×10^{3}
4	4.0×10^{-1}	1.06×10^{5}

   (a) What is the rate law equation?

   (b) Calculate the value of the rate constant.

3. **Table 9** shows experimental data obtained at constant temperature for the reaction described by the following balanced chemical equation:

   $I^-(aq) + OCl^-(aq) \rightarrow IO^-(aq) + Cl^-(aq)$ K/U T/I

Table 9 Initial Data from Constant Temperature Runs

Run	Initial $[I^-(aq)]$ (mol/L)	Initial $[OCl^-(aq)]$ (mol/L)	Initial rate (mol/(L·s))
1	0.12	0.18	7.91×10^{-2}
2	0.060	0.18	3.95×10^{-2}
3	0.090	0.030	9.88×10^{-3}
4	0.090	0.24	7.91×10^{-2}

   (a) What is the rate law equation for this reaction?

   (b) Calculate the value of the rate constant, including units.

   (c) Calculate the initial rate for an investigation where both $[I^-(aq)]$ and $[OCl^-(aq)]$ are initially present at 0.15 mol/L.

4. The rate law equation for a reaction is rate $= k[Cl_2(g)][NO(g)]^2$. K/U T/I

   (a) What is the order of the reaction for each reactant?

   (b) How would the rate change if the initial concentration of $Cl_2(g)$ were tripled?

   (c) How would the rate change if the initial concentration of NO(g) were doubled?

   (d) Calculate the rate constant, *k*, given the following information: initial rate = 0.0242 mol/L·s, initial $[Cl_2(g)] = 0.20$ mol/L, and initial $[NO(g)] = 0.20$ mol/L.

   (e) Calculate the reaction rate predicted for the following conditions: $k = 3.0\ L^2/(mol^2 \cdot s)$, initial $[Cl_2(g)] = 0.44$ mol/L, initial $[NO(g)] = 0.025$ mol/L

Rate Law

6.5

Industries continually search for ways to increase efficiency. Their aim is to maximize output while minimizing costs of production. Achieving this balance requires finding an optimal rate of production.

One strategy industries use to change their production rate is to vary the concentrations of reactants. This strategy requires much experimental work, because chemists cannot predict the effect of changing reactant concentrations on the rate of a reaction simply by looking at a balanced chemical equation. They can only determine rates of reaction from data obtained during experimental testing (**Figure 1**). One goal of this testing is to create a chemical rate law for the reaction. A chemical **rate law** is an equation that connects the rate of a reaction with the concentrations of its reactants at a given temperature and pressure.

Figure 1 To determine how the concentration of a reactant may affect the rate of a reaction, chemists carry out several runs using different initial concentrations, and determine the initial rate resulting from each run. They then compare the results to observe how the initial rate depends on the initial concentrations.

rate law the mathematical expression that allows calculation of reaction rate as a function of reactant concentration

Determining a Rate Law Equation

The concentration of a reactant may affect the rate of a reaction. In most reactions, the concentrations of the reactants and the temperature inside the reaction vessel change as soon as the reaction begins. Therefore, in gathering data to determine a rate law for a reaction, chemists look at the initial concentrations of the reactants at a specified temperature.

Consider the following equation for a chemical reaction:

$$aA + bB \rightarrow \text{products}$$

A and B represent the reactants, and *a* and *b* are the coefficients used to balance the equation. Experimental evidence has shown that the rate of a reaction is proportional to the product of the initial concentrations of the reactants, where each concentration is raised to some exponential value. This can be expressed as

$$\text{rate} \propto [A]^m[B]^n$$

This expression relates the reaction rate to the initial concentrations of reactants using exponents *m* and *n*. Note that exponents in a rate law cannot be obtained from the balanced equation; they can only be determined experimentally. The values of the exponents can be any real number. For the relatively simple reactions we will consider here, however, all exponents will be positive integers or 0.

Instead of using a proportionality sign, we can write the relationship between reactant concentrations and reaction rate as an equation:

$$\text{rate} = k[A]^m[B]^n$$

This equation is called the **rate law equation**. Notice that this equation includes a constant, *k*, known as the **rate constant**. The rate constant is unique for each reaction, and must be determined experimentally. For any reaction, *k* varies with temperature, so the temperature must be kept constant in all runs of an investigation of a chemical reaction carried out to determine the rate law for that reaction.

Each exponent in the rate law equation is called an **order of reaction** with respect to the particular reactant with which it is associated. For example, if the exponent of [A] is 1, then the reaction is *first order* with respect to A. If the exponent of [A] is 2, the reaction is *second order* with respect to A, and so on. The **total order of reaction** is the sum of the individual orders of reaction for each reactant. The orders of reaction can be used to predict reaction rates. Suppose you are given this equation,

$$2A + 2B + 3C \rightarrow \text{products}$$

and are told that the experimental evidence gives the following rate law equation:

$$\text{rate} = k[A]^1[B]^2[C]^0$$

This equation tells us that the rate of the reaction is proportional to each of the initial concentrations of the reactants raised to a given power:

$$\text{rate} \propto [A]^1 \quad \text{rate} \propto [B]^2 \quad \text{rate} \propto [C]^0$$

rate law equation the relationship among rate, the rate constant, the initial concentrations of reactants, and the orders of reaction with respect to the reactants

rate constant determined empirically and is unique for a single reaction at a specified temperature

order of reaction the exponent used to describe the relationship between the initial concentration of a particular reactant and the rate of the reaction

total order of reaction the sum of the exponents in the rate law equation

The rate of the reaction is proportional to [A] raised to the power 1. If the exponent of the concentration of a reactant is 1, when we multiply the initial concentration by 2, the rate will be multiplied by 2^1. When we multiply the initial concentration by 3, the rate will be multiplied by 3^1. Since a number raised to the power 1 is the number itself, when we double the initial concentration, the rate will double; when we triple the initial concentration, the rate will triple; and so on.

The rate of the reaction is proportional to [B] raised to the power 2. A number raised to the power 2 is the number squared. So, if the exponent of the concentration of a reactant is 2, when we double the initial concentration, the rate will be multiplied by 2^2, or 4. When we multiply the initial concentration by 3, the rate will be multiplied by 3^2, or 9, and so on.

The rate of the reaction is proportional to [C] raised to the power 0. Any non-zero number raised to the power 0 is 1. So, if the exponent of the concentration of a reactant is 0, this means that the concentration of that reactant does not affect the rate of reaction. If we double the concentration of the reactant, the rate will be multiplied by $2^0 = 1$. In other words, the rate will not change. Similarly, if we triple the initial concentration of the reactant, the rate will still not change, because the rate will be multiplied by $3^0 = 1$. Since in this reaction the rate does not depend on the initial concentration of (C), we would write the rate law equation as

$$\text{rate} = k[\text{A}]^1[\text{B}]^2$$

We can use graphs to help us recognize the order of reaction with respect to a particular reactant. Plotting experimental data as shown in **Figure 2** and looking for a straight line (indicating a direct relationship) will determine the value of *n*.

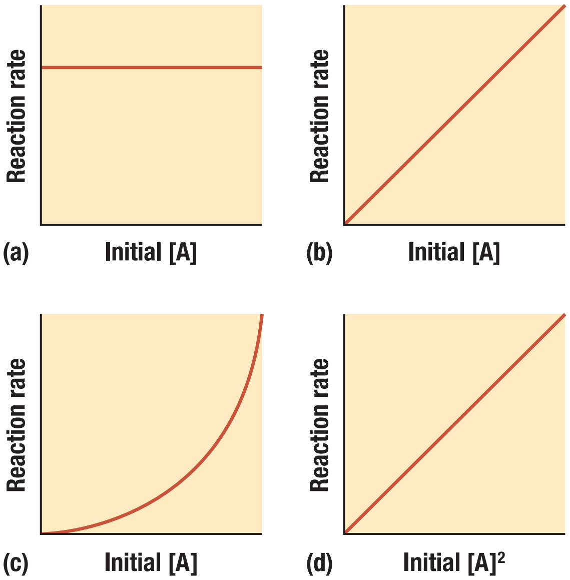


Figure 2 When a series of kinetics experiments is performed on a given system, the rates of reaction are measured for different initial concentrations of a reactant. When the evidence is graphed, you may see one or more of these results.

(a) In this plot, $r \propto [\text{A}]^0$. The reaction is zero order with respect to [A].
(b) In this plot, $r \propto [\text{A}]^1$. The reaction is first order with respect to [A].
(c) In this plot, $r \propto [\text{A}]^n$, where n is greater than 1.
(d) In this plot, $\text{r} \propto [\text{A}]^2$. The reaction is second order with respect to [A].

Chemists commonly use the method of initial rates to determine the rate law equation for a reaction. The **initial rate** of a reaction is the instantaneous rate determined just after the reaction begins (just after $t = 0$ s).

initial rate the rate determined just after the reaction begins (just after $t = 0$ s)

The steps in the method of initial rates are as follows:

1. Measure the instantaneous rate of reaction before there are any significant changes in concentration of the reactants.
2. Carry out several runs using different initial concentrations, determining the initial rate resulting from each run.
3. Compare these results to observe how the initial rate depends on the initial concentrations.

Note that the concentrations of the products are not expressed in the rate law equation. Since we deal with the initial instantaneous rate, we do not worry about the products, because at this stage none or close to none have been formed.

A rate law equation establishes the specific mathematical relationship between the reaction rate for a given reaction and the concentrations of reactants at the start of the reaction. We can use experimentally determined reaction rates to illustrate this. Consider the following chemical equation, which summarizes the reaction between nitric oxide, NO(g), and hydrogen gas, $H_2(g)$:

$$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$$

Table 1 shows several experimentally determined rates for our sample reaction under various initial concentrations of each reactant. In order to determine the value of an exponent of the rate law equation and therefore the effect of the concentration of that reactant on the reaction rate, it is necessary to keep all other variables constant. Therefore, in runs 1 and 2 the concentration of nitric oxide gas was kept constant to see if changes in the concentration of hydrogen gas have an effect on the reaction rate. Likewise, in runs 2 and 3 the concentration of hydrogen gas was kept constant to see if changes in the concentration of nitric oxide gas have an effect on the rate.

Table 1 Initial Rates from Three Investigations for the Reaction at 800 °C Represented by $2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$

Run	Initial [NO(g)] (mol/L)	Initial $[H_2(g)]$ (mol/L)	Initial rate (mol/L·s)
1	0.400	0.100	1.10×10^{-5}
2	0.400	0.200	2.20×10^{-5}
3	0.800	0.200	8.80×10^{-5}

Compare the data shown in the first two runs in Table 1. The nitric oxide gas concentration is identical in both cases; only the hydrogen gas concentration has been changed. Notice what happens to the rate of the reaction when the concentration of nitric oxide gas is kept constant and the concentration of hydrogen gas is doubled—the rate of the reaction doubled from 1.10×10^{-5} to 2.20×10^{-5} mol/L·s. As the concentration of hydrogen gas doubles, the rate doubles, so the reaction rate in runs 1 and 2 is directly proportional to the concentration of hydrogen gas, that is, proportional to the hydrogen gas concentration raised to the power 1:

$$\text{rate} \propto [H_2(g)]^1 \quad \text{or} \quad \text{rate} = k[H_2(g)]^1$$

Next, compare the data shown in runs 2 and 3 in Table 1. In these runs, the hydrogen gas concentration is constant and the nitric oxide gas concentration has been doubled. This time, the reaction rate went up fourfold, from 2.20×10^{-5} to 8.80×10^{-5} mol/L·s. As the concentration of nitrogen monoxide gas doubles, the rate goes up four times. The rate of the reaction in runs 2 and 3 is proportional to the square of the concentration of nitrous oxide gas:

$$\text{rate} \propto [\text{NO(g)}]^2 \quad \text{or} \quad \text{rate} = k[\text{NO(g)}]^2$$

Therefore, the rate law equation for this reaction is

$$\text{rate} = k[\text{NO(g)}]^2[\text{H}_2\text{(g)}]^1$$

The reaction is second order with respect to nitric oxide gas and first order with respect to hydrogen gas. Notice that the exponent for hydrogen gas does not match the coefficient for this reactant in the balanced equation.

Note that the rate constant, *k*, is not a true constant. It varies if you change the temperature of the reaction, add a catalyst, or change the catalyst.

In Tutorial 1. you will use experimental data to analyze a sample reaction. You will write the complete rate law equation for the sample reaction, including the rate constant, *k*, and the order with respect to each reactant.

Tutorial 1 Using Experimental Data to Formulate the Rate Law

In this tutorial, you will use experimental data to determine the rate law equation for a reaction.

Sample Problem 1: Predicting a Rate and Finding the Rate Constant

An investigation indicates that the initial rate of the reaction represented by the equation

$$\text{BrO}_3^-\text{(aq)} + 5\,\text{Br}^-\text{(aq)} + 6\,\text{H}^+\text{(aq)} \rightarrow 3\,\text{Br}_2\text{(l)} + 3\,\text{H}_2\text{O(l)}$$

at 25 °C is 3.2×10^{-3} mol/(L·s) when the initial concentration of bromate, BrO_3^-(aq), is 0.10 mol/L; the initial concentration of bromide, Br^-(aq), is 0.10 mol/L; and the initial concentration of hydrogen ion, H^+(aq), is 0.20 mol/L. The reaction is first order with respect to bromate, first order with respect to bromide, and second order with respect to hydrogen ion. Determine the initial rate of reaction if the initial concentration of hydrogen ion is doubled with no change in the bromate or bromide concentrations, and find the rate constant, *k*.

Given: $[\text{BrO}_3^-\text{(aq)}]_{\text{initial}} = 0.10$ mol/L; $[\text{Br}^-\text{(aq)}]_{\text{initial}} = 0.10$ mol/L; $[\text{H}^+\text{(aq)}]_{\text{initial}} = 0.20$ mol/L; $\text{rate}_{\text{initial}} = 3.2 \times 10^{-3}$ mol/(L·s); orders of reactions

Required: initial rate if $[\text{H}^+\text{(aq)}]_{\text{initial}}$ is doubled, and the rate constant, *k*

Solution:

Step 1. The rate law for the reaction is

$$\text{rate} = k[\text{BrO}_3^-\text{(aq)}]^1[\text{Br}^-\text{(aq)}]^1[\text{H}^+\text{(aq)}]^2$$

Since the rate is second order with respect to hydrogen ion, if the initial concentration of hydrogen ion is doubled (multiplied by 2), the initial rate will be multiplied by 2^2, or 4. The new rate is

$$4 \times (3.2 \times 10^{-3}\ \text{mol/(L·s)}) = 1.3 \times 10^{-2}\ \text{mol/(L·s)}$$

Step 2. To find *k*, rearrange the rate law equation to solve for *k* and enter the values provided:

$$k = \frac{\text{rate}}{[\text{BrO}_3^-\text{(aq)}]^1[\text{Br}^-\text{(aq)}]^1[\text{H}^+\text{(aq)}]^2}$$

$$= \frac{3.2 \times 10^{-3}\,\dfrac{\cancel{\text{mol}}}{\cancel{\text{L}}\cdot\text{s}}}{\left(0.10\,\dfrac{\cancel{\text{mol}}}{\cancel{\text{L}}}\right)\left(0.10\,\dfrac{\text{mol}}{\text{L}}\right)\left(0.20\,\dfrac{\text{mol}}{\text{L}}\right)^2}$$

$$k = 8.0\ \text{L}^3/(\text{mol}^3\cdot\text{s})$$

Statement: If the initial concentration of hydrogen ion is doubled, the initial rate of reaction will be 1.3×10^{-2} mol/(L·s). The rate constant, *k*, is 8.0 $\text{L}^3/(\text{mol}^3\cdot\text{s})$.

Sample Problem 2: Determining the Rate Law Equation

Under acidic conditions, hydrogen peroxide, H_2O_2(aq), oxidizes iodide ions, I^-(aq), to triiodide ions, I_3^-(aq). The balanced equation describing this reaction is

$$H_2O_2(aq) + 3\,I^-(aq) + 2\,H^+(aq) \rightarrow I_3^-(aq) + 2\,H_2O(l)$$

A chemist runs a series of reactions using the method of initial rates. She varies the initial concentrations of the 3 reactants as shown in **Table 2**. Using these data, determine the reaction orders with respect to H_2O_2(aq), I^-(aq), and H^+(aq). State the rate law equation for the reaction.

Table 2 Initial Data from Runs at 25 °C of the Reaction Represented by $H_2O_2(aq) + 3\,I^-(aq) + 2\,H^+(aq) \rightarrow I_3^-(aq) + 2\,H_2O(l)$

Run	Initial [H_2O_2(aq)] (mol/L)	Initial [I^-(aq)] (mol/L)	Initial [H^+(aq)] (mol/L)	Initial rate (mol/(L·s))
1	0.100	0.100	0.00030	1.5×10^{-5}
2	0.200	0.100	0.00030	3.0×10^{-5}
3	0.100	0.200	0.00030	3.0×10^{-5}
4	0.100	0.100	0.00060	1.5×10^{-5}

Given: experimental data provided in Table 2

Required: the order of reaction with respect to each reactant and the rate law equation

Analysis: Use the general form of the rate law equation to begin writing the rate law for this reaction:

$$\text{rate} = k[H_2O_2(aq)]^m[I^-(aq)]^n[H^+(aq)]^p$$

To determine the orders of reaction, look for pairs of data in which the initial concentration of only 1 reactant changes. Then, insert values for m, n, and p into the rate equation along with 1 set of data from the table.

Solution:

Step 1. Find m.

Look at the data from runs 1 and 2, because the initial concentration of hydrogen peroxide changed while the concentrations of iodide and hydrogen remained constant. When the initial concentration of hydrogen peroxide doubled, the rate of reaction doubled. Thus, the rate of reaction and the initial concentration are directly proportional. The exponent m in the rate law equation is therefore 1, and the order of reaction with respect to H_2O_2(aq) is 1.

Step 2. Find n.

Look at the data from runs 1 and 3, because the initial concentration of iodide changed while the concentrations of hydrogen peroxide and hydrogen remained constant. When the initial concentration of iodide doubled, the rate of reaction doubled. The exponent n in the rate law equation is therefore 1, and the order of reaction with respect to I^-(aq) is 1.

Step 3. Find p.

Look at the data from runs 1 and 4, because the initial concentration of hydrogen changed while the concentrations of hydrogen peroxide and iodide remained constant. When the initial concentration of hydrogen doubled, the rate of reaction remained unchanged. The exponent p in the rate law equation is therefore 0, and the order of reaction with respect to H^+(aq) is 0.

Step 4. Therefore, for this reaction,

$$\text{rate} = k[\mathrm{H_2O_2(aq)}]^1[\mathrm{I^-(aq)}]^1[\mathrm{H^+(aq)}]^0$$

The total order of this reaction is

$$\begin{aligned} m + n + p &= 1 + 1 + 0 \\ &= 2 \end{aligned}$$

You do not need to include the exponent when it is 1. Since the exponent of $[\mathrm{H^+(aq)}]$ is 0, the rate does not depend on the initial concentration of hydrogen, so you do not include it in the rate law equation. The rate law equation is

$$\text{rate} = k[\mathrm{H_2O_2(aq)}][\mathrm{I^-(aq)}]$$

Statement: The rate law equation is rate $= k[\mathrm{H_2O_2(aq)}][\mathrm{I^-(aq)}]$. The total order of the reaction is 2.

Investigation **6.5.1**

The Iodine Clock Reaction System (page 392)
Now that you have learned about the rate law equation, you will run experiments to collect the data needed to determine the order of reaction with respect to one of the reactants involved in the reaction of iodate ions and bisulfite ions.

Practice

1. A series of investigations is performed for the theoretical reaction $2\mathrm{A} + 3\mathrm{B} + \mathrm{C} \rightarrow \mathrm{D} + 2\mathrm{E}$.

   When the initial concentration of A is doubled, the rate increases by a factor of 4.

   When the initial concentration of B is doubled, the rate is doubled.

   When the initial concentration of C is doubled, there is no effect on rate. T/I
   (a) What is the order of reaction with respect to each of the reactants? [ans: A = 2, B = 1, C = 0]
   (b) Write the rate law equation for the reaction. [ans: rate = $k[\mathrm{A}]^2[\mathrm{B}]^1$]

2. The reaction represented by the balanced chemical equation

   $\mathrm{CO(g)} + \mathrm{NO_2(g)} \rightarrow \mathrm{CO_2(g)} + \mathrm{NO(g)}$

   is first order with respect to carbon monoxide and first order with respect to nitrogen dioxide. The initial rate of the reaction at 175 °C is 2.5 mol/(L·s) when the concentration of carbon monoxide is 0.025 mol/L and the concentration of nitrogen dioxide is 0.055 mol/L. T/I
   (a) Determine the rate of reaction if the carbon monoxide concentration is doubled with no change in the nitrogen dioxide concentration. [ans: 5.0 mol/(L·s)]
   (b) Determine the rate if the nitrogen dioxide concentration is tripled with no change in carbon monoxide concentration. [ans: 7.5 mol/(L·s)]
   (c) Determine the rate if the carbon monoxide concentration is doubled and the nitrogen dioxide concentration is tripled. [ans: 15 mol/(L·s)]

3. The reaction represented by the balanced chemical equation

   $2\,\mathrm{NO(g)} + \mathrm{Cl_2(g)} \rightarrow 2\,\mathrm{NOCl(g)}$

   was studied at –10 °C. The initial rate of reaction was determined by measuring the rates of change in the concentrations of $\mathrm{NO(g)}$ and $\mathrm{Cl_2(g)}$ near the beginning of the reaction **(Table 3)**. T/I

   Table 3 Initial Data from Runs at 25 °C of the Reaction Represented by $2\,\mathrm{NO(g)} + \mathrm{Cl_2(g)} \rightarrow 2\,\mathrm{NOCl(g)}$

Run	Initial [NO(g)] (mol/L)	Initial [$\mathrm{Cl_2(g)}$] (mol/L)	Initial rate (mol/(L·s))
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.44

(a) What is the rate law equation? [ans: rate = $k[\text{NO(g)}]^2[\text{Cl}_2\text{(g)}]$]

(b) What is the value of the rate constant? [ans: 1.8×10^2 $\text{L}^2/\text{mol}^2\cdot\text{s}$]

4. The reaction represented by the balanced chemical equation

$$2\,\text{I}^-\text{(aq)} + \text{S}_2\text{O}_8^{\,2-}\text{(aq)} \rightarrow \text{I}_2\text{(aq)} + 2\,\text{SO}_4^{\,2-}\text{(aq)}$$

was studied at 25 °C. The initial rate of reaction was determined by measuring the rates of change in the concentrations of I^-(aq) and $\text{S}_2\text{O}_8^{\,2-}$(aq) near the beginning of the reaction (**Table 4**). T/I

Table 4 Initial Rates from Runs at 25 °C of the Reaction Represented by $2\,\text{I}^-\text{(aq)} + \text{S}_2\text{O}_8^{\,2-}\text{(aq)} \rightarrow \text{I}_2\text{(aq)} + 2\,\text{SO}_4^{\,2-}\text{(aq)}$

Run	Initial $[\text{I}^-\text{(aq)}]$ (mol/L)	Initial $[\text{S}_2\text{O}_8^{\,2-}\text{(aq)}]$ (mol/L)	Initial rate (mol/(L·s))
1	0.080	0.040	12.5×10^{-6}
2	0.040	0.040	6.25×10^{-6}
3	0.080	0.020	6.25×10^{-6}
4	0.032	0.040	5.00×10^{-6}
5	0.060	0.030	7.00×10^{-6}

(a) Determine the rate law equation. [ans: rate = $k[\text{I}^-\text{(aq)}][\text{S}_2\text{O}_8^{\,2-}\text{(aq)}]$]

(b) Calculate a value for the rate constant for each investigation and an average value for the initial rate constant. Include units. [ans: average $k = 3.9 \times 10^{-3}$ L/mol·s]

5. The experimental observations in **Table 5** were obtained for the reaction represented by the following balanced chemical equation:

$2\,\text{A} + \text{B} + 2\,\text{C} \rightarrow 3\,\text{D}$ T/I

(a) What is the order of reaction with respect to each of the reactants? [ans: A = 2, B = 0, C = 1]

(b) Write the rate law equation for the reaction. [ans: rate = $k[\text{A}]^2[\text{C}]$]

(c) Calculate a value for the rate constant, including units. [ans: 0.30 $\text{L}^2/\text{mol}^2\cdot\text{s}$]

(d) Calculate the rate of production of D when [A] = [B] = [C] = 0.40 mol/L. [ans: 1.9×10^2 mol/L·s]

Table 5 Initial Rates from Four Runs at 25 °C of the Reaction Represented by $2\,\text{A} + \text{B} \rightarrow 3\,\text{D}$

Run	1	2	3	4
Initial [A] (mol/L)	0.10	0.20	0.10	0.10
Initial [B] (mol/L)	0.10	0.10	0.30	0.10
Initial [C] (mol/L)	0.10	0.10	0.10	0.20
D formation rate (mol/(L·s))	3.0×10^{-4}	1.2×10^{-3}	3.0×10^{-4}	6.0×10^{-3}

Units for *k*

The order of a reaction can be determined from the units of the rate constant, *k*. Rate is always measured in mol/(L·s). Therefore, a first-order reaction has the unit s^{-1} because

$$\text{rate} = k[\text{A}]$$

Inserting units for rate into this expression gives

$$\frac{\text{mol}}{\text{L}\cdot\text{s}} = k \times \frac{\text{mol}}{\text{L}}$$

Dividing both sides of this equation by (mol/L) gives

$$\frac{\dfrac{\cancel{\text{mol}}}{\cancel{\text{L}}\cdot\text{s}}}{\cancel{\dfrac{\text{mol}}{\text{L}}}} = \frac{k \times \cancel{\dfrac{\text{mol}}{\text{L}}}}{\cancel{\dfrac{\text{mol}}{\text{L}}}}$$

Simplifying,

$$\frac{1}{\text{s}} = k$$

Therefore, *k* for a first-order reaction has units of s^{-1}.

Table 6 contains a summary of the units for *k*. These units vary depending on the total order of reaction. It is useful to go through the same process shown above to check the units for *k* that correspond to each reaction order.

Table 6 Units of *k* by Total Reaction Order

Total reaction order	Units of *k*
0	mol/(L·s)
1	1/s or s^{-1}
2	L/(mol·s)
3	$\text{L}^2/(\text{mol}^2\cdot\text{s})$

6.5 Review

Summary

- A rate law equation describes the relationship between the rate of a reaction and reactant concentrations. It follows the general format rate $= k[\mathrm{A}]^m[\mathrm{B}]^n$, where [A] and [B] are the concentrations of reactants, *m* and *n* are the orders of reaction, and *k* is the rate constant. Values of *m*, *n*, and *k* must be determined by experimentation.
- If the exponent of [A] is 1, then the reaction is first order with respect to A. If the exponent of [A] is 2, then the reaction is second order with respect to A, and so on.
- The total order of a reaction can be determined from the rate constant units.

Questions

1. The gas-phase decomposition of dinitrogen pentoxide, represented by the following balanced chemical equation, was studied:

   $2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$

   The initial rate of reaction was determined by measuring the rate of change in the concentration of dinitrogen pentoxide gas, $N_2O_5(g)$, at constant temperature near the beginning of the reaction (**Table 7**).

   Write the rate law equation for the reaction, and calculate the value of the rate constant. K/U T/I

Table 7 Initial Data from Constant Temperature Runs

Run	Initial $[N_2O_5(g)]$ (mol/L)	Initial rate (mol/(L·s))
1	0.0750	8.90×10^{-4}
2	0.190	2.26×10^{-3}
3	0.275	3.26×10^{-3}
4	0.410	4.85×10^{-3}

2. The decomposition of nitrosyl chloride, NOCl(g), represented by the following balanced chemical equation, was studied:

   $2\ NOCl(g) \rightarrow 2\ NO(g) + Cl_2(g)$

   The initial rate of reaction was determined by measuring the rate of change in the concentration of nitrosyl chloride gas at constant temperature near the beginning of the reaction (**Table 8**). K/U T/I

Table 8 Initial Data from Constant-Temperature Runs

Run	Initial [NOCl(g)] (mol/L)	Initial rate (mol/(L·s))
1	3.0×10^{-1}	5.98×10^{4}
2	2.0×10^{-1}	2.66×10^{4}
3	1.0×10^{-1}	6.64×10^{3}
4	4.0×10^{-1}	1.06×10^{5}

   (a) What is the rate law equation?
   (b) Calculate the value of the rate constant.

3. **Table 9** shows experimental data obtained at constant temperature for the reaction described by the following balanced chemical equation:

   $I^-(aq) + OCl^-(aq) \rightarrow IO^-(aq) + Cl^-(aq)$ K/U T/I

Table 9 Initial Data from Constant Temperature Runs

Run	Initial $[I^-(aq]$ (mol/L)	Initial $[OCl^-(aq]$ (mol/L)	Initial rate (mol/(L·s))
1	0.12	0.18	7.91×10^{-2}
2	0.060	0.18	3.95×10^{-2}
3	0.090	0.030	9.88×10^{-3}
4	0.090	0.24	7.91×10^{-2}

   (a) What is the rate law equation for this reaction?
   (b) Calculate the value of the rate constant, including units.
   (c) Calculate the initial rate for an investigation where both $[I^-(aq)]$ and $[OCl^-(aq)]$ are initially present at 0.15 mol/L.

4. The rate law equation for a reaction is rate $= k[Cl_2(g)][NO(g)]^2$. K/U T/I

   (a) What is the order of the reaction for each reactant?
   (b) How would the rate change if the initial concentration of $Cl_2(g)$ were tripled?
   (c) How would the rate change if the initial concentration of NO(g) were doubled?
   (d) Calculate the rate constant, *k*, given the following information: initial rate = 0.0242 mol/L·s, initial $[Cl_2(g)] = 0.20$ mol/L, and initial $[NO(g)] = 0.20$ mol/L.
   (e) Calculate the reaction rate predicted for the following conditions: $k = 3.0\ L^2/(mol^2 \cdot s)$, initial $[Cl_2(g)] = 0.44$ mol/L, initial $[NO(g)] = 0.025$ mol/L

Reaction Mechanisms

6.6

To get from home to a concert, you might walk a few blocks, take a bus, transfer to the subway, and then walk a few more blocks. If you tell a friend you are going from home to the concert, this gives information about where you will be starting from and where you will end up, but not where you will be and what you will be doing in the stages in between. Like the trip from home to the concert, chemical reactions rarely occur in a single step.

What Is a Reaction Mechanism?

Balanced chemical equations provide an overall summary of a chemical reaction. They provide information about the types of reactants and products as well as their stoichiometric relationships. However, chemists think that most chemical reactions occur by a sequence of simpler reactions. An **elementary step** is a step that only involves one-, two-, or three-entity collisions and that cannot be explained in terms of simpler reactions. A **reaction mechanism** is the series of elementary steps by which the chemical reaction occurs. Chemists perform experiments that provide clues about the steps of a reaction mechanism.

elementary step a step involving a one-, two-, or three-entity collision that cannot be explained by simpler reactions

reaction mechanism a series of elementary steps by which a chemical reaction occurs

To understand a chemical reaction completely, we must know its mechanism. However, reaction mechanisms cannot be 100 % confirmed. One of the main purposes for studying reaction rates is to learn as much as possible about the steps involved in a chemical reaction.

Consider the reaction between gaseous nitrogen dioxide and carbon monoxide. The overall balanced chemical equation that summarizes this chemical reaction is

$$\mathrm{NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)}$$

The rate law equation for this reaction has been determined experimentally to be

$$\text{rate} = k[\mathrm{NO_2(g)}]^2$$

The mechanism of the reaction is thought to involve the following two elementary steps, or elementary reactions.

$$\text{Step 1: } \mathrm{NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g)} \quad \text{slow step}$$

$$\text{Step 2: } \mathrm{NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)} \quad \text{fast step}$$

Experiments show that the first step in this reaction mechanism is much slower than the second step. Since the first step is the slowest step in the reaction mechanism, the overall reaction must proceed at the rate of the first step. That is, the products of the overall reaction, gaseous nitrogen dioxide and carbon dioxide, can be produced only as fast as the slowest step, Step 1. Step 1 is therefore called the **rate-determining step**, which is the step in a reaction mechanism that determines the rate of the overall reaction.

rate-determining step the step in a reaction mechanism that determines the rate of the overall reaction; the slowest step in a reaction mechanism

In this mechanism, gaseous nitrogen trioxide, $\mathrm{NO_3(g)}$, is a reaction intermediate. A **reaction intermediate** is an entity that is neither a reactant nor a product but is formed and consumed during the reaction sequence. Note that when the two steps are combined, the resulting equation is the overall balanced chemical equation for the reaction:

reaction intermediate an entity that is neither a reactant nor a product but is formed and consumed during the reaction sequence

$$\mathrm{NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)}$$

Step 1 in the mechanism for the reaction between nitrogen dioxide and carbon monoxide has two reactant molecules, as does Step 2. Most reaction steps have either 1 or 2 reactant entities. Reaction steps that involve only 1 reactant entity include those in which a single entity collides with the sides of the container and breaks apart into smaller entities.

Elementary steps involving 3 reactant molecules are very rare. Why? According to collision theory, a chemical reaction must involve collision of chemical entities with each other or the walls of the container. Logical analysis and calculations indicate that collisions of 3 entities simultaneously must be much less frequent than collisions of 2 entities. Picture yourself in a circle of friends, tossing Velcro-covered Ping-Pong balls toward the centre of the circle. The chances of any 2 balls colliding and sticking together in the air is small: the probability of 3 balls colliding and sticking together is much smaller still.

Rate law equations cannot be written using information from an overall balanced equation for a reaction. However, rate law equations can be written directly from the balanced equations representing elementary steps. Examples of the common types of elementary steps and the corresponding rate law equations are shown in **Table 1**. Notice that the rate law equation for an elementary step with 1 reactant molecule is always first order, and the rate law equation for an elementary step with 2 reactant molecules is always second order, either of the form $k[\mathrm{A}]^2$ for a step with a single reactant or of the form $k[\mathrm{A}][\mathrm{B}]$ for a step involving 2 reactants.

Table 1 Examples of Elementary Steps

Elementary step	Rate law equation
$\mathrm{A} \rightarrow$ products	rate $= k[\mathrm{A}]$
$\mathrm{A} + \mathrm{A} \rightarrow$ products	rate $= k[\mathrm{A}]^2$
$\mathrm{A} + \mathrm{B} \rightarrow$ products	rate $= k[\mathrm{A}][\mathrm{B}]$

We may now describe the requirements of a plausible reaction mechanism. To be plausible, a reaction mechanism must satisfy two requirements:

1. Summing the elementary steps in the reaction mechanism must give the overall balanced equation for the reaction.
2. The reaction mechanism must agree with the experimentally determined rate law.

To see how these requirements are applied, we will consider the reaction mechanism given previously for the reaction between nitrogen dioxide gas and carbon monoxide gas. The following equations show that the sum of the two steps gives the overall balanced equation.

$$\mathrm{NO_2(g)} + \mathrm{NO_2(g)} \rightarrow \mathrm{NO_3(g)} + \mathrm{NO(g)}$$

$$\mathrm{NO_3(g)} + \mathrm{CO(g)} \rightarrow \mathrm{NO_2(g)} + \mathrm{CO_2(g)}$$

$$\cancel{\mathrm{NO_2(g)}} + \mathrm{NO_2(g)} + \cancel{\mathrm{NO_3(g)}} + \mathrm{CO(g)} \rightarrow \cancel{\mathrm{NO_3(g)}} + \mathrm{NO(g)} + \cancel{\mathrm{NO_2(g)}} + \mathrm{CO_2(g)}$$

Overall reaction: $\mathrm{NO_2(g)} + \mathrm{CO(g)} \rightarrow \mathrm{NO(g)} + \mathrm{CO_2(g)}$

The first requirement for a correct mechanism is therefore met. To determine whether the mechanism meets the second requirement, we need to evaluate the rate-determining step. Recall that experiments show that the first step in this reaction is much slower than the second step. Why? The theoretical interpretation is that the first elementary step is relatively slow because it has a fairly high activation energy. The rate of the overall reaction is primarily controlled by the rate of this step, just as the slowest part of a journey to a concert might be the bus ride.

The first elementary step of this reaction mechanism is the rate-determining step,

$$NO_2(g) + NO_2(g) \xrightarrow{k_1} \text{products}$$

so the rate law equation will be

$$\text{overall rate} = k_1[NO_2]^2$$

This rate law equation agrees with the experimentally determined rate law equation given earlier,

$$\text{rate} = k[NO_2(g)]^2$$

Therefore, this reaction mechanism satisfies the two requirements stated above. Experimental evidence can be used to confirm or refute this reaction mechanism.

Tutorial 1 Evaluating a Rate Law Mechanism

In this tutorial, you will use rate law equations to evaluate the plausibility of a proposed reaction mechanism and then use the rate law to identify the rate-limiting step in a reaction mechanism.

Sample Problem 1: Using the Experimental Rate Law Equation

Nitryl fluoride gas, $NO_2F(g)$, is a strong oxidizer that is sometimes used as rocket propellant (**Figure 1**). Nitryl fluoride gas can be synthesized from gaseous nitrogen dioxide and fluorine. The balanced equation for the reaction of nitrogen dioxide gas and fluorine gas is

$$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$$

The experimentally determined rate law equation is

$$\text{rate} = k[NO_2(g)][F_2(g)]$$

A suggested mechanism for this reaction is

$$NO_2(g) + F_2(g) \xrightarrow{k_1} NO_2F(g) + F(g) \quad \text{slow}$$

$$NO_2(g) + F(g) \xrightarrow{k_2} NO_2F(g) \quad \text{fast}$$

Does this mechanism satisfy the two requirements for a plausible reaction mechanism?

Solution

Step 1. Analyze the first requirement. Add the two elementary steps given for the mechanism to determine whether the sum yields the balanced equation for the overall reaction.

$$\begin{array}{r}
NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g) \\
F(g) + NO_2(g) \rightarrow NO_2F(g) \\
\hline
2\ NO_2(g) + F_2(g) + \cancel{F(g)} \rightarrow 2\ NO_{2F}(g) + \cancel{F(g)}
\end{array}$$

Overall reaction: $2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$

The first requirement has been met.

Step 2. Analyze the second requirement. Determine whether the mechanism agrees with the experimentally determined rate law equation. Since the proposed mechanism states that the first step is rate determining, the overall reaction rate must be defined by the first step. The rate law equation for the first step is

$$\text{rate} = k[NO_2(g)][F_2(g)]$$

This has the same form as the experimentally determined rate law, meaning that the second requirement has been met.

Statement: The proposed reaction mechanism satisfies both requirements for a plausible reaction mechanism.

Figure 1 Rocket propellants, such as nitryl fluoride gas, provide the thrust to counteract the force of gravity.

UNIT TASK BOOKMARK

How will you apply what you have learned about reaction mechanism and rate-determining steps to the Unit Task described on page 402?

Sample Problem 2: Identifying the Rate-Determining Step

The rate law of a chemical reaction was found to be

$\text{rate} = k[\text{NO(g)}][\text{Cl}_2\text{(g)}]$

The following elementary steps have been proposed:

$\text{NO(g)} + \text{Cl}_2\text{(g)} \rightarrow \text{NOCl}_2\text{(g)}$

$\text{NOCl}_2\text{(g)} + \text{NO(g)} \rightarrow 2\ \text{NOCl(g)}$

(a) Determine the overall reaction.

(b) Identify any reaction intermediates.

(c) Determine the slowest step in the mechanism. Explain your choice.

(d) Determine the rate law equation for the fast step.

Solution:

(a)

$$\begin{array}{r} \text{NO(g)} + \text{Cl}_2\text{(g)} \rightarrow \text{NOCl}_2\text{(g)} \\ \text{NOCl}_2\text{(g)} + \text{NO(g)} \rightarrow 2\ \text{NOCl(g)} \\ \hline \text{NO(g)} + \text{Cl}_2\text{(g)} + \cancel{\text{NOCl}_2\text{(g)}} + \text{NO(g)} \rightarrow 2\ \text{NOCl(g)} + \cancel{\text{NOCl}_2\text{(g)}} \end{array}$$

Overall reaction: $2\ \text{NO(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\ \text{NOCl(g)}$

(b) The reaction intermediate is NOCl_2(g).

(c) The experimentally determined rate law for the overall reaction indicates that the first step is rate determining, because it matches the rate law written for this elementary step.

(d) $\text{rate} = k[\text{NOCl}_2\text{(g)}][\text{NO(g)}]$

Practice

1. Write the rate law equations for the following elementary reactions: T/I
   (a) $\text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)} \rightarrow \text{AgCl(s)}$ [ans: $\text{rate} = k[\text{Ag}^+\text{(aq)}][\text{Cl}^-\text{(aq)}]$]
   (b) $\text{O}_3\text{(g)} + \text{NO(g)} \rightarrow \text{O}_2\text{(g)} + \text{NO}_2\text{(g)}$ [ans: $\text{rate} = k[\text{O}_3\text{(g)}][\text{NO(g)}]$]
   (c) $\text{O}_3\text{(g)} \rightarrow \text{O}_2\text{(g)} + \text{O(g)}$ [ans: $\text{rate} = k[\text{O}_3\text{(g)}]$]
   (d) $\text{O}_3\text{(g)} + \text{O(g)} \rightarrow 2\ \text{O}_2\text{(g)}$ [ans: $\text{rate} = k[\text{O}_3\text{(g)}][\text{O(g)}]$]

2. A proposed mechanism for the reaction between iodine chloride gas, ICl(g), and hydrogen gas, H_2(g), is
   $\text{ICl(g)} + \text{H}_2\text{(g)} \rightarrow \text{HI(g)} + \text{HCl(g)}$ slow
   $\text{HI(g)} + \text{ICl(g)} \rightarrow \text{HCl(g)} + \text{I}_2\text{(g)}$ fast K/U T/I
   (a) Determine the overall reaction. [ans: $2\ \text{ICl(g)} + \text{H}_2\text{(g)} \rightarrow 2\ \text{HCl(g)} + \text{I}_2\text{(g)}$]
   (b) The rate law equation was experimentally determined to be $\text{rate} = k[\text{ICl(g)}]^2[\text{H}_2]$. Does the proposed mechanism agree with the rate law equation? If it does agree, explain why.

3. A two-step reaction is outlined below:
   $\text{I}_2\text{(g)} \rightarrow 2\ \text{I(g)}$ slow
   $\text{H}_2\text{(g)} + 2\ \text{I(g)} \rightarrow 2\ \text{HI(g)}$ fast K/U T/I
   (a) What is the overall reaction? [ans: $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightarrow 2\ \text{HI(g)}$]
   (b) Are there any intermediates? What are they? [ans: I(g)]
   (c) What is the rate law equation if the proposed mechanism is correct? [ans: $\text{rate} = k[\text{I}_2\text{(g)}]$]

6.6 Review

Summary

- Most chemical reactions occur in a series of elementary steps. The sequence of elementary steps making up a reaction is known as its reaction mechanism.
- A rate law equation can be written for each elementary step of a reaction, and the overall rate law equation for a reaction may be deduced from these.
- The slowest elementary step in a reaction mechanism is the rate-determining step.
- There are two requirements for a plausible reaction mechanism:
  1. The elementary steps must combine to give the correct overall balanced equation.
  2. The mechanism must agree with the experimentally determined rate law equation.

Questions

1. Define each of the following terms: K/U
   (a) elementary step
   (b) reaction mechanism
   (c) reaction intermediate
   (d) rate-determining step
2. Using an example from your daily life as an analogy, explain the concepts of reaction mechanism and rate-determining step. Try to use an analogy that includes a reaction intermediate as well. C A
3. The following reaction can occur between iodine fluoride and hydrogen:

   $2\,\text{IF(g)} + \text{H}_2\text{(g)} \rightarrow 2\,\text{HF(g)} + \text{I}_2\text{(g)}$

   One of your classmates thinks that this is probably a one-step reaction. Explain why this is unlikely. K/U
4. A proposed mechanism for a reaction is

   $\text{O}_3\text{(g)} \rightarrow \text{O}_2\text{(g)} + \text{O(g)}$ fast

   $\text{O}_3\text{(g)} + \text{O(g)} \rightarrow 2\text{O}_2\text{(g)}$ slow K/U T/I

   (a) Write the rate law equation expected for this reaction mechanism.
   (b) What is the overall balanced chemical equation for the reaction?
   (c) What is the intermediate in the proposed reaction mechanism?
5. A proposed mechanism for a reaction is

   $\text{C}_4\text{H}_9\text{Br(aq)} \rightarrow \text{C}_4\text{H}_9^+\text{(aq)} + \text{Br}^-\text{(aq)}$ slow

   $\text{C}_4\text{H}_9^+\text{(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{C}_4\text{H}_9\text{OH}_2^+\text{(aq)}$ fast

   $\text{C}_4\text{H}_9\text{OH}_2^+\text{(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{H}_3\text{O}^+\text{(aq)}$ fast K/U T/I

   (a) Write the rate law equation expected for this reaction mechanism.
   (b) What is the overall balanced chemical equation for the reaction?
   (c) What are the intermediates in the proposed reaction mechanism?
6. What two requirements must be met for a mechanism to be plausible? K/U
7. A friend of yours says, "A balanced equation describes how chemical entities interact. Therefore, we can determine a rate law equation directly from an overall balanced equation." Evaluate your friend's explanation. K/U T/I
8. The steps of a proposed reaction mechanism for a reaction are

   $\text{NO(g)} + \text{NO(g)} \rightarrow \text{N}_2\text{O}_2\text{(g)}$

   $\text{N}_2\text{O}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$ K/U T/I

   (a) What is the overall balanced chemical equation for the reaction?
   (b) What is the intermediate in the proposed reaction mechanism?
   (c) The rate law equation was experimentally determined to be rate $= k[\text{NO}]^2[\text{O}_2]$. If this mechanism is correct, which is the rate-determining step?
9. A proposed mechanism for a reaction is

   $\text{NH}_4^+\text{(aq)} \rightarrow \text{NH}_3\text{(aq)} + \text{H}^+\text{(aq)}$ fast

   $\text{H}^+\text{(aq)} + \text{HNO}_2\text{(aq)} \rightarrow \text{H}_2\text{O(l)} + \text{NO}^+\text{(aq)}$ fast

   $\text{NH}_3\text{(aq)} + \text{NO}^+\text{(aq)} \rightarrow \text{NH}_3\text{NO}^+\text{(aq)}$ slow

   $\text{NH}_3\text{NO}^+\text{(aq)} \rightarrow \text{N}_2\text{(g)} + \text{H}_2\text{O(l)} + \text{H}^+\text{(aq)}$ fast

   K/U T/I

   (a) What is the overall balanced chemical equation for the reaction?
   (b) What are the intermediates in the proposed reaction mechanism?
   (c) The rate law equation was determined to be rate $= k[\text{HNO}_2\text{(aq)}][\text{NH}_4^+\text{(aq)}]$. Is the proposed mechanism plausible? Support your answer.

Global Warming and Reaction Rates

SKILLS HANDBOOK A4, A5.1

ABSTRACT

Greenhouse gases absorb energy from solar radiation and store it as thermal energy. Atmospheric concentrations of greenhouse gases are increasing, which is complicating efforts to limit global warming. In 2009, the G8 (six of the world's major economies, plus Canada and Russia) set a goal to keep the average global temperature within 2 °C of the pre-industrial level of 14.4 °C. Through this goal, the G8 hope to minimize the negative consequences of global warming. Important to this goal are gases that persist in the upper atmosphere, which can make a significant contribution to global warming even in low concentrations. Also, some "super" greenhouse gases have a global warming potential significantly higher than that of carbon dioxide. An understanding of the average lifespan of these super greenhouse gases therefore is needed to better manage the contribution of these gases to global warming.

Global warming is an increase in Earth's average temperature. We are presently in a period of global warming, which is leading to climate change. In 2009, representatives of the G8 countries met in Copenhagen, Denmark, and agreed to limit global warming so that, by 2020, Earth's average temperature will have risen no more than 2 °C above pre-industrial levels. In other words, the average global temperature would be no higher than 16.4 °C. Since the G8 is composed of the world's six largest economies plus Canada and Russia, reaching this limit could have profound effects on the whole planet. European countries had made a similar agreement in 1996.

The global warming we are currently experiencing is due in large part to increases in the concentration of greenhouse gases in the atmosphere. A greenhouse gas is any gas that absorbs incoming solar radiation and infrared radiation re-irradiated from Earth's surface and stores it. Some of this stored energy is re-emitted as infrared radiation back to Earth's surface. This process is called the greenhouse effect. Without the greenhouse effect, Earth would be too cold to support life as we know it. However, since the Industrial Revolution of the 1800s, many human activities have caused a large increase in the concentration of greenhouse gases. The atmosphere can therefore store and re-emit more energy and, as a result, Earth is getting warmer. Scientists believe that an increase beyond the 2 °C mark agreed upon by the G8 will likely cause dramatic, irreversible climate change.

The most abundant greenhouse gases are water vapour, $H_2O(g)$; carbon dioxide, $CO_2(g)$; methane, $CH_4(g)$; nitrous oxide, $N_2O(g)$; and ozone, $O_3(g)$. Evidence supports the idea that the increased atmospheric concentration of each of these gases is related to increases in industrial activity. For example, combustion of fossil fuels releases large quantities of carbon dioxide gas as well as water vapour (**Figure 1**).

Figure 1 Every combustion reaction of a fossil fuel releases carbon dioxide and water vapour into the atmosphere

Global Warming Potential

It is not just the general concentration of greenhouse gases in the atmosphere that affects global warming. Each gas has a particular ability to capture, store, and return energy back to Earth's surface. Further, each gas remains in the atmosphere for a distinct length of time, which depends on the reaction rate of its decomposition. To compare the contribution of different gases to global warming, scientists came up with the concept of global warming potential (GWP). GWP is the ratio of the quantity of energy stored by a certain mass of a greenhouse gas (for example, 1 kg of methane) to the quantity of thermal energy stored by the same mass of carbon dioxide, usually over 100 years. The GWP of a gas is affected both by its ability to absorb energy and its lifetime in the atmosphere. **Table 1** shows the GWP and average atmospheric lifespan of several greenhouse gases produced by human activity.

Table 1 Global Warming Potential and Average Lifespan of Some Atmospheric Gases

Greenhouse gas	GWP over 100 years	Average atmospheric lifespan (years)
carbon dioxide	1	50–200
methane	25	12
nitrous oxide	298	120

Figure 2 The greenhouse gas nitrogen trifluoride is used in the manufacture of energy-efficient LCD televisions.

New Greenhouse Gases

Human activities continue to release greenhouse gases, some of which have never been in the atmosphere. For example, in 2010 scientists found three new "super" greenhouse gases in the atmosphere: sulfuryl fluoride, $SO_2F_2(g)$, trifluoromethyl sulfur pentafluoride, $SF_5CF_3(g)$, and nitrogen trifluoride, $NF_3(g)$. These synthetic substances have extremely high GWP. For example, the GWP of nitrogen trifluoride is reported to be 17 200 over 100 years! These three gases have only recently been manufactured and their atmospheric concentrations are increasing. Sulfuryl fluoride is a fumigant used in pest control, which was believed to be more environmentally friendly than older fumigants. Trifluoromethyl sulfur pentafluoride is likely released from electronic devices and microchips as a by-product. Nitrogen trifluoride is used in the electronics industry for plasma etching and equipment cleaning (**Figure 2**). This gas replaced perfluorocarbons, which damage Earth's ozone layer. The ozone layer filters out much of the damaging ultraviolet rays in solar radiation.

Why do these gases have such high GWP values? Any substance with polar bonds can absorb the infrared portion of solar radiation very efficiently. These three gases are all fluorinated compounds, and fluorine atoms have the highest electronegativity of any element. As a result, they form highly polar bonds with sulfur and carbon, which are found in these three gases. These three gases can absorb and store a lot of energy. All fluorinated compounds also have very slow rates of decomposition, so they will persist in the atmosphere for a very long time.

Faster Decomposition, Slower Global Warming?

Progress in limiting global warming and, hopefully, climate change, depends on finding more environmentally friendly substitutes for harmful substances and continuing to monitor for harmful effects. In one approach, scientists are making progress in finding other fluorinated compounds or appropriate substitutes that will decompose at a much faster rate than those used currently. These new substances will not last as long in the atmosphere. They may even absorb less infrared radiation than fluorinated compounds used today. A second approach is to look for ways to speed up the rate of the decomposition reactions of greenhouse gases. Such studies must be done very carefully, however, since we already know that altering the gases in our atmosphere can have unforeseen consequences.

Further Reading

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Canadian Space Agency. (2010, May 3). NASA, Purdue study offers recipe for global warming-free industrial materials. *SpaceRef*.

6.7 Questions

1. Why is the 2 °C limit to an increase in Earth's average temperature so important? K/U A
2. Describe how limits in scientific understanding affected the choice to use the three super greenhouse gases. T/I
3. Do you think that the people who approved the use of these super gases should be held accountable for their potential effect on global warming? Give reasons for your answer. T/I A
4. Conduct research to find out if scientists have made any progress in increasing the decomposition rate of any greenhouse gases. Report your findings to the class. C A

WEB LINK

CHAPTER 6 Investigations

Investigation 6.1.1 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Reaction Rates

Limestone is composed mainly of calcium carbonate, $CaCO_3(s)$. Limestone formations are also geological indicators of petroleum deposits. Geologists use hydrochloric acid in a field test to detect limestone (**Figure 1**). The reaction between hydrochloric acid and calcium carbonate produces carbon dioxide gas:

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Figure 1 A positive reaction to hydrochloric acid indicates the presence of calcium carbonate in a geological sample.

Purpose

To determine the reaction rate at various points during the reaction of hydrochloric acid and calcium carbonate, using given data

Hypothesis/Prediction

SKILLS HANDBOOK A2.1

Write a hypothesis that explains the change in rate of a chemical reaction over time. Then, write a prediction for the shape of the curve for the given data, based on this hypothesis.

Procedure

SKILLS HANDBOOK A6.5

1. Using the data in **Table 1**, plot a graph of the concentration of hydrochloric acid over time (6 min).
2. Calculate the average rate of consumption of hydrochloric acid from 0 s to 120 s and from 180 s to 300 s.
3. Calculate the instantaneous rate of consumption of hydrochloric acid at 60 s and 240 s.

Table 1 Concentration of Hydrochloric Acid Over Time

[HCl(aq)] (mol/L)	Time (s)
1.90	0.0
1.40	60.0
1.10	120.0
0.90	180.0
0.80	240.0
0.75	300.0
0.72	360.0

Analyze and Evaluate

SKILLS HANDBOOK A2.4

(a) What variables were recorded in this investigation? What type of relationship was being tested? T/I

(b) Describe in words the change in reaction rates determined in Steps 2 and 3. T/I

(c) Calculate the slope of the line. What does this represent? T/I

(d) Using your graph, determine the instantaneous reaction rate of hydrochloric acid with calcium carbonate at

(i) 1 min

(ii) 2 min

(iii) 6 min T/I C

(e) What are the possible sources for error in your analysis of the data? T/I

Apply and Extend

(f) To determine the concentration of hydrochloric acid at the different times, an investigator measured the pH of the solution. Referring to the chemical equation, suggest other ways that could be used to determine the rate of this reaction at various points. T/I

Investigation 6.2.1 CONTROLLED EXPERIMENT

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Factors Affecting the Rate of Chemical Reactions

There are five factors that affect reaction rate: concentration, nature of the reactant, surface area, catalysts, and temperature. In this investigation, you will explore factors that might increase the rate of a particular reaction. You will choose one of the following chemical reactions to investigate:

Metals react with acids as follows:

$$X(s) + H_2SO_4(aq) \rightarrow XSO_4(aq) + H_2(g)$$

Carbonate or carbonate salts react with acids as follows:

$$XCO_3(s) + 2\,HCl(aq) \rightarrow XCl_2(aq) + H_2O(g) + CO_2(g)$$

Hydrogen peroxide decomposes as follows:

$$2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g)$$

Testable Question

SKILLS HANDBOOK A2.2

Write an appropriate question that you will attempt to answer in this investigation. Your question must state the manipulated and responding variables.

Hypothesis/Prediction

Write a hypothesis outlining how the factor or factors you have chosen affect chemical reaction rates. Then, predict the results of your investigation based on this hypothesis.

Variables

Identify all major independent, dependent, and controlled variables in your investigation.

Experimental Design

SKILLS HANDBOOK A2.1

Describe your experimental set-up and procedure in one paragraph. Include the manipulated, responding, and controlled variables.

Equipment and Materials

SKILLS HANDBOOK A1.2

- chemical safety goggles
- lab apron
- all necessary chemicals and equipment
- MSDS for the chemicals

Hydrochloric acid is corrosive and poisonous. Avoid splashing it on your skin, in your eyes, or on clothing. Immediately rinse any spills with plenty of cool water and inform your teacher of the spill. Carefully follow your teacher's instructions for disposal.

Hydrogen peroxide solutions should be no more than 6 % w/v. Higher concentrations are corrosive and highly reactive, so should not be used.

Procedure

Part A: Evaluation of the Effect of a Catalyst on Reaction Rates

1. Plan a step-by-step procedure to evaluate the effect of a catalyst on the reaction rate. Include any safety equipment you will need and precautions you should follow, based on the information in the relevant MSDS. Outline what you will observe and how you will record your observations.
2. Once your teacher has approved it, carry out your procedure.

Part B: Evaluation of Factors Affecting Reaction Rate

3. Write a detailed procedure to evaluate at least two other factors that affect reaction rate. Include appropriate safety measures. Outline what you will observe and how you will record your observations. Your procedure must allow you to collect data at enough time points to generate graphs.
4. Once your teacher has approved it, carry out your procedure.

Analyze and Evaluate

SKILLS HANDBOOK A6.5

(a) What variables were measured/recorded and/or manipulated in this investigation? T/I

(b) Create graphs and conduct calculations to determine the rates of the reaction(s) you investigated. T/I C

(c) Answer your testable question using your results. Was your prediction correct? Explain. T/I

(d) Suggest ways that you could improve your procedure if you were to repeat your investigation. T/I

Apply and Extend

(e) Which of the factors you tested had an effect on the rate of reaction in your investigation? T/I

(f) What was happening at the level of atoms, ions, and/or molecules to change the reaction rate when you modified the factors in (d)? T/I

Investigation 6.5.1 CONTROLLED EXPERIMENT

The Iodine Clock Reaction System

The iodine clock reaction system allows you to see changes in reaction rate by colour changes. Two colourless solutions are combined and the combined solution initially stays colourless. After a certain amount of time, the combined solution suddenly changes colour (**Figure 1**).

Figure 1 During the iodine clock reaction, the solution suddenly changes from clear to blue-black.

The iodine clock reaction system has three reactions that occur in sequence. In the first reaction, the iodate ions, $IO_3^-(aq)$, are reduced to iodide ions, $I^-(aq)$.

$$IO_3^-(aq) + 3\ HSO_3^-(aq) \rightarrow 3\ SO_4^{2-}(aq) + I^-(aq) + 3\ H^+(aq)$$

In the second reaction, iodate ions, $IO_3^-(aq)$, are changed to molecular iodine, $I_2(aq)$.

$$6\ H^+(aq) + IO_3^-(aq) + 5\ I^-(aq) \rightarrow 3\ I_2(aq) + 3\ H_2O(l)$$

In the last, the iodine, $I_2(aq)$, reacts with starch to form a blue-black complex.

$$I_2(aq) + \text{starch} \rightarrow \text{blue-black complex}$$

The third reaction is extremely fast compared to the previous two reactions, so the time it takes for the colour change to happen is approximately the same it takes to complete the first two reactions.

In this investigation, you will use the iodine clock reaction system to investigate the relationship between the rates of the first two reactions and the initial concentration of iodate ions.

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Testable Question

SKILLS HANDBOOK A2.2

In the iodine clock reaction, system, how does the initial concentration of iodate ions affect the rate and/or the sequence of the first two reactions?

Hypothesis/Prediction

State a hypothesis relating the concentration of reactants to reaction rate. Predict what will happen to the rate and sequence of each reaction in the iodine clock reaction system when the initial concentration of iodate ions is increased.

Variables

Identify the independent (sometimes called manipulated) and dependent (sometimes called responding) variables, and the variables that will be controlled.

Experimental Design

Using dropper bottles, solutions with varying iodate ion concentrations will be combined with equal amounts of sulfuric acid, starch, and sodium bisulfite in spot plates. The time from mixing to the appearance of the blue-black product will be measured and then graphed.

Equipment and Materials

- chemical safety goggles
- lab apron
- 2 spot plates, labelled A and B
- 1 transfer pipette
- timer
- dropper bottles with
  - distilled water
  - 0.020 mol/L solution of potassium iodate (solution A)
  - 0.0200 mol/L sodium bisulfite mixed with sulfuric acid and starch solution (solution B)

Procedure

1. Put on your safety goggles and lab apron.
2. Place spot plates on a flat surface. In spot plate 1, use the dropper bottle of solution A to place 1 drop of solution A in well 1, 2 drops in well 2, 3 drops in well 3, and so on, up to 10 drops of solution A in well 10.

3. Still using spot plate 1, place 9 drops of water in well 1, 8 drops of water in well 2, 7 drops in well 3, and so on, to 1 drop of water in well 9. There are now 10 drops of solution in each well and you have created a dilution series of solution A (**Figure 1**).

Figure 2 Create a dilution series for solution A.

4. Using spot plate 2, place 10 drops of solution B in each of the first 10 wells.
5. Using the transfer pipette held vertically, transfer the contents of spot plate 1, well 10, to spot plate 2, well 10. Make sure to push the tip of the transfer pipette below the surface of the liquid in spot plate 2, and stir gently so the solutions mix thoroughly (**Figure 3**). Start timing the instant the transfer pipette is squeezed and stop timing when the colour first appears. Record your observations.
6. Rinse the transfer pipette at least twice with water. Ensure that no water remains in the transfer pipette.
7. Using the rinsed transfer pipette, repeat Steps 4 and 5 for each of the other pairs of wells. Record your observations.

Analyze and Evaluate

(a) What variables were measured/recorded and/or manipulated in this investigation? T/I

(b) Calculate the concentration of iodate ions in each of the wells at the end of Step 2. T/I

Figure 3 Ensure that the tip of the pipette is below the surface of the liquid.

(c) Calculate the concentration of iodate ions in each of the wells at the instant of mixing with an equal value of solution B. T/I

(d) Using tables and graphs of your observations, identify the order of the reaction with respect to the concentration of iodate ions. T/I C

(e) Answer the testable question using your results. T/I

(f) Evaluate your hypothesis and prediction. Was your prediction correct? Explain your answer. T/I

(g) Suggest ways that you could improve your procedure if you were to repeat your investigation. T/I

Apply and Extend

(h) The manufacture of many plastics depends on series of linked chemical reactions. One role of chemical engineers in this area is to ensure that these linked reactions take place as efficiently as possible. Research the Internet and other sources to learn more about this career. Communicate your findings in an interesting way. 🌐 C A CAREER LINK

WEB LINK

Summary Questions

1. Create a study guide based on the Key Concepts on page 344. For each point, create three or four sub-points that provide further information, relevant examples, explanatory diagrams, or general equations.
2. Look back at the Starting Points questions on page 344. Answer these questions using what you have learned in this chapter. Compare your latest answers with those that you wrote at the beginning of the chapter. Note how your answers have changed.

Vocabulary

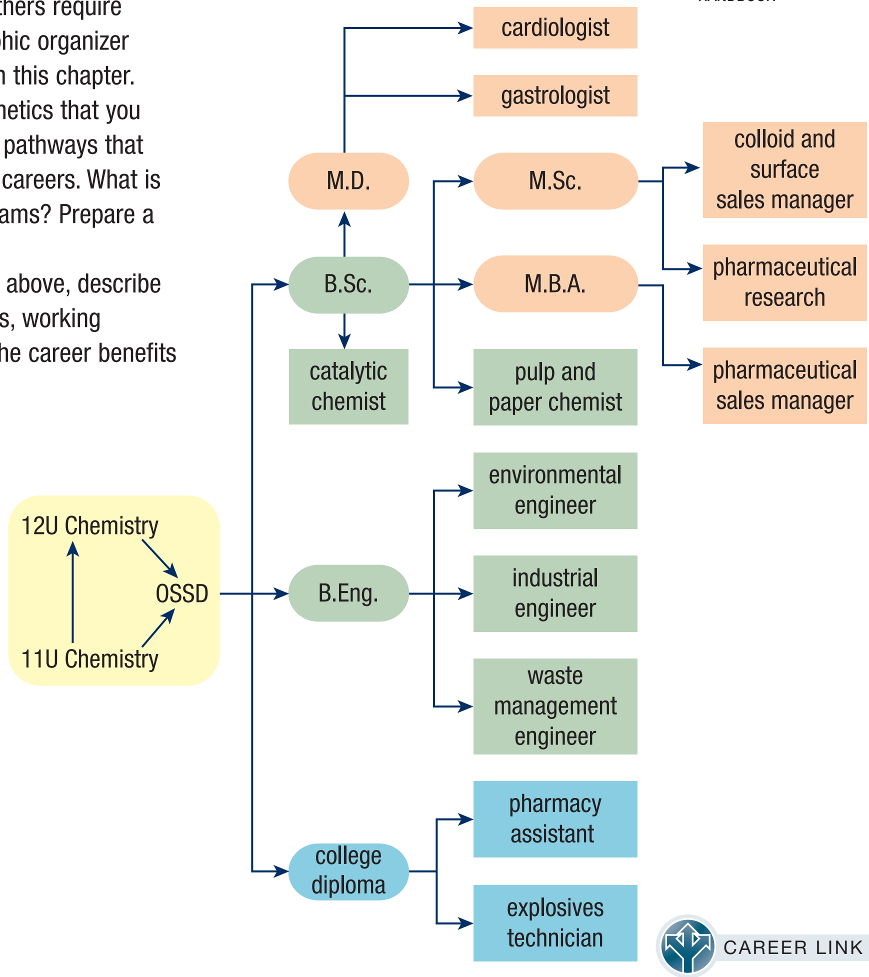
chemical kinetics (p. 346)
reaction rate (p. 346)
average reaction rate (p. 347)
instantaneous reaction rate (p. 353)
catalyst (p. 364)
biological catalyst (p. 364)
heterogeneous catalyst (p. 364)
homogeneous catalyst (p. 364)
collision theory (p. 366)
activation energy (E_a) (p. 367)
activated complex (p. 367)
rate law (p. 375)
rate law equation (p. 375)
rate constant (p. 375)
order of reaction (p. 375)
total order of reaction (p. 375)
initial rate (p. 376)
elementary step (p. 383)
reaction mechanism (p. 383)
rate-determining step (p. 383)
reaction intermediate (p. 383)

CAREER PATHWAYS

Grade 12 chemistry can lead to a wide range of careers. Some require a college diploma or a B.Sc. degree. Others require specialized or postgraduate degrees. This graphic organizer shows a few pathways to careers mentioned in this chapter.

1. Select two careers related to Chemical Kinetics that you find interesting. Research the educational pathways that you would need to follow to pursue these careers. What is involved in the required educational programs? Prepare a brief report of your findings.
2. For one of the two careers that you chose above, describe the career, main duties and responsibilities, working conditions, and setting. Also outline how the career benefits society and the environment.

SKILLS HANDBOOK A7



CAREER LINK

CHAPTER 6 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. In the chemical rection
   $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$
   the rate of consumption of oxygen gas is observed to be 4 mol/(L·min). What is the rate of production of carbon dioxide gas? (6.1) K/U
   (a) 1 mol/(L·min)
   (b) 2 mol/(L·min)
   (c) 4 mol/(L·min)
   (d) 8 mol/(L·min)
2. The rate of reaction depends upon
   (a) the concentration and nature of the reactants
   (b) the temperature of the reaction
   (c) whether or not a catalyst was used
   (d) all of the above (6.2) K/U
3. Which of the following factors that affect rate of reaction applies only to heterogeneous systems? (6.2) K/U
   (a) surface area (c) temperature
   (b) concentration (d) catalysis
4. The catalytic converter on a vehicle is
   (a) a biological catalyst
   (b) a heterogeneous catalyst
   (c) a homozygous catalyst
   (d) a reactant (6.2) K/U
5. The activation energy of a chemical reaction is affected by
   (a) the kinetic energy of the reactant(s)
   (b) the potential energy of the product(s)
   (c) the presence of a catalyst
   (d) none of the above (6.3) K/U
6. If the initial rate of reaction is observed to increase by a factor of 9 when the concentration of a reactant is tripled, what is the order of reaction with respect to that reactant? (6.5) K/U
   (a) 0 (c) 2
   (b) 1 (d) 3
7. The gas phase reaction $A + B \rightarrow C$ has a reaction rate that is experimentally observed to follow the relationship rate $= k[A]^2$. What is the reaction order with respect to B? (6.5) K/U
   (a) 0 (c) 2
   (b) 1 (d) 3
8. Which of the following statements is incorrect? (6.5) K/U
   (a) The reaction rate for a zero-order reaction is independent of concentrations.
   (b) The rate constant for a second-order reaction is dependent on temperature.
   (c) The rate law expression relates rate and concentration.
   (d) The rate constant for a first-order reaction never varies with temperature or pressure.
9. What are the units of the rate constant, *k*, in a second-order equation if rate is measured in mol/(L·s) and all concentrations are in mol/L? (6.5) K/U
   (a) s^{-1}
   (b) L/(mol·s)
   (c) $L^2/(mol^2 \cdot s)$
   (d) $mol^2/(L^2 \cdot s)$
10. Recent scientific research shows that the emerging "super" greenhouse gases include
    (a) sulfuryl fluoride, SO_2F_2
    (b) nitrogen trifluoride, NF_3
    (c) trifluoromethylsulfurpentafluoride, SF_5CF_3
    (d) all of the above (6.7) K/U

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

11. The concentration of the product or reactant in a reaction changes over time. (6.1) K/U
12. Reaction rates can only be determined by studying the change in concentration of the products. (6.1) K/U
13. The instantaneous rate of reaction is determined graphically from the slope of a tangent. (6.1) K/U
14. Rates of reaction can only be determined from theoretical data. (6.1) K/U
15. A decrease in the frequency of collisions leads to a higher reaction rate. (6.3) K/U
16. An enzyme is a biological catalyst. (6.4) K/U
17. If one reactant molecule is involved in the rate-determining step, the reaction is a first-order reaction. (6.5, 6.6) K/U
18. The elementary steps in a mechanism must add up to the overall equation. (6.6) K/U
19. A reaction intermediate may be used in the rate law if required. (6.6) K/U
20. Methane has a global warming potential about 12 times that of carbon dioxide. (6.7) K/U

Go to Nelson Science for an online self-quiz.
WEB LINK

CHAPTER 6 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Chemical kinetics is the study of factors that affect
    - (a) the rate of a chemical reaction
    - (b) the chemical properties of substances
    - (c) the rate of a change in concentration
    - (d) the physical properties of substances (6.1) K/U
2. Which of the following conditions will change the rate of a reaction? (6.2) K/U
    - (a) chewing food
    - (b) heating in an oven
    - (c) exposure to high oxygen concentration
    - (d) all of the above
3. Enzymes are
    - (a) highly porous substances that activate acids and bases
    - (b) substances synthesized by chemists to decrease the reaction rate
    - (c) extremely poor in catalytic activity
    - (d) catalysts found in organisms (6.2) K/U
4. Which of the following statements is true, according to the collision theory? (6.3) K/U
    - (a) All collisions result in reactions.
    - (b) Entities must collide to react.
    - (c) Entities that collide but are incorrectly oriented will form a different product.
    - (d) All entities in a collision have the same quantity of kinetic energy.
5. Which of the following is *not* an example of a biocatalyst? (6.4) K/U
    - (a) yeast
    - (b) Rubisco
    - (c) cellulose
    - (d) laccases
6. A rate law equation expresses how
    - (a) the concentrations of entities in a reaction depend on time
    - (b) the rate of a reaction depends on the concentrations of the reactants
    - (c) the concentrations of entities in the reaction depend on temperature
    - (d) the rate of a reaction depends on temperature (6.5) K/U
7. Which of the following describes a reaction intermediate? (6.6) K/U
    - (a) a starting material
    - (b) a product
    - (c) something formed and consumed during a reaction
    - (d) a step in a reaction mechanism
8. In a reaction mechanism, the rate-determining step is always
    - (a) the reaction intermediate
    - (b) the last step
    - (c) the slowest step
    - (d) the fastest step (6.6) K/U
9. The average atmospheric lifespan of a greenhouse gas depends on its
    - (a) global warming potential (GWP)
    - (b) concentration in the atmosphere
    - (c) rate of decomposition
    - (d) rate of emission (6.7) K/U

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

10. The instantaneous reaction rate is always equal and constant. (6.1) K/U
11. Similar elements tend to react similarly, but may do so at different reaction rates. (6.2) K/U
12. It is not necessary to break existing bonds in molecules in order to form new bonds. (6.3) K/U
13. Chemical entities can be in any orientation during an effective collision. (6.3) K/U
14. The frequency of collisions and the proportion of those collisions that are effective determine the rate of a given reaction. (6.3) K/U
15. Biocatalysts are catalysts that are made by living systems or are themselves living systems. (6.4) K/U
16. The rate constant for a zero-order reaction has no units. (6.5) K/U
17. The rate law for a chemical reaction is always expressed as a product of the initial concentrations of the products of the reaction. (6.5) K/U
18. The units for the rate law constant, k, are always $L/(mol \cdot s)$. (6.5) K/U
19. The reaction mechanism explains exactly what occurs in a chemical reaction. (6.6) K/U
20. The increase in thermal energy trapped in Earth's atmosphere is contributing to climate change. (6.7) K/U

Understanding

Write a short answer to each question.

21. Why do the average and instantaneous rates of a reaction usually differ? (6.1) T/I
22. Define "reaction rate" in your own words. (6.1) K/U
23. Describe three different methods a chemist might use to quantify the appearance of a product or the disappearance of a reactant. (6.1) K/U
24. What is the purpose of enzymes in our bodies? (6.2) K/U
25. In terms of reaction kinetics, explain why each of the following increases reaction rate: (6.2) K/U
    (a) catalyst
    (b) increase in temperature
    (c) increase in concentration
26. Explain the difference between homogeneous and heterogeneous catalysts, and provide an example of each. (6.2) K/U
27. There are five factors that affect the rate of a reaction. For each of the five factors, draw a series of diagrams showing how it affects the rate of reaction. Include captions with your diagrams to clarify your ideas. (6.2) K/U C
28. Consider the equation $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ Predict the rate law for this reaction. Justify your prediction. (6.2) K/U C
29. Why do reactions of substances containing covalent bonds take longer than reactions of ions in solution? (6.3) K/U
30. Explain the collision theory, using diagrams in your answer. (6.3) K/U C
31. What is the Maxwell–Boltzmann distribution? (6.3) K/U
32. Define "activation energy" in your own words. (6.3) K/U
33. Explain why all chemical reactions have an activation energy. (6.3) K/U
34. According to the collision theory, what are two reasons why the rates of most reactions increase with increasing temperature? (6.3) K/U
35. Use a potential energy graph to differentiate between endothermic and exothermic reactions. (6.3) K/U
36. What is a potential drawback of using biocatalysts? (6.2, 6.4) K/U
37. Why are the initial rates used to measure the rate of reaction? (6.5) K/U
38. What is the overall order of reaction for the one-step reaction represented by the following? $A + B \rightarrow$ products (6.5) K/U
39. Use collision theory to explain why it is unlikely that three or more chemical entities (atoms, ions, or molecules) will be involved in an elementary step. (6.3, 6.6) K/U
40. (a) Why do average rates of reaction decrease with time?
    (b) How does the instantaneous rate of a reaction depend on time?
    (c) Why are initial rates used by convention? (6.5) K/U
41. State in your own words the relationship between the rate law and the reaction mechanism. (6.5, 6.6) K/U
42. Distinguish between the rate of a chemical reaction and the rate constant for the reaction. (6.1, 6.5) K/U
43. What is the relationship between the rate law and the rate-determining step? (6.5, 6.6) T/I
44. What is a reaction mechanism? Include and explain the term "elementary step" in your answer. (6.6) K/U
45. How many chemical entities are generally involved in an elementary step in a reaction mechanism? (6.6) K/U
46. Why is it not effective to simply use a balanced chemical equation to understand a reaction rate? (6.6) K/U
47. Why is it necessary to consider the atmospheric lifespan of a gas when considering the gas's impact on global warming? (6.7) K/U
48. Describe the concerns surrounding greenhouse gases. (6.7) K/U

Analysis and Application

49. A chemist conducted a study of the decomposition of phosphine gas, $PH_3(g)$, into phosphorus gas, $P_4(g)$, and hydrogen gas. This reaction is represented by the following balanced chemical equation:

    $4\ PH_3(g) \rightarrow P_4(g) + 6\ H_2(g)$

    She determined the rate of reaction with respect to the consumption of phosphine gas to be -0.0024 mol/L·s. What are the rates of formation of phosphorus gas and hydrogen gas in this experiment? (6.1) T/I
50. In the reaction represented by the general equation

    $A + 2\ B \rightarrow 3\ C + 4\ D$

    the initial concentration of B was 0.0431 mol/L. After 11.3 min, the concentration of B was 0.0307 mol/L. (6.1) T/I
    (a) Calculate the average rate of consumption of B for the first 11.3 min in mol/L·s.
    (b) Calculate the average rate of formation of C.
51. In the reaction represented by the general equation

    $A + 2\ B \rightarrow 3\ C + 4\ D$

    the initial concentration of A was 0.0367 mol/L. After 21.8 min, the concentration of A was 0.0240 mol/L. What is the average rate of disappearance, in mol/L·s, of reactant B? (6.1) T/I

52. Use **Figure 1** to answer these questions. (6.1) T/I C
   (a) How many reactants are there?
   (b) How many products are there?
   (c) What was the initial concentration of each of the entitites involved in the reaction?
   (d) Based on the graph, write the balanced chemical equation for this reaction. Explain how you determined the coefficients in the equation.

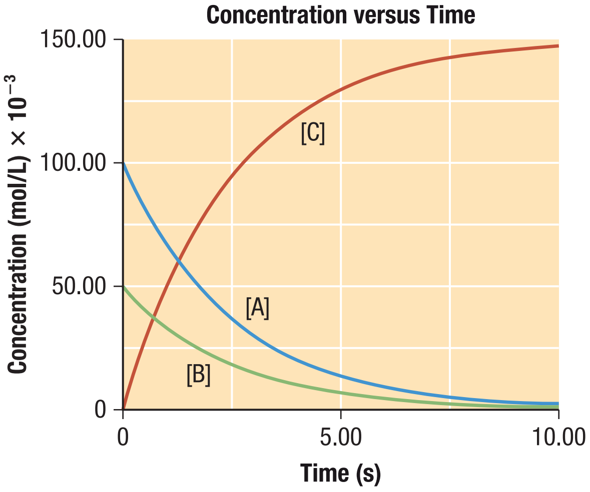


Figure 1

53. **Table 1** shows data collected during an investigation in which the concentration of nitrogen dioxide, $NO_2(g)$, was measured as a function of time. (6.1) K/U T/I C

Table 1 Concentration of Nitrogen Dioxide over Time

Time (s)	$[NO_2]$ mol/L
0	0.560
15	0.445
30	0.350
45	0.282
60	0.210
75	0.171
90	0.142
105	0.123
120	0.102

   (a) Graph the data.
   (b) Determine the average rate of consumption of nitrogen dioxide between 15 s and 90 s.
   (c) Determine the instantaneous rate of reaction at 15 s.
   (d) Determine the instantaneous rate of reaction at 90 s.
   (e) Explain why the instantaneous rate of reaction changes so dramatically over the course of the reaction.

54. When zinc metal, Zn(s), is placed in a solution of hydrochloric acid, HCl(aq), a chemical reaction occurs that forms hydrogen gas, $H_2(g)$, and aqueous zinc chloride, $ZnCl_2(aq)$. This reaction is exothermic, as shown by the following balanced chemical equation:

$$2\,HCl(aq) + Zn(s) \rightarrow H_2(g) + ZnCl_2(aq) + \text{thermal energy}$$

For each of the following, predict the effect on the rate of this reaction. Justify your predictions using the collision theory. Use diagrams in your explanations. (6.3) K/U T/I C A
   (a) The concentration of hydrochloric acid is increased.
   (b) The reaction mixture is cooled.
   (c) Finely ground zinc is used instead of large chunks of zinc.
   (d) A solution of copper(II) sulfate, $CuSO_4(aq)$, is used as a catalyst.

55. During the process of making bread, at one stage you let yeast act on the dough and, at another stage, you place the finished dough in a hot oven. Explain how temperature affects each of these two processes (that is, the action of yeast and baking), referring to the effect on reaction rates. (6.2) K/U A

56. Explain why dust control is an important part of industrial safety, and give an example of what can happen if dust builds up in a workplace. Refer to reaction rate in your answer. (6.2) K/U A

57. Refer to the reactivity information given in **Figure 2** (6.2) T/I A
   (a) Explain why copper is commonly used in plumbing.
   (b) If copper were not available, what other metal might be suitable to make plumbing pipes? Refer to the costs and benefits of the metal in your answer.

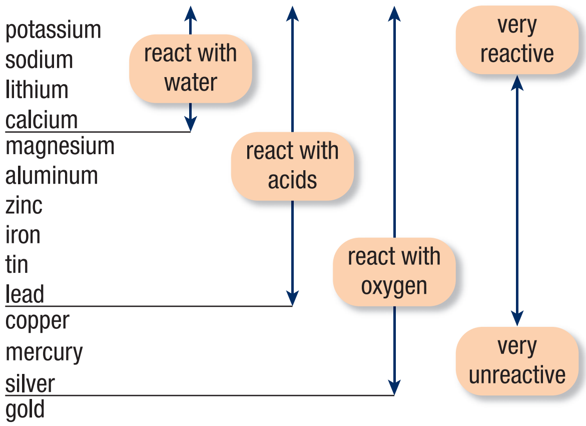


Figure 2

58. Sulfuric acid, $H_2SO_4(aq)$, can be produced by a number of different methods. One process, called the wet sulfuric acid process, can be summarized by the following reaction equations: (6.2) T/I C A

$S(s) + O_2(g) \rightarrow SO_2(g)$

$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$, possible catalyst V_2O_5

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

(a) Suggest ways that could be used to increase the rate of each step of the reaction.

(b) Discuss the costs and benefits of each factor you suggested in (a) with respect to both expense and safety. Use a chart or other visual tool to organize your answer.

59. The instantaneous rate of a highly exothermic reaction is measured at the start of the reaction, $t = 0$. After 5 s, the instantaneous rate is measured again, and is found to be higher than at the start of the reaction. How is this increase possible? (6.1, 6.3) T/I

60. **Figure 3** illustrates the energy of a system during a chemical change. Sketch a new diagram showing how the energy of the system would change if a catalyst were added. Explain your answer. (6.3) K/U T/I C

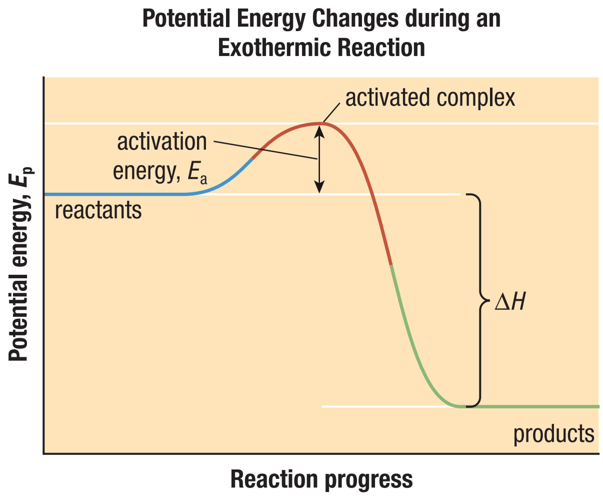


Figure 3

61. Why do large piles of timber in a lumberyard not catch fire spontaneously, even though they are surrounded by oxygen? (6.3) T/I A

62. When cobalt metal, Co(s), is placed in a solution of chlorine, $Cl_2(aq)$, it undergoes a chemical reaction to form cobalt (II) chloride, $CoCl_2(aq)$. The balanced chemical equation is

$Co(s) + Cl_2(aq) \rightarrow CoCl_2(aq)$

(a) Suggest three ways that you could increase the rate of this reaction, and explain each one, referring to the collision theory.

(b) What techniques could you use to measure the rate of this reaction? State as many as you can, and briefly describe how you could carry out each. (6.2, 6.3) K/U T/I

63. In solution, chlorine dioxide, $ClO_2(aq)$, and hydroxide ions, $OH^-(aq)$, react to form chlorate ions, $ClO_3^-(aq)$, chlorite ions, $ClO_2^-(aq)$, and water. The balanced chemical equation for this reaction is

$$2\ ClO_2(aq) + 2\ OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$$

The reaction is found to be second order with respect to chlorine dioxide and first order with respect to hydroxide ions. (6.5) K/U T/I

(a) Write a rate equation for the reaction.

(b) What is the overall order of the reaction?

(c) How would doubling the concentration of chlorine dioxide affect the reaction rate?

(d) How would doubling the concentration of hydroxide ions affect the reaction rate?

64. Explain the steps you need to follow to determine the exponents of the reactant concentrations in the rate law equation. Use a flow chart, point-form list, or series of diagrams with explanations. (6.5) K/U T/I C

65. An investigator carried out a chemical reaction between molecules of a haloalkane, RX, and hydroxide ions, OH^-, three times at constant temperature. **Table 2** shows his experimental data. Determine the order of the reaction with respect to RX and OH^- then write the rate law equation for the reaction. (6.5) K/U T/I

Table 2 Initial Data from Constant Temperature Runs of the Reaction between a Haloalkane and Hydroxide

Run	Initial [RX] (mol/L)	Initial [OH^-] (mol/L)	Initial rate (mol/(L·s))
1	0.01	0.04	8×10^{-6}
2	0.01	0.02	4×10^{-6}
3	0.005	0.04	4×10^{-6}

66. Identify the order of reaction associated with the shape of each of the curves shown in **Figure 4(a–d)**. Explain each of your answers. (6.5) T/I C

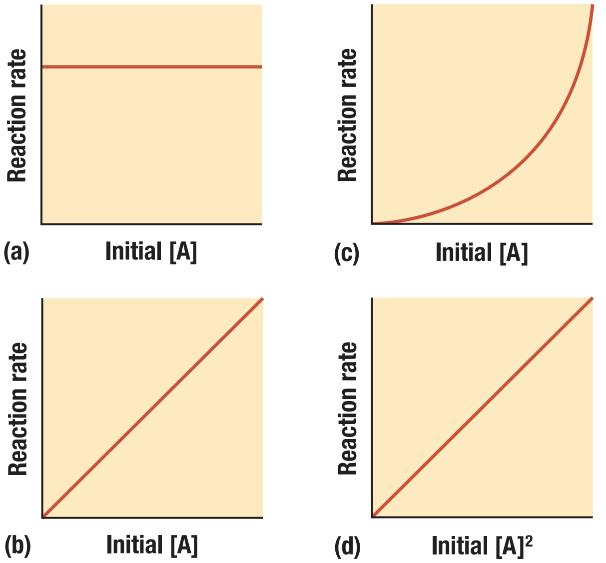


Figure 4

67. The rate law for the reaction between chlorine and nitric oxide can be expressed as

$r = k[Cl_2][NO]^2$ (6.5) K/U T/I

(a) What is the order of the reaction with respect to chlorine and nitric oxide?

(b) What is the overall order of the reaction?

(c) What are the units of the rate constant?

68. Magnesium ribbon, Mg(s), will burn in the presence of oxygen gas, forming solid magnesium oxide, MgO(s). The balanced chemical equation for this reaction is

$2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$

A chemical technician carries out this reaction three times at the same temperature, and collects the data given in **Table 3**. From the given information, determine the rate law, the rate constant, and the overall reaction order. (6.5) T/I

Table 3 Initial Data from Constant Temperature Runs of the Combustion Reaction of Magnesium Metal

Run	Initial [Mg] (mol/L)	Initial $[O_2]$ (mol/L)	Rate (mol/(L·s))
1	0.10	0.10	2.0×10^{-3}
2	0.20	0.10	4.0×10^{-3}
3	0.10	0.20	8.0×10^{-3}

69. Hydrogen bromide gas, HBr(g), can form from the reaction of hydrogen gas and bromide gas, as represented by the balanced chemical equation

$H_2(g) + Br_2\ (g) \rightarrow 2\ HBr(g)$

A researcher carries out this reaction in a sealed vessel at 50 °C and determines the reaction rate to be 2.5 mol/(L·s). She repeats the reaction twice. She starts with the same initial reactant concentrations, but changes one other factor. Under the new conditions, she finds the reaction rate is 1.75 mol/(L·s) for the first repetition and 2.35 mol/(L·s) for the second repetition. She double-checks her calculations and finds no errors. Suggest what factor she changed to achieve these different reaction rates. (6.2, 6.5) T/I

70. Thioethanamide, CH_3CSNH_2, reacts with hydroxide ions as follows:

$$CH_3CSNH_2(aq) + 2\ OH^-(aq) \rightarrow CH_3CO_2^-(aq) + HS^-(aq) + NH_3(g)$$

The reaction is first order with respect to both thioethanamide and hydroxide ions. (6.5, 6.6) K/U T/I

(a) Write the rate law equation for this reaction.

(b) What is the overall order of the reaction?

(c) The reaction occurs in two steps and the rate-determining step is

$CH_3CSNH_2 + OH^- \rightarrow CH_3CONH_2 + HS^-$

Write an equation for the second step in the reaction.

71. For the theoretical reaction represented by the balanced chemical equation

$2\ A + B + C \rightarrow 2\ D + E$

the data given in **Table 4** were obtained at 50 °C. (6.5, 6.6) K/U T/I

Table 4 Initial Data from Runs at 50 °C for the Theoretical Reaction Given by

$2\ A + B + C \rightarrow 2\ D + E$

Run	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial [C] (mol/L)	Rate
1	0.025	0.035	0.022	0.0060
2	0.025	0.035	0.044	0.012
3	0.025	0.140	0.022	0.0060
4	0.050	0.035	0.044	0.048

(a) Determine the order of the reaction with respect to each reactant.

(b) Write the specific rate law equation for the reaction, making sure to include units for *k*.

(c) The following proposed mechanism is being studied:

1. $A + C \rightarrow D + F + G$ (slow)
2. $F + B \rightarrow E$ (fast)
3. $A + G \rightarrow D$ (very slow)

Which is the rate-determining step?

(d) What are the reaction intermediates?

(e) Show that this mechanism results in the overall reaction being studied.

(f) Does the reaction mechanism agree with the experimental rate law? Explain your answer.

(g) Is this mechanism correct? Justify your response.

72. Assuming a reaction occurs in one elementary step, propose a chemical equation using P as the symbol for the product. (6.6) T/I

Evaluation

73. A solution of permanganate ions, $MnO_4^-(aq)$, causes the solution to be purple. When oxalic acid, $H_2C_2O_4(aq)$, is added, a chemical reaction occurs and the solution becomes nearly colourless. The balanced chemical equation for this reaction is

$$2\ MnO_4^-(aq) + 5\ H_2C_2O_4(aq) + 6\ H_3O^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(aq) + 14\ H_2O(l)$$

A student carried out this reaction and determined the concentration of permanganate ions by measuring the intensity of the colour of the solution. His results are given in **Table 5**.

Table 5 Concentration of Reactants and Product over Time

Time (s)	$[MnO_4^-(aq)]$ (mol/L)	$[H_2C_2O_4(aq)]$ (mol/L)	$[Mn^{2+}(aq)]$ (mol/L)
0	0.10	1.0	0
10	0.049		
20	0.024		
30	0.011		
40	0.005		

(a) Copy and complete Table 5.

(b) Calculate the average reaction rate over the first 30 s, with respect to permanganate ions.

(c) Using your answer from (b), determine the average rate of the disappearance of oxalic acid and the appearance of carbon dioxide.

(d) A classmate thinks that measuring colour intensity is the only way to determine concentration of reactants and products over time. Do you agree? If so, explain why. If not, suggest other ways to determine changes in concentration for this reaction. (6.1) K/U T/I A

74. At a hardware store, the clerk directs you to a type of paint that will dry much more quickly when you add a small amount of an accelerant to the can before you use it. When you ask him about the accelerant, he tells you that it is a catalyst. Do you think the clerk is using this term correctly in describing this particular accelerant? Justify your position based on what you know about catalysts. (6.2, 6.3) K/U A

75. You read an article that states that a gas station is much more likely to catch fire spontaneously on a hot day than on a cold day. Do you think this is statement is accurate? Support your answer by referring to the collision theory. (6.3) K/U A

Reflect on Your Learning

76. Write a paper detailing how chemical kinetics makes an impact on your daily life. You may want to include examples from manufacturing, the environment, or biology. C A

77. Identify and describe three ways to change a reaction rate that you studied in this chapter that you might apply in your everyday life. For each way, give an example of a situation where you would want to change a reaction rate, and state whether you would be trying to increase or decrease the reaction rate. K/U A

78. What concepts in this chapter did you find the easiest to understand? Which ones were the most difficult? What tools did you use to help you understand the difficult concepts? K/U A

Research

WEB LINK

79. Catalysts used by industry may be either heterogeneous or homogeneous. Research catalysts and find a specific example of an industrial use of each type. For each example, briefly describe how it is used. Determine whether most catalysts used in industry are heterogeneous or homogeneous, and explain why. Report your findings as a written report, poster, or computer-based presentation. T/I C A

80. What is autocatalysis? Describe a reaction in which it occurs and an industrial or medical use for that reaction. T/I A

81. Ozone is a molecule that is helpful in the upper atmosphere but harmful at ground level. Use a web page, computer-based presentation, or other interesting format to explain the effects of this gas. Answer the following questions in your work. T/I C A

(a) Why is ground-level ozone a problem?

(b) What are the mechanisms of the reactions that lead to its production?

(c) What is the connection between the production of ozone and kinetics?

82. John Polanyi, a scientist at the University of Toronto, won the 1986 Nobel Prize for his work in chemical kinetics. Imagine that you are a newspaper reporter describing Polanyi's work in an article written the day after he received the Nobel Prize. Include in your article a description of his area of research and the experiments he performed. T/I C A

Evaluating Different Catalysts

Our unhealthy dependence on non-renewable energy sources such as gasoline and natural gas has triggered unprecedented research into the production of green fuels from renewable resources. Bioethanol, a green fuel, can be used to run motor vehicles or as an additive to conventional gasoline. The production of bioethanol is costly. It is currently produced from high-quality biomass such as sugar and starch. As a result, corn, grain, and soy are no longer being produced solely for use as food. Their value on the food market is therefore rising, making them very expensive and inaccessible to people in poorer countries as food sources.

Another type of plant matter that could be used to produce bioethanol is cellulose (**Figure 1**). Cellulose is a complex sugar polymer and differs from the simple sugars found in starch. Sources of cellulose include

- forestry waste (wood chips, sawdust from saw mills, and dead trees)
- municipal solid waste (household garbage and paper products)
- energy crops (fast-growing trees and grasses)
- garden waste (grass clippings, tree branches)

Figure 1 Cellulose obtained from biomass such as wood chips can be converted into ethanol, a biofuel.

Cellulose is a polysaccharide made from glucose, a 6-carbon sugar. Cellulose is highly resistant to hydrolysis. Hydrolysis is the chemical reaction that breaks down cellulose into simple sugars. The simple sugars can then be fermented into ethanol. In animals that eat plants and grass, enzymes known as cellulases facilitate the breakdown of cellulose in an energy-efficient manner.

Scientists are currently searching for alternative catalysts that will break down biomass cellulose into glucose molecules. Japanese scientists are comparing different metal catalysts. Australian, Canadian, and American scientists are investigating methods that use alternative enzymes or acid catalysts.

Scientists must compare the rate of catalysis, the purity of product, the availability of the catalyst, and the cost of using each catalyst and its associated process.

The Task

In this Unit Task, imagine that you are a chemist who is responsible for comparing different catalysts that will be used to break down cellulose into glucose. In order to do so, you must conduct a preliminary study on basic catalytic properties that you will apply to catalytic cellulose decomposition. For your study, you have chosen the decomposition of hydrogen peroxide. You will quantitatively analyze the rate of reaction associated with the breakdown of hydrogen peroxide into oxygen and water using three chemical catalysts: potassium iodide, KI; manganese dioxide, MnO_2; and zinc oxide, ZnO. This analysis will help you understand how chemists compare the efficiency of different types of catalysts in a specific reaction. Furthermore, in this activity, you will further develop your understanding of experimental design and application of results.

Purpose

To understand the relationship between the type of catalyst used and its effect on the rate of a specific reaction

To model a system that may be applied to current research in isolating viable catalysts for breaking down cellulose into glucose for the production of bioethanol

Equipment and Materials

- graduated cylinder
- dishwashing detergent
- scoopula
- stopwatch
- hydrogen peroxide (4 %)
- potassium iodide, KI(s)
- manganese dioxide, MnO_2(s)
- zinc oxide, ZnO(s)
- goggles and gloves
- any other equipment approved by your teacher

Procedure

SKILLS HANDBOOK A1.2, A2.2

Design an experiment that will allow you to compare the effectiveness of different catalysts that may be used to decompose hydrogen peroxide. Collect data that will allow you to calculate the rate of reaction for each catalyst used in the decomposition reaction. Outline the variables you will measure and any controls you will need. Include a sample observation table(s).

Analyze and Evaluate

SKILLS HANDBOOK A5.1, A6.5

(a) Write the chemical equation for the decomposition of hydrogen peroxide. K/U

(b) What variables did you measure in the task? What did you change? What was the result of each change? T/I

(c) Calculate the reaction rate for each catalyst. Use volume of gas produced per unit time. You may wish to use a graph. T/I C

(d) How do the catalysts compare in terms of reaction rate qualitatively and quantitatively? Support your answer with observations and calculations directly from your results. T/I

(e) Which of the catalysts you used was most effective in breaking down hydrogen peroxide? Consider in your analysis the mass of catalyst used versus the volume of gas produced. T/I

(f) Calculate which of the catalysts is the most economical to use in breaking down hydrogen peroxide. Obtain the cost of each chemical catalyst from your teacher. T/I

(g) List two errors that occurred during the execution of your experiment and explain how they may have affected your results. T/I

(h) Propose two modifications to your experimental design that would provide you with more conclusive results. T/I

Apply and Extend

SKILLS HANDBOOK A5.1, A5.2

(i) Use the Internet or other electronic resources to find the chemical equation for the hydrolysis of cellulose. T/I

(j) What are the products of the hydrolysis of cellulose? Describe the process by which the products of hydrolysis are turned into viable biofuel. T/I A

(k) Why is ethanol a good alternative fuel source? T/I A

(l) Using the Internet or other electronic resources, research different catalytic methods being investigated to break down cellulose. T/I A

(m) Compare your investigation to the process research scientists use to evaluate different catalysts in the breakdown of cellulose. Was your investigation a good model of what catalytic research scientists undertake in their studies? Why or why not? T/I A

(n) Using the Internet or other electronic resources, research how much energy is obtained from the combustion of ethanol. How does this value compare to the combustion of conventional gasoline? T/I A

(o) Currently in Canada, ethanol is used as an additive to gasoline. Why is ethanol added? What percentage of gasoline would you expect to consist of ethanol at a Canadian gas station? T/I A

(p) List some sources of biomass that could be used as viable sources of cellulose. T/I A

(q) Besides cellulose, hemicellulose and lignin can be used as sources of ethanol once they are broken down. What are the advantages and disadvantages of using these polymers as a starting material versus cellulose? Communicate your answer as a chart, poster, webpage, or other visually interesting manner. T/I A C

WEB LINK

ASSESSMENT **CHECKLIST**

Your completed Unit Task will be assessed according to the following criteria:

Knowledge/Understanding

- ✓ Identify the manipulated and controlled variables.

Thinking/Investigation

- ✓ Correctly use the variables in the experiment.
- ✓ Fill out an observation table correctly.
- ✓ Analyze the results.
- ✓ Evaluate the procedure as a model for cellulose breakdown research.

Communication

- ✓ Prepare a suitable lab report that includes a complete procedure, results, analysis, and evaluation.

Application

- ✓ Research current methods used to break down cellulose into glucose for use in fermentation.
- ✓ Compare this student-designed investigation with current studies of cellulose breakdown being conducted by research scientists.

UNIT 3 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. Identify the correct order of relative magnitude of potential energy changes from the following:
   (a) nuclear change > phase change > chemical change
   (b) phase change > nuclear change > chemical change
   (c) chemical change > phase change > nuclear change
   (d) nuclear change > chemical change > phase change (5.1) K/U
2. Consider the reaction system represented by the following thermochemical equation:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H° = -286 \text{ kJ}$$

   Which of the following is true? (5.1, 5.2) K/U
   (a) Thermal energy is absorbed by the system.
   (b) The reaction is endothermic.
   (c) The reaction is exothermic.
   (d) none of the above
3. One-gram samples of two metals that have different heat capacities are subjected to the same quantity of thermal energy. Which of the following statements is true for this experiment? (5.2) K/U
   (a) Both metals undergo the same change in temperature.
   (b) The metal with the higher heat capacity undergoes the smaller temperature change.
   (c) The metal with the lower heat capacity undergoes the smaller temperature change.
   (d) You need to know the initial temperature of the metals to predict their temperature change.
4. A 4.0 g sample of heated metal is placed in a coffee-cup calorimeter that contains 1.00 kg of water. The temperature of the water increases by 5.0 °C. How much thermal energy was transferred to the water, given that the heat capacity of water, *c*, is 4.18 J/g·°C? (5.2) T/I
   (a) 0 kJ/g
   (b) 5.2 kJ/g
   (c) 5.4 kJ/g
   (d) 21 kJ/g
5. The balanced chemical equation for the combustion of 1 mol of ethyne gas, $C_2H_2(g)$, is

$$C_2H_2(g) + 2.5\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(g)$$

   Estimate the heat of combustion for 1 mol of ethyne gas, using the bond energy values given in, Table 1, page 307. (5.3) T/I
   (a) −1228 kJ
   (b) −447 kJ
   (c) 447 kJ
   (d) 1228 kJ
6. Given the following two balanced thermochemical equations:

$$C(s) + O_2(g) \rightarrow CO_2(g)\ \Delta H = -393.6 \text{ kJ}$$
$$CO(g) + ½\ O_2 \rightarrow CO_2(g)\ \Delta H = -283.3 \text{ kJ}$$

   use Hess's law to determine the ΔH for the reaction

$$2\ C(s) + O_2(g) \rightarrow 2\ CO(g)$$

   (a) −576.9 kJ
   (b) −220.8 kJ
   (c) 220.8 kJ
   (d) 576.9 kJ (5.4) T/I
7. Identify which of the following statements concerning petroleum is inaccurate: (5.6) K/U
   (a) All of its hydrocarbon chains contain the same number of carbon atoms.
   (b) It is a thick, dark liquid composed mostly of hydrocarbons.
   (c) It must be separated into fractions by boiling to be used.
   (d) It likely was formed from the remains of ancient marine organisms.
8. The type of coal that releases the highest quantity of thermal energy per unit burned is
   (a) anthracite
   (b) bituminous
   (c) lignite
   (d) sub-bituminous (5.6) K/U
9. Which of the following is not a potential drawback of a wind farm? A wind farm
   (a) requires large tracts of land.
   (b) may produce noise pollution.
   (c) allows farmers to generate additional revenue while still using the land for crops.
   (d) must be located in an area where there are strong, steady winds. (5.7) K/U
10. For the chemical reaction that occurs when zinc metal, Zn(s), is placed in a hydrochloric acid solution, HCl(aq), the rate of reaction could *not* be determined by measuring the
    (a) change in pH
    (b) volume of gas produced
    (c) temperature change
    (d) mass of zinc consumed (6.1) K/U T/I

11. A chemical reaction is represented by the following balanced chemical equation:

$$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$$

Identify the catalyst, given that the following two equations represent the accepted reaction mechanism:

$$H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq)$$

$$H_2O_2(aq) + IO^-(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq)$$

(a) $H_2O(l)$
(b) $H_2O_2(aq)$
(c) $I^-(aq)$
(d) $IO^-(aq)$ (6.2) K/U T/I

12. Which of the following will occur when the kinetic energy of reactants is not equal to or greater than the activation energy? (6.3) K/U
(a) The activated complex will convert to products.
(b) The products will form at an unstable energy state.
(c) The rate of the reaction will tend to increase.
(d) The reactants will re-form.

13. Which of the following is NOT true? (6.4) K/U
(a) Reactions involving a biocatalyst are thought to have a lower activation energy than the same reaction carried out without a biocatalyst.
(b) Biocatalysts often make a chemical process more environmentally friendly.
(c) Sodium hydroxide is a biocatalyst used in the kraft process.
(d) Biocatalysts can increase the rate of a chemical process.

14. A sample of zinc with a mass of 6.54 g is dropped into dilute acetic acid. At the end of 2.00 min, the unreacted zinc is removed, dried, and found to have a mass of 6.00 g. The average rate of the reaction over this time period was
(a) 4.13×10^{-3} mol/min
(b) 4.13×10^{-3} mol/s
(c) 5.00×10^{-2} mol/min
(d) 4.59×10^{-2} mol/min

15. For the chemical reaction represented by the balanced chemical equation

$$2\ NO(g) \rightarrow N_2(g) + O_2(g)$$

the rate law equation is

$$-\frac{\Delta[NO(g)]}{\Delta t} = 2k[NO(g)]^2$$

After a period of 2.0×10^3 s, the concentration of nitric oxide, NO(g), decreases from an initial value of 2.8×10^{-3} mol/L to 2.0×10^{-3} mol/L. What is the rate constant, k? (6.5) T/I
(a) 3.6×10^{-2} mol/L·s
(b) 7.2×10^{-2} mol/L·s
(c) 1.7×10^{-4} mol/L·s
(d) 4.0×10^{-4} mol/L·s

16. The catalyzed pathway of a reaction mechanism has _________ activation energy and thus causes a _______ reaction rate. (6.6) K/U
(a) higher, lower
(b) higher, higher
(c) lower, higher
(d) lower, lower

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

17. The energy of the universe is constant. (5.1) K/U

18. When a reaction is reversed in enthalpy calculations, the sign of ΔH remains the same but its magnitude changes. (5.4) K/U

19. Elements in their standard states are not included in the ΔH_f° calculations. (5.5) K/U

20. Nuclear reactions constitute a potentially valuable energy source. (5.6) K/U

21. Combining 2 light nuclei to form a heavier, more stable nucleus is called fission. (5.6) K/U

22. One of the least abundant energy sources is the energy that binds the atomic nucleus together. (5.6) K/U

23. A modern wind turbine can generate enough electricity to supply several small towns. (5.7) K/U

24. For the chemical reaction in which hydrogen gas and oxygen gas form water vapour, the rate of water vapour formation is equal to the rate of the consumption of hydrogen gas. (6.1) K/U

25. The effect of changing reactant concentrations on the rate of a reaction can be predicted by looking at a balanced chemical equation. (6.2) K/U

26. A catalyst is a substance that increases reaction rate by lowering the activation energy and that is consumed in the reaction. (6.2) K/U

27. Chemical entities must be oriented in a certain way and have sufficient kinetic energy when they collide for a chemical reaction to occur. (6.3) K/U

28. Biocatalysts are thought to increase reaction rate by providing an alternative reaction mechanism with a higher activation energy. (6.4) K/U

29. The initial rate of a reaction is the instantaneous rate determined just after the reaction begins (just after $t = 0$). (6.5) K/U

30. The rate constant, k, is the same for all chemical reactions. (6.5) K/U

31. Most chemical reactions occur in a series of steps called the reaction mechanism. (6.6) K/U

32. The global warming potential of "super" greenhouse gases is similar to that of carbon dioxide. (6.7) K/U

UNIT 3 REVIEW

K/U Knowledge/Understanding   C Communication   T/I Thinking/Investigation   A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Potential energy can be defined as energy (5.1) K/U
   (a) associated with an object's location or composition
   (b) related to the motion of an object
   (c) of moving particles
   (d) that is dependent on an object's mass and velocity
2. Which of the following terms describes the study of the transfer of energy that occurs in chemical reactions? (5.1) K/U
   (a) thermal energy
   (b) thermodynamics
   (c) thermochemistry
   (d) none of the above
3. Which of the following defines an endothermic reaction? (5.1) K/U
   (a) a reaction in which matter is not allowed to move into or out of a system
   (b) a reaction in which energy flows out of a system
   (c) a reaction in which energy flows into a system
   (d) all of the above
4. Which of the following is an accepted way to communicate the enthalpy change of a reaction? (5.2) K/U
   (a) writing the energy term into the thermochemical reaction equation
   (b) writing the enthalpy change separately from the reaction equation
   (c) drawing a potential energy diagram
   (d) all of the above
5. A bond in which 3 pairs of electrons are shared by 2 atoms is a (5.3) K/U
   (a) single bond
   (b) double bond
   (c) triple bond
   (d) ionic bond
6. The complete combustion of propane in oxygen is represented by the equation

   $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$

   Which of the following reactions would *not* be required to calculate the enthalpy of combustion of propane? (5.4) K/U
   (a) $3\ C(s) + 4\ H_2(g) \rightarrow C_3H_8(g)$
   (b) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$
   (c) $C(s) + O_2(g) \rightarrow CO_2(g)$
   (d) $CO(g) + O_2(g) \rightarrow CO_2(g)$
7. Which of the following statements about Hess's law is true? (5.4) K/U
   (a) The enthalpy change of a reaction is the same whether the reaction takes place in one step or in a series of steps.
   (b) You can manipulate and combine different chemical reactions to determine the enthalpy change of a reaction.
   (c) If you multiply the coefficients in a balanced equation by an integer, then you also have to multiply the value of ΔH by the same integer.
   (d) all of the above
8. The standard state of a pure substance is
   (a) a pressure of exactly 100 kPa when the substance is in the gas phase
   (b) the most stable form of the substance under standard conditions, 25 °C and 100 kPa
   (c) a concentration of exactly 100 mol/L when the substance is dissolved in water
   (d) the substance in the solid phase (5.5) K/U
9. What is/are the primary component(s) of syngas? (5.6) K/U
   (a) oxygen gas
   (b) hydrogen liquid
   (c) carbon dioxide gas
   (d) hydrogen gas and carbon monoxide gas
10. The rate of a chemical reaction
    (a) tells you how quickly a reactant is consumed or a product is formed
    (b) is expressed as a change in concentration per unit time
    (c) can be determined from a graph of the change in concentration of a reactant or product
    (d) all of the above (6.1) K/U
11. In which state of matter will a reactant undergo a chemical change most slowly? (6.2) K/U
    (a) aqueous
    (b) liquid
    (c) gas
    (d) solid
12. Simple reactions often have an elementary step that is called the rate-determining step, which is
    (a) only for first-order reactions
    (b) faster than the rest of the steps
    (c) known with 100 % certainty
    (d) the step in the reaction that has a much slower rate than the other steps (6.6) K/U

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

13. The terms "thermal energy" and "temperature" mean the same thing. (5.1) K/U
14. Much of the energy emitted from the Sun is released during the nuclear process called fission. (5.1) K/U
15. The quantity of energy needed to increase the temperature of a substance depends on the amount of the substance present. (5.2) K/U
16. The quantity of energy required to break a chemical bond is known as thermal energy. (5.3) K/U
17. According to Hess's law, if you reverse a reaction, you must reverse the sign of ΔH for the reaction. (5.4) K/U
18. An enthalpy of formation is always reported per mole of product in its standard state. (5.5) K/U
19. Electricity generated by wind turbines is far more expensive than electricity generated by other sources. (5.7) K/U
20. The instantaneous reaction rate is the slope of the tangent line to the curve of a graph of concentration versus time. (6.1) K/U
21. Product concentration(s) can be used to express the rate law equation. (6.5) K/U

Understanding

Write a short answer to each question.

22. Distinguish between potential energy and kinetic energy. (5.1) K/U
23. State whether each of the following is an open system or a closed system: (5.1) K/U
    (a) combustion of methane gas to heat a home
    (b) combustion of methane gas in a sealed bomb calorimeter
    (c) water boiling in a kettle with a closed lid
    (d) an acid–base neutralization reaction in a sealed flask
24. Classify each of the following reactions as endothermic or exothermic: (5.1) K/U
    (a) splitting a large gas molecule into smaller gas molecules
    (b) forming a cation from an atom in the gas phase
    (c) mixing elemental sodium and chlorine to form table salt
    (d) nuclear fission
25. Explain the difference between nuclear fission and nuclear fusion. (5.1) K/U
26. List three examples of endothermic reactions. (5.1) K/U
27. List three examples of exothermic reactions. (5.1) K/U
28. Describe how the enthalpy change of a chemical reaction is consistent with the law of conservation of energy. (5.1, 5.2) K/U
29. Explain how bond energies are used. (5.3) K/U
30. Which releases more energy: breaking an N–O bond or forming a P–Cl bond? Refer to Table 1 on page 307 for bond energy values. (5.3) K/U
31. Why is more energy needed to form and break triple bonds than single or double bonds? (5.3) K/U
32. State the two rules you need to apply when calculating enthalpy changes using Hess's law. (5.4) K/U
33. What is the standard enthalpy of formation? (5.5) K/U
34. What are the three main forms of fossil fuels used for energy? Explain the major concern with using fossil fuels as energy sources. (5.6) K/U
35. Suggest any three physical properties that can change during a reaction and that may be used to measure the rate of a reaction. (6.1) K/U
36. In each of the following examples, identify the factor that affects the rate of the reaction: (6.2) K/U
    (a) Gold and copper are both used in jewellery, but copper bracelets turn green over time.
    (b) Milk kept in a refrigerator will keep for a week or more, but milk left out on the counter will quickly turn sour.
    (c) Papain is a food additive that is sometimes added to meat to make it more tender.
    (d) The dust in grain silos has been known to explode, whereas kernels of grain are almost non-flammable.
    (e) Vinegar is safe to add to food and to consume, but pure acetic acid will burn skin on contact.
37. In chart form, summarize the factors that affect reaction rate, and explain, using collision theory, how each factor affects reaction rate. Include an example in each case. (6.3) K/U C
38. How do biocatalysts support the tenets of green chemistry? (6.4) K/U A
39. Explain, with an example, the difference between order of reaction with respect to each reactant and the total order of reaction. (6.5) K/U
40. Explain the difference between an elementary step and the rate-determining step. (6.6) K/U

Analysis and Application

41. Give an example of an endothermic change that you have encountered in your everyday life. Where did the energy for the endothermic change come from? (5.1) K/U A

42. Physical changes in substances often depend on energy released during chemical changes. Suppose you are boiling a pan of water by placing it over a hot campfire. Draw a series of labelled diagrams to show the transfer of energy as the water starts to boil, consistent with the law of conservation of energy. (5.1) K/U C A

43. Calculate the amount of thermal energy, in J and kJ, that is required to heat 1.5 kg of water from 20 °C to 75 °C. The specific heat capacity of liquid water is 4.18 J/(g·°C). (5.2) T/I

44. The molar enthalpy of vaporization of elemental chlorine, Cl_2, is +20.7 kJ/mol. Calculate the enthalpy change during the vaporization of 2.25 kg of elemental chlorine. (5.2) T/I

45. A coffee-cup calorimeter is filled with 200.0 mL of water at 22.1 °C. A piece of metal at 48.6 °C with a mass of 5.1 g is added. The final temperature of the water in the calorimeter is 26.8 °C. The density of liquid water is 1.00 g/mL, and its specific heat capacity is 4.18 J/(g·°C). Determine the specific heat capacity of the metal. (5.2) T/I

46. When 0.40 g of sodium hydroxide is dissolved in 100 mL of water in a coffee-cup calorimeter, the temperature of the water changes from 20.02 °C to 21.12 °C. The specific heat capacity of water is 4.18 J/(g·°C). Determine the heat of dissolution. (5.2) T/I

47. In a coffee-cup calorimeter, 60.0 mL of 0.700 mol/L sodium hydroxide solution was neutralized with 40.0 mL of excess sulfuric acid solution. The temperature increased by 5.6 °C. (5.2) T/I
    (a) Calculate the molar enthalpy of neutralization for sodium hydroxide.
    (b) What assumptions did you make to answer this question?

48. In developing countries, solar ovens are sometimes used to boil water. If 2.00 L of water is heated from 26.5 °C to 100.0 °C, determine the amount of energy that was transferred to the water from sunlight. (5.2) T/I

49. For reactions carried out in a copper flame calorimeter, you must consider the specific heat capacities of the copper metal that makes up the calorimeter and the water contained in the calorimeter. This is because, during a physical or chemical change in this calorimeter type, thermal energy is transferred to both the calorimeter walls and the water. A chemist burns a sample of propanal, C_3H_6O, in a copper flame calorimeter. Her data are presented in **Table 1**. What is the enthalpy of combustion of propanal? (5.2) T/I A

Table 1 Data for the Combustion of Propanal in a Copper Flame Calorimeter

Variable	Value
mass of calorimeter	305 g
mass of water	255 g
mass of propanal	1.01 g
temperature change of calorimeter and contents	+28.8 °C
specific heat capacity of copper	0.385 J/(g · °C)
specific heat capacity of water	4.18 J/(g · °C)

50. Using bond energies given in Table 1 on page 307, determine the enthalpy change for the reaction given by the following balanced chemical equation: (5.3) T/I

$$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$$

51. Using bond energies given in Table 1 on page 307, estimate the enthalpy change for the reactions represented by each of the following chemical equations. Make sure to balance the equations first. (5.3) T/I
    (a) $H_2O_2(aq) \rightarrow H_2O(l) + O_2(g)$
    (b) $CH_3OH(aq) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$
    (c) $CHF_2CHF_2(g) \rightarrow CHCH(g) + F_2(g)$

52. Nitromethane gas, $CH_3NO_2(g)$, is a rapidly burning fuel often used in dragsters, where rate, not energy yield, is important. The combustion of nitromethane gas is given by the equation

$$4\ CH_3NO_2(g) + 3\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ N_2(g) + 6\ H_2O(g)$$

Use Hess's law and the known thermochemical equations given below to calculate the enthalpy change for the combustion of 1 mol of nitromethane: (5.4) T/I

$$C(g) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5\ kJ$$

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g) \quad \Delta H = -483.6\ kJ$$

$$2\ C(g) + 3\ H_2(g) + 2\ O_2(g) + N_2(g) \rightarrow 2\ CH_3NO_2(g) \quad \Delta H = -226.2\ kJ$$

53. The combustion of glucose, $C_6H_{12}O_6$, forms carbon dioxide gas and water vapour. When a 1.00 g sample of glucose was burned, it raised the temperature of 100.0 mL of water by 37.0 °C. (5.2, 5.3, 5.5) T/I A
    (a) Write a balanced chemical equation for this reaction.
    (b) Use ΔH_f° to calculate the enthalpy change of this reaction.
    (c) Use bond energies in Table 1 on page 307 to calculate the enthalpy change of this reaction. The structural formula of glucose is shown in **Figure 1**.

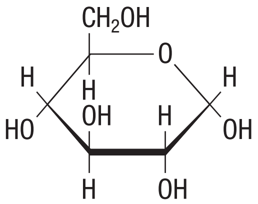


Figure 1

(d) Use the given experimental data to calculate the enthalpy change of this reaction.

(e) Give reasons for any differences in your answers to (b), (c), and (d).

54. The standard molar enthalpy of formation for vinyl chloride gas, $C_2H_3Cl(g)$, is $+37.3$ kJ/mol. Express this information in three different ways. (5.5) T/I

55. The standard enthalpy of formation of sulfur dioxide gas, $SO_2(g)$, is -296.8 kJ/mol. (5.5) T/I C
    (a) Write a thermochemical equation for the formation reaction.
    (b) Sketch a potential energy diagram for the reaction. Label the axes, enthalpy of reactants, enthalpy of products, and ΔH.
    (c) If 9.63 g of sulfur dioxide is formed under standard conditions, what quantity of thermal energy is released?

56. (a) Write an equation for the combustion of 1 mol of pentane gas, $C_5H_{12}(g)$, to form carbon dioxide gas and liquid water.
    (b) Use the standard enthalpies of formation in Table 1 on page 320, and the standard enthalpy of formation of pentane, -146 kJ/mol, to calculate the enthalpy change associated with the combustion of 1 mol of pentane.
    (c) How much thermal energy would be released in the combustion of 20 g of pentane? (5.5) T/I

57. For five different uses of fossil fuels, create and complete a table with the following headings: "Fossil fuel," "Use," "Possible alternative fuel," "Advantage(s) of alternative," and "Disadvantage(s) of alternative." (5.6) K/U C A

58. Summarize the advantages and disadvantages of wind energy using a graphic organizer. Consider social, economic, and environmental factors. (5.7) K/U C

59. **Table 2** shows data collected from an investigation of the chemical reaction between gaseous carbon monoxide and nitrogen dioxide, represented by the balanced chemical equation

    $CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$ (6.1) T/I

    (a) Copy and complete Table 2 by predicting the missing concentration values.
    (b) If the initial concentration of nitrogen dioxide gas, $NO_2(g)$, is 0.250 mol/L, what is its concentration after 80 s? (*Hint*: Refer to Table 2.)
    (c) Use the data in your completed table to create a graph of the changes in concentration of carbon monoxide gas and carbon dioxide gas over time. Plot the data from both gases on one graph.
    (d) Does your graph reflect the stoichiometry of the balanced equation? Explain.

Table 2 Concentration of Carbon Monoxide and Carbon Dioxide

Time (s)	[CO(g)] (mol/L)	[CO_2(g)](mol/L)
0	0.100	
20	0.050	0.050
40	0.033	
60	0.026	0.074
80	0.020	0.080
100		0.083

60. **Table 3** shows observations made during the decomposition of the theoretical gas $X_2O_5(g)$, given by the balanced chemical equation

    $2\ X_2O_5(g) \rightarrow 4\ XO_2(g) + O_2(g)$ (6.1) T/I C

Table 3 Concentration of Reactant and Products during Decomposition

Time (h)	[X_2O_5(g)] (mol/L)	[XO_2(g)] (mol/L)	[O_2(g)] (mol/L)
0.0	1.20	0	0
2.0	0.80		0.20
4.0	0.55		0.325
7.0	0.30		0.45
12.0	0.10		0.55

   (a) On the same axes, plot concentration versus time on a graph to show
      (i) [$X_2O_5(g)$] versus time
      (ii) [$O_2(g)$] versus time
   (b) Complete Table 3.
   (c) Calculate the rate of consumption or formation production in the first 12 h of
      (i) $X_2O_5(g)$
      (ii) $O_2(g)$
      (iii) $XO_2(g)$
   (d) Determine the instantaneous rates of consumption of $X_2O_5(g)$ at 2.0 h and 7.0 h.
   (e) Describe and explain the observed trend in the rate of consumption of X_2O_5 (g).

61. What is the overall rate of production of nitrogen dioxide for the chemical reaction represented by the balanced equation

    $N_2(g) + 2\ O_2(g) \rightarrow 2\ NO_2(g)$

    if the concentration of nitrogen dioxide gas changes from 0.32 mol/L to 0.80 mol/L in 3 min? (6.1) T/I

62. Under certain conditions, gas phase ammonia, $NH_3(g)$, and oxygen gas react as shown by the following balanced chemical equation:

$$4\,NH_3(g) + 5\,O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O(g)$$

When the instantaneous rate of consumption of ammonia is 2.0×10^{-2} mol/(L·s), what will be the instantaneous rate of

(a) consumption of oxygen?

(b) formation of water vapour? (6.1) T/I

63. A student draws the two graphs in **Figure 2** from data he collected during an investigation. Use these graphs to answer the following questions. (6.1) T/I C

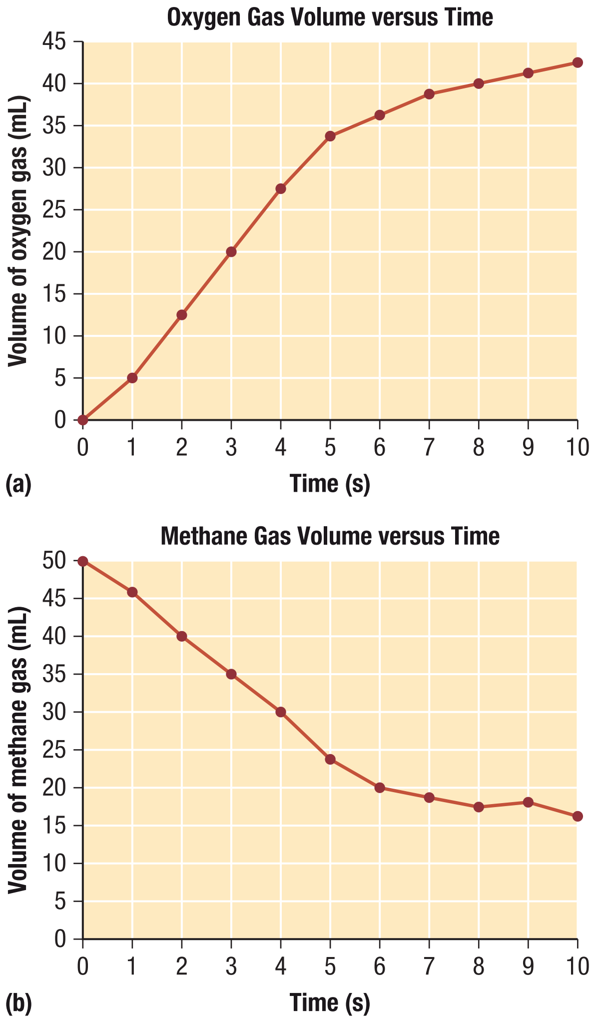


Figure 2

(a) Determine the reaction rate of the decomposition of methane between 3 s and 7 s.

(b) Determine the reaction rate of the production of oxygen gas between 2 s and 6 s.

(c) Identify the reactant and product, based on the graphs. Explain your answer.

64. Predict which of the following reactions you expect to have a higher rate at room temperature. Explain your answer. (6.2) T/I A

$$Pb^{2+}(aq) + 2\,Cl^{-}(aq) \rightarrow PbCl_2(s)$$

$$Pb(s) + Cl_2(g) \rightarrow PbCl_2(s)$$

65. Containers of powdered aluminum metal, a chemical used in laboratory investigations, must carry a warning that the contents are dangerously combustible. Aluminum metal is used in many everyday objects, from frying pans to screen-door frames to the bodies of buses. Why are such objects not required to carry the same warning? (6.2) K/U A

66. At 25 °C, a catalyzed solution of formic acid, $CH_2O_2(aq)$, undergoes a chemical reaction that forms 44.2 mL of carbon monoxide gas, $CO(g)$, in 30.0 s. (6.2) K/U T/I A

(a) Calculate the rate of reaction with respect to carbon monoxide gas production in mL/s.

(b) The experiment was repeated under various conditions, listed below. Predict the effect of each of these conditions on the rate of formation of carbon monoxide. Explain your reasoning.

(i) at 30 °C

(ii) without the catalyst

(iii) with formic acid that is half as concentrated

67. Hydrogen peroxide, $H_2O_2(aq)$, decomposes to oxygen gas, $O_2(g)$, and water under certain conditions. Hydrogen peroxide can be stored for months on the shelf, but will bubble strongly when applied to an open cut. Suggest an explanation for this effect. (6.2, 6.3) T/I A

68. Hydrogen gas and bromine gas can combine to form hydrogen bromide, as shown in the following balanced equation:

$$H_2(g) + Br_2\,(g) \rightarrow 2HBr(g)$$

Using a molecular model kit, illustrate a collision between a hydrogen molecule and a bromine molecule that is likely to be an effective collision. Draw a series of sketches showing the molecular orientation of the 2 entities. (6.3) T/I C

69. A strip of magnesium metal can be safely stored at room temperature for long periods of time (over a year). When a magnesium strip is heated in a flame, it will undergo a rapid, highly exothermic reaction that forms magnesium oxide. When a container of magnesium metal granules is stored at room temperature for about one year, essentially all the magnesium metal will be converted to magnesium oxide. Explain these observations. (6.3) K/U T/I A

70. Create a graphic organizer that summarizes the advantages of biocatalysts over traditional catalysts. (6.4) K/U C

71. A chemical reaction is highly exothermic. How will this affect the rate of this reaction? Explain your answer using the collision theory. (5.1, 6.2, 6.3) K/U

72. Calcium ions, found in hard water, will form solid calcium oxide, CO(s), which builds up over time in plumbing pipes and fixtures. This buildup can be dissolved by soaking the affected hardware in vinegar (dilute acetic acid). Suggest two ways that the rate at which calcium oxide dissolves could be increased. Explain how these would work, using the collision theory. (6.2, 6.3) K/U A

73. The iodine clock reaction can be represented by the following balanced equation:

$$ClO^-(aq) + I^-(aq) \rightarrow Cl^-(aq) + lO^-(aq)$$

A researcher found that the rate was first order with respect to each of the reactants.

(a) Predict what would happen to the initial rate, *r*, when
  (i) the initial $[ClO^-(aq)]$ is doubled
  (ii) the initial $[I^-(aq)]$ is halved
  (iii) the same initial numbers of moles of reactants are placed in a container with half the volume of water

(b) Design an experiment that would enable you to study the effect of change in temperature using the iodine clock reaction. Write a question, prediction, experimental design, equipment and materials list, and procedure, including safety and disposal precautions. (6.5) T/I C A

74. Phosgene, $COCl_2(g)$, is a toxic gas that was used as a chemical weapon in World War I. It is now used primarily in the manufacture of the plastic polyurethane. Phosgene gas is produced when carbon monoxide gas combines with chlorine gas according to the following balanced equation:

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

The reaction is first order with respect to chlorine, and the rate constant is 1.3×10^{-2} L/(mol · s). (6.5) T/I

(a) What is the order of the reaction with respect to carbon monoxide?

(b) You want to increase the reaction rate as much as you can by doubling the initial concentration of one of the reactants. Which reactant would you choose? Explain your reasoning.

75. Using the rate law, determine the rate constant, *k*, of a zero-order reaction if the initial concentration of substance A is 1.5 mol/L and, after 120 s, the concentration of substance A is 0.75 mol/L. (6.5) T/I

76. The bimolecular reaction given by the balanced chemical equation

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2\,H_2O(l)$$

has a rate constant of 1.0×10^{11} L/mol·s. Calculate the rate of the reaction when equal volumes of 0.10 mol/L solutions of hydrochloric acid and sodium hydroxide are mixed. (6.5) T/I

77. The combustion of propane gas, $C_3H_8(g)$, is represented by the following equation: (6.5, 6.6) K/U T/I

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(g)$$

(a) Explain whether you would expect this reaction to occur in a single step or in a series of steps.

(b) If the rate of consumption of propane gas is 4×10^{-2} mol/(L · s), write expressions and numerical values to represent the rate of reaction with respect to oxygen and carbon dioxide gases.

78. Nitrogen monoxide reacts with hydrogen gas to produce nitrogen and water vapour. The reaction mechanism is believed to be

Step 1. $2\,NO(g) \rightarrow N_2O_2(g)$
Step 2. $N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$
Step 3. $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$

(a) Write the overall balanced equation for this process.

(b) Identify the reaction intermediates.

(c) If Step 1 is the slow step, write the rate law equation for this reaction. (6.5, 6.6) T/I

79. For the reaction represented by the balanced chemical equation

$$2\,NO_2Cl(g) \rightarrow 2\,NO_2(g) + Cl_2(g)$$

an investigator proposed the following mechanisms:

(i) $NO_2Cl \rightarrow NO_2 + Cl$ (slow)
$NO_2Cl + Cl \rightarrow NO_2 + Cl_2$ (fast)
(ii) $2\,NO_2Cl \rightarrow N_2O_4Cl_2$ (slow)
$N_2O_4Cl_2 \rightarrow 2\,NO_2 + Cl_2$ (fast)
(iii) $NO_2Cl \rightarrow NO_2 + Cl$ (fast)
$NO_2Cl + Cl \rightarrow NO_2 + Cl_2$ (slow)

He carried out the reaction three times and gathered the data in **Table 4**. (6.5, 6.6) K/U T/I

Table 4 Initial Data from Constant-Temperature Runs

Run	Initial $[NO_2Cl]$(mol/L)	Rate (mol/(L • s))
1	0.0025	3.5×10^{-2}
2	0.0050	7.0×10^{-2}
3	0.0075	1.0×10^{-1}

(a) Use the experimental data to generate the rate law for this reaction.

(b) Using the rate law, determine which of the proposed mechanisms are incorrect.

(c) Is it appropriate to ask which mechanism is correct? Why or why not?

80. A chemist studying the reaction given by the balanced chemical equation

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

obtained the results in **Table 5**. (6.5, 6.6) K/U T/I

Table 5 Initial Data from Constant Temperature Runs

Run	Initial [NO(g)] (mol/L)	Initial [O_2(g)] (mol/L)	Rate (mol/(L • s))
1	0.22	0.15	0.45
2	0.22	0.30	0.90
3	0.44	0.15	1.80

(a) Determine the order of the reaction with respect to nitrogen monoxide.

(b) Determine the order of the reaction with respect to oxygen.

(c) Determine the total order of the reaction.

(d) A proposed mechanism for this reaction is

$NO(g) + O_2(g) \rightarrow NO_2(g) + O(g)$ (fast)

$NO(g) + O(g) \rightarrow NO_2(g)$ (slow)

Does this mechanism agree with the proposed rate law? Support your answer.

Evaluation

81. The per capita energy use of Canadians is one of the highest of any country in the world. (5.6) K/U A

(a) Suggest reasons why this is true.

(b) What changes could Canadians make as a society to decrease our energy use?

(c) What things in Canadian life that affect our energy use cannot be changed?

(d) A classmate believes that the per capita energy use in Canada will always be one of the highest in the world. Do you share this opinion? Give reasons for your answer.

82. There are many different sources of energy that may be used as fuel in the future. Which source or sources of energy do you think we should be looking to develop as an alternative to fossil fuels? Explain your position in the form of a letter to a politician. (5.6) K/U C A

83. Would you be concerned if a wind farm was in your area? Justify your opinion. (5.7) K/U A

84. Fire departments warn people against leaving large masses of paper near a potential source of sparks, such as a furnace or spaceheater. Compare the fire hazard of equal masses of paper and lumber. Do you think similar warnings should be made about storing lumber near potential sources of sparks? Why or why not? (6.2) K/U A

85. Many industries in Canada apply many of the methods to alter the rate of chemical reactions that you explored in this chapter. Which of these methods do you think would be used in industrial processes to increase the rate of a reaction? Refer to the costs and benefits of the various methods available. K/U A

86. Sucrose, fructose, and glucose are all sugars. Sucrose (table sugar) is the sweetest of these, followed by fructose (fruit sugar) and glucose. Sucrose is extracted and purified from sugar cane or sugar beets. An alternative sweetener is a fructose solution produced from corn starch, known as high fructose corn syrup. Starch is extracted from corn and decomposed to glucose. The glucose is converted to sweeter fructose by adding a biocatalyst called glucose isomerase.

(a) What are the advantages to society of producing sugars using a biocatalyst such as glucose isomerase?

(b) High fructose corn syrup is cheaper to produce than sucrose and is used to sweeten many products. What are the disadvantages to society of the use of high fructose corn syrup as a sweetener?

(c) Do you think glucose isomerase has had a positive or a negative effect on society? Explain your answer. (6.4) K/U T/I A

87. Three scientists are independently studying the reaction given by the following balanced chemical equation:

$2\ AB + C_2 \rightarrow 2\ ABC$

The rate law of the reaction was determined to be

rate = $[AB][C_2]$.

Each scientist proposed one of the following reaction mechanisms:

Proposed mechanism 1:

$AB + C_2 \rightarrow ABC + C$ (slow)

$AB + C \rightarrow ABC$ (fast)

Proposed mechanism 2:

$C_2 \rightarrow 2\ C$ (slow)

$C + AB \rightarrow ABC$ (fast)

Proposed mechanism 3:

$AB + C_2 \rightarrow ABC_2$ (fast)

$ABC_2 \rightarrow ABC + C$ (slow)

$AB + C \rightarrow ABC$ (fast)

Which scientist do you agree with? Support your decision. (6.5, 6.6) T/I

88. In an investigation of the reaction given by the balanced chemical equation

$$2\ H_2(g) + 2\ NO(g) \rightarrow N_2(g) + 2\ H_2O(g)$$

the data in **Table 6** were obtained.

Table 6 Initial Data from Constant Temperature Runs

Run	Initial [$H_2(g)$] (mol/L)	Initial [NO(g)] (mol/L)	Rate (mol/(L•s))
1	0.031	0.0025	2.0×10^{-3}
2	0.062	0.0025	4.0×10^{-3}
3	0.031	0.0050	8.0×10^{-3}
4	0.062	0.0050	1.60×10^{-2}

The scientist proposed the following reaction mechanism:

Step 1. $H_2(g) + NO(g) \rightarrow H_2O(g) + N(g)$
Step 2. $N(g) + NO(g) \rightarrow N_2(g) + O(g)$
Step 3. $O(g) + H_2(g) \rightarrow H_2O(g)$

Which step in the proposed mechanism is the rate-determining step? Support your answer. (6.6) T/I

89. (a) Why is it important to know the rate of decomposition of greenhouses gases in the atmosphere?
    (b) Why is the lifespan of a molecule considered in determining the global warming potential (GWP) of an atmospheric gas? (6.7) A

Reflect on Your Learning

90. In this unit you studied a number of ways to determine the enthalpy of a reaction. In a chart, summarize what you know about each method. Include column titles such as Name of method, Summary of method, Strengths, and Weaknesses. T/I C A

91. What did you learn in this unit that you found most surprising? Explain. A

92. State and explain something that you learned in this unit about chemical reactions that you had not known before. A

93. In this unit, you encountered a number of theoretical concepts that scientists do not have direct evidence for, such as an activated complex. Do you think science will ever reach a point where there are no longer any theoretical concepts? Explain your answer. A

94. Many of the concepts that you explored in this unit are relevant to the environmental issues facing society today, such as pollution, global warming, or sustainable practices. Other concepts were not obviously connected to everyday life. Do you think all scientific research should directly address a human issue, or should some of it be driven solely by the desire to understand? Support your position with your own experiences or events in the world at large. K/U A

Research

WEB LINK

95. Design an experiment to test the feasibility of the mass production of ethanol as a replacement for automobile fuel sources. Evaluate the effectiveness of this method in producing fuel and reducing costs to consumers. T/I A

96. Conduct research to investigate the reasoning behind the disparity in coal consumption of each of the Canadian provinces. Why are some provinces consuming far more coal than others? Report your findings as a news article. T/I C A

97. Research how wind power technology has been developed in other parts of the world. Are the same methods employed throughout the globe? Why are some countries turning to this alternative energy source? Share your findings as a web page, blog, or on social media. T/I C A

98. Conduct research to investigate recent developments in finding possible solutions to reducing the concentration of greenhouse gases in the atmosphere. Report your findings in a manner of your choice, but make sure you provide details of ways to reduce each major greenhouse gas. T/I C A

99. Why might pharmaceutical chemists be interested in biological catalysts? (6.2) K/U A

100. Catalysts used in industry can work in two different ways. They are either adsorption catalysts or catalysts that form intermediate compounds. Research each of these types of catalysts, and describe how they work in one or two sentences. Give an example of a situation in which each is most useful and explain why. T/I C A

UNIT 4 Chemical Systems and Equilibrium

OVERALL EXPECTATIONS

- analyze chemical equilibrium processes, and assess their impact on biological, biochemical, and technological systems
- investigate the qualitative and quantitative nature of chemical systems at equilibrium, and solve related problems
- demonstrate an understanding of the concept of dynamic equilibrium and the variables that cause shifts in the equilibrium of chemical systems

BIG IDEAS

- Chemical systems are dynamic and respond to changing conditions in predictable ways.
- Applications of chemical systems at equilibrium have significant implications for nature and industry.

UNIT TASK **PREVIEW**

In the Unit Task, you will choose an acidic or basic consumer product, and then ask and explore a question related to the acidic or basic characteristics of the product.

The Unit Task is described in detail on page 582. As you work through the unit, look for Unit Task Bookmarks to see how information in the section relates to the Unit Task.

FOCUS ON **STSE**

STRIKING A BALANCE: BREATHING, BLOOD, AND BASKETBALL

An athlete living near the coast of Nova Scotia wanted to improve his stamina on the basketball court. He knew that athletes living in Calgary, Alberta, get some benefit just from living in the mountains. The air pressure at higher altitudes is lower than the air pressure at sea level. To simulate this environment, the athlete had devices installed in his home to create an area in which the air pressure was decreased. He hoped that sleeping in this area every night would make a difference in his body's energy reserves during ball games. Why might lower air pressure lead to improved stamina? Stamina is the body's ability to maintain adequate energy levels during periods of more intense activity. Energy is released in the body by cellular respiration. Since oxygen is a reactant in cellular respiration, you tend to run out of energy when your cells do not receive enough oxygen. The oxygen supply of the body depends on a dynamic balance between two substances in red blood cells in the blood: hemoglobin and hemoglobin–oxygen complex.

Oxygen gas diffuses into blood in the lungs and is then bound to hemoglobin in a hemoglobin–oxygen complex. This complex travels to cells where oxygen is needed. Here, the reverse reaction occurs, producing free oxygen and hemoglobin. The body can shift the balance between unbound hemoglobin and hemoglobin–oxygen complex to meet its changing needs. For example, if your muscle cells needed more energy to make a jump shot, the balance would shift in favour of unbound hemoglobin.

This balance is also sensitive to oxygen levels in the air. Air at high altitudes has a lower oxygen concentration than air at low altitudes. If you were to live at high altitude for a long enough time, your body would adapt to the low oxygen levels by producing more hemoglobin. If you were then to go to a lower altitude, the additional hemoglobin would allow your body to supply oxygen to its cells more quickly. By lowering the air pressure in part of his home, the basketball player from Nova Scotia mimicked the high-altitude environment of Calgary. His body therefore made more hemoglobin and his stamina increased.

In this unit, you will explore many other reversible reactions and the factors that affect their balance. You will also explore the important role that some of them play in our health, environment, economy, and industry.

Questions

1. Should all athletes either train at high altitudes or set up their sleeping quarters to simulate high altitudes? Explain your reasoning.
2. Do you think that the effects of training at high altitudes are long term, or do athletes need to maintain high-altitude training?
3. In your opinion, would an athlete who has trained or lived at higher altitudes automatically have an advantage over an athlete who has not? Explain your reasoning.

UNIT 4 ARE YOU READY?

CONCEPTS

- states of matter
- formation of solutions
- acids and bases
- gas laws
- kinetic-molecular theory

SKILLS

- convert between mass and amount
- determine concentration of solutions
- write and balance chemical equations
- solve algebraic equations
- plan an investigation
- analyze experimental data and form conclusions

Concepts Review

1. Solid sucrose, $C_{12}H_{22}O_{11}(s)$, has a crystalline structure. Rock candy is an example of the large crystal size that sucrose can achieve. **Figure 1** shows a series of diagrams in which a large piece of rock candy was suspended in an aqueous solution of sucrose. The system was maintained at SATP for 10 days. K/U

Figure 1 Changes observed when a sucrose crystal was suspended in an aqueous sucrose solution for 10 days.

   (a) What does SATP stand for?
   (b) List the states of matter that you observe in the jar for day 1.
   (c) From your observations of Figure 1, when does the solution become saturated? Explain.
   (d) Explain what would happen to the liquid in the jar if the lid were removed on day 10.
   (e) Would you expect the crystal to change in size in the open jar after day 10? Explain.

2. Zinc metal, $Zn(s)$, reacts with aqueous hydrochloric acid, $HCl(aq)$, to produce aqueous zinc chloride, $ZnCl_2(aq)$, and hydrogen gas, $H_2(g)$. T/I
   (a) Write a balanced chemical equation for this reaction.
   (b) What mass of aqueous zinc chloride will be produced when 250 mL of 0.80 mol/L aqueous hydrochloric acid reacts with excess zinc metal?
   (c) Calculate the concentration of aqueous zinc chloride, c_{ZnCl_2}, in the resulting solution. Assume that the volume remains constant.

3. (a) Explain how an acid can be both weak and concentrated. Use an example to illustrate.
   (b) Identify the ions present in an aqueous solution of nitric acid, $HNO_3(aq)$. K/U

4. Explain why a substance goes into solution at a faster rate when the temperature is raised. K/U

5. Create a diagram to show what happens to an ideal gas in a closed, rigid container when the volume is decreased. Which gas law does your diagram illustrate? K/U C

6. On a chilly October morning, you notice that your car's tires look a bit flat. Use the kinetic-molecular theory to explain why all your tires need to be filled, assuming that none of them were damaged. K/U A

Skills Review

7. Calculate the mass of magnesium chloride, $MgCl_2(aq)$, that is present in 4.0 L of a solution with a concentration of 0.5 mol/L. T/I

8. Nitric acid is important in the manufacture of fertilizer. Concentrated nitric acid, $HNO_3(aq)$, can be produced from ammonia gas, $NH_3(g)$, in a series of reactions known as the Oswald process. The steps in the Oswald process are shown by the following unbalanced equations:

$$NH_3(g) + O_2(g) \longrightarrow NO(g) + H_2O(g)$$

$$NO(g) + O_2(g) \longrightarrow NO_2(g)$$

$$NO_2(g) + H_2O(l) \longrightarrow HNO_3(aq) + NO(g)$$

T/I A

   (a) Balance each of the equations above so that the number of nitrogen atoms from ammonia gas is equal to the number of nitrogen atoms in the products in the third equation (that is, liquid nitric acid and nitrogen monoxide gas). *Hint*: Begin by balancing the third equation and then work backwards.
   (b) A chemist carries out the Oswald process beginning with 405 g of ammonia gas. She produces 1.0 L of a solution of nitric acid. Determine the concentration of this solution, c_{HNO_3}, assuming that plenty of all the other reactants is available.
   (c) Do you think the actual solution produced would have the exact concentration you determined in (b)? Why or why not?

9. Write a brief procedure to compare the solubility of carbon dioxide gas, $CO_2(g)$, in pop at different temperatures. T/I A

10. (a) The solubility of solid calcium hydroxide, $Ca(OH)_2(s)$, is 0.10 g/100 mL at 60 °C. Calculate the concentration of aqueous hydroxide ions, $OH^-(aq)$, in mol/L for a saturated calcium hydroxide solution at this temperature.
    (b) If you added more solid calcium hydroxide to the solution described in (a), would the concentration of hydroxide ions in solution increase? Explain. K/U T/I

11. (a) Write the balanced chemical, total ionic, and net ionic equations for the reaction between aqueous sodium hydroxide, $NaOH(aq)$, and sulfuric acid, $H_2SO_4(aq)$.
    (b) Identify the type of reaction that occurs between aqueous sodium hydroxide and sulfuric acid.
    (c) The apparatus in **Figure 2** is used to carry out the above reaction. Name the container that holds the aqueous sodium hydroxide and delivers it in measured volumes to the flask.

Figure 2

    (d) Name the laboratory procedure that would be carried out using the apparatus shown in Figure 2.
    (e) Predict the volume of 1.00 mol/L sodium hydroxide solution that would be required to completely react with 20.0 mL of 1.50 mol/L sulfuric acid.

12. Solve the following equations for x: T/I

    (a) $\dfrac{(0.20)(0.30)}{(0.010)x} = 2.3 \times 10^{-4}$

    (b) $\dfrac{(2x)^2}{(x - 0.10)^2} = 36$

    (c) $\dfrac{(3.0x)^2}{(x - 2.0)(x - 4.0)} = 2.0$

13. Residents of a small community noticed that their tap water has developed an acidic taste. To try to solve the problem, the water commissioner ordered that the pH of the town's water supply be measured every month for a year. **Table 1** shows the pH measurements made from January to December.

    The commissioner reviewed these results and used them to calculate the average water pH for the year. She then issued a report stating that an average pH of 5.7 is not a concern and no action would be taken. She defended her decision by stating that at pH 5.7, the water was much less acidic than foods such as salad dressing and citrus fruits. Do you agree with the commissioner's analysis? Why or why not? A

Table 1 Measured pH in Tap Water each Month

Month	J	F	M	A	M	J	J	A	S	O	N	D
pH	6.0	6.4	5.8	6.2	5.9	5.6	5.3	4.9	4.8	5.6	5.7	6.1

CAREER PATHWAYS **PREVIEW**

Throughout this unit you will see Career Links. Go to the Nelson Science website to find information about careers related to Chemical Systems and Equilibrium. On the Chapter Summary page at the end of each chapter you will find a Career Pathways feature that shows you the educational requirements of the careers. There are also some career-related questions for you to research.

CHAPTER 7

Chemical Equilibrium

KEY CONCEPTS

After completing this chapter you will be able to

- demonstrate an understanding of dynamic equilibrium in a variety of situations, and use the equilibrium law to solve problems
- apply Le Châtelier's principle to predict how various factors affect a chemical system at equilibrium
- carry out laboratory investigations to explore equilibrium systems and to determine equilibrium constants
- explain how equilibrium principles may be applied to optimize the production of industrial chemicals
- identify the effects of solubility on biological systems

How Do Reversible Reactions Affect Living Organisms and the Environment?

Atmospheric carbon dioxide, $CO_2(g)$, is often in the news in its role as a greenhouse gas. Carbon dioxide gas is released during many human activities, especially the combustion of fossil fuels. Since greenhouse gases absorb and retain thermal energy, increasing levels of atmospheric carbon dioxide gas contribute to climate change. A number of natural processes absorb carbon dioxide gas from the atmosphere. Unfortunately, some of these processes can also have negative effects on the environment. For example, carbon dioxide can dissolve in water, $H_2O(l)$, to form a solution of carbonic acid, $H_2CO_3(aq)$. This reaction is reversible. In the reverse direction, carbonic acid decomposes to form carbon dioxide gas and water.

When the concentrations of the reactants and products are stable, there is a balance between the rates of the forward and reverse reactions. However, since the concentration of carbon dioxide gas in the atmosphere is increasing, the rate of carbonic acid formation is also increasing. As a result, many bodies of water, including the oceans, are becoming more acidic. Some ocean ecosystems are extremely sensitive to changes in pH. At particular risk are organisms that have exoskeletons composed of calcium carbonate, $CaCO_3(s)$, such as corals and shellfish. Calcium carbonate dissolves in acidic solutions. Scientists have shown that ocean acidification causes bleaching and death of coral reefs.

To slow down or reverse the acidification of oceans due to increasing concentrations of atmospheric carbon dioxide, we must find a way to re-establish the balance in the reversible chemical reaction between water and carbon dioxide. We could reduce the concentration of atmospheric carbon dioxide, so that less carbonic acid forms, or increase the rate of carbonic acid decomposition in ocean water.

STARTING **POINTS**

Answer the following questions using your current knowledge. You will have a chance to revisit these questions later, applying concepts and skills from the chapter.

1. A store clerk notices that there are always exactly 7 customers in the store, even though people continually enter and leave.
   (a) How does the number of customers in the store remain constant over time?
   (b) What would happen to the total number of customers if the number entering the store were greater than the number leaving?
   (c) How is the situation in (a) different from inviting 7 customers to the store for a product demonstration and then closing the doors to other customers?
2. When running on a treadmill, a person must move forward at a rate that equals the rate of the reverse motion of the treadmill's belt. Describe two situations in your daily life that, like the treadmill, are examples of a state of balance between two opposing processes.
3. The molar solubility of solid lead(II) iodide, $PbI_2(s)$, in pure water, $H_2O(l)$, is 1.3×10^{-3} mol/L. If water were replaced by a solution of 0.1 mol/L sodium iodide, $NaI(aq)$, predict whether the solubility of lead(II) iodide would increase or decrease. Provide a reason for your prediction.
4. (a) The following balanced chemical equation represents the formation of carbonic acid, $H_2CO_3(aq)$, from carbon dioxide and water. Why is there a double arrow?

   $$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \quad \Delta H^\circ = -20.3 \text{ kJ}$$

   (b) What does ΔH° stand for? What does it tell you about this reaction?
   (c) If the reaction in (a) were carried out in a closed container and the container were heated, would the production of carbonic acid increase or decrease? Explain.

Mini **Investigation**

Back to Blue?

Skills: Predicting, Observing, Evaluating

SKILLS HANDBOOK **A1.2, A2.1, A3.2**

Most familiar chemical reactions come to an end once all the reactants are used up. For example, if an iron object is left outside, the iron will react with oxygen and water in the environment to form rust. Eventually, all the iron is converted to rust and the chemical reaction has to end. In this activity, you will observe a chemical reaction that does not have a definite end point.

Equipment and Materials: lab apron; chemical safety goggles; gloves; 250 mL graduated cylinder; 400 mL flask; weighing paper; balance; stirring rod; stopper; water; 1 % methylene blue; 5.0 g potassium hydroxide crystals, KOH(s); 3.0 g glucose, $C_6H_{12}O_6$(s)

Potassium hydroxide is toxic and corrosive, both as a solid and as a solution. Eye protection must be worn. Any spills on the skin, in the eyes, or on clothing should be washed immediately with plenty of cool water. Report any spills to your teacher.

1. Put on your lab apron, safety goggles, and gloves.
2. Measure 250 mL of water with the graduated cylinder, then pour it into the flask. Add 6 drops of methylene blue.
3. Using the balance, measure 5.0 g of potassium hydroxide onto weighing paper. Transfer it to the flask. Then, measure and transfer 3.0 g of glucose.
4. Stir the liquid in the flask with the stirring rod until all the solids have dissolved. Put the stopper in the flask. Observe and record the colour of the solution.
5. Pick up the flask and, holding the stopper in place, shake the solution vigorously. Place the flask down on a surface. Observe and record any changes.
6. Continue to observe the flask until another colour change occurs. Record your observations.

A. Suggest an explanation for the observations you recorded in Steps 4 to 6. T/I

B. Predict whether the colour will continue to change over an extended period of time. Then, describe how you might test your prediction. T/I

7.1

Equilibrium Systems

When doing stoichiometry calculations, we generally assume that chemical reactions proceed until one of the reactants runs out. At this point, we say that the reaction has gone to completion. This is true for most chemical reactions. However, some chemical reactions do not proceed to completion. **Figure 1** shows the changes that take place when nitrogen dioxide gas, $NO_2(g)$, is placed in a sealed, evacuated chamber at 25 °C. Nitrogen dioxide gas reacts to form dinitrogen tetroxide gas, $N_2O_4(g)$, as is represented by the equation

$$2\ NO_2(g) \rightarrow N_2O_4(g)$$

The sealed chamber ensures that the reaction takes place in a closed chemical reaction system. In a closed system, energy may transfer from the surroundings to the chemical system, or from the chemical system to the surroundings, but matter cannot. (You encountered this term in Chapter 5.) Nitrogen dioxide is a dark brown gas, whereas dinitrogen tetroxide gas is colourless, so the colour in the chamber provides visual evidence of their relative quantities. The initial dark brown colour of the gas decreases in intensity as it is converted to colourless dinitrogen tetroxide gas.

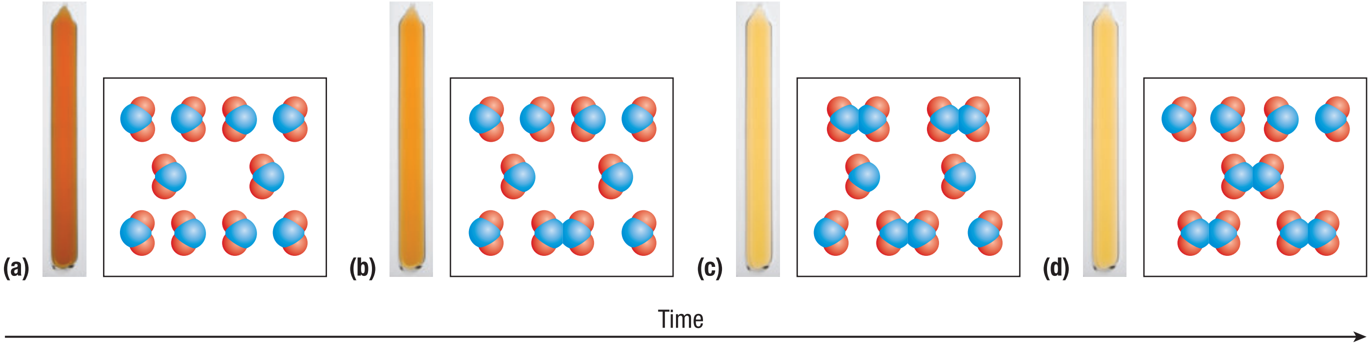


Figure 1 (a) Initially, the vial contains only molecules of brown nitrogen dioxide gas. In the vial shown in (b) some of the nitrogen dioxide gas has been converted to dinitrogen tetroxide gas, which is colourless. Eventually, in (c) and (d), an equilibrium is established, so the gas remains the same colour.

However, even over a long time, the intensity of the brown colour eventually remains constant. The gas never becomes completely colourless. This indicates that the concentration of nitrogen dioxide is no longer changing. The reaction has clearly stopped short of completion. When the concentrations of all reactants and products of a chemical reaction remain constant over time, we say that this system has reached **chemical equilibrium**. Any chemical reaction carried out in a closed system will eventually reach chemical equilibrium. All of the reactions explored in this chapter take place in closed systems.

chemical equilibrium the state of a reaction in which all reactants and products have reached constant concentrations in a closed system

The Equilibrium Condition

dynamic equilibrium a balance between forward and reverse processes that are occurring simultaneously at equal rates

All chemical equilibria are dynamic equilibria. A **dynamic equilibrium** is an equilibrium in which the rates of forward and reverse processes are equal. To help picture a dynamic equilibrium, imagine 18 000 people attending a sporting event. Most of them are in their seats for most of the time, but there are always about 400 people at the concession stands buying snacks. This means that on average 17 600 people are in their seats. Throughout the event, people continuously move back and forth from the seats to the concessions but the total number in each area remains constant. Since it is a closed system, we can therefore describe this as a closed system in dynamic equilibrium.

Why is a chemical equilibrium always a dynamic equilibrium? To answer this, consider the chemical reaction between steam, $H_2O(g)$, and carbon monoxide gas, $CO(g)$, in a closed vessel at a high temperature. The balanced equation for this reaction is

$$H_2O(g) + CO(g) \rightarrow H_2(g) + CO_2(g)$$

Assume that we start with equal amounts of carbon monoxide gas and water vapour. From the balanced equation, we know these substances react in a 1:1 molar ratio. Therefore, if we start off with equal concentrations, the concentrations of these two gases will always be equal. Similarly, since hydrogen gas, $H_2(g)$, and carbon dioxide gas, $CO_2(g)$, are formed in equal amounts, the concentrations of these gases will also always be equal.

Under the conditions of a closed vessel at a high temperature, the chemical reaction begins immediately and progresses very quickly. **Figure 2** shows the changes in the concentrations of reactants and products of this reaction over time. Notice how, as the concentrations of the products increase, the concentrations of the reactants decrease. At the time indicated by the dashed vertical line in Figure 2, the concentrations of reactants and products remain stable. This is the point at which chemical equilibrium has been reached. No further changes in the concentrations of reactants or products will occur (unless the chemical system is changed in some way, as you will see in Section 7.2). WEB LINK

LEARNING **TIP**

Concentration Notation

By convention, when the formula of a substance is placed between square brackets, we are referring to the concentration of that substance. For example, the concentration of carbon dioxide gas is labelled $[CO_2(g)]$ in Figure 2. Concentration also may be denoted by the symbol *c*.

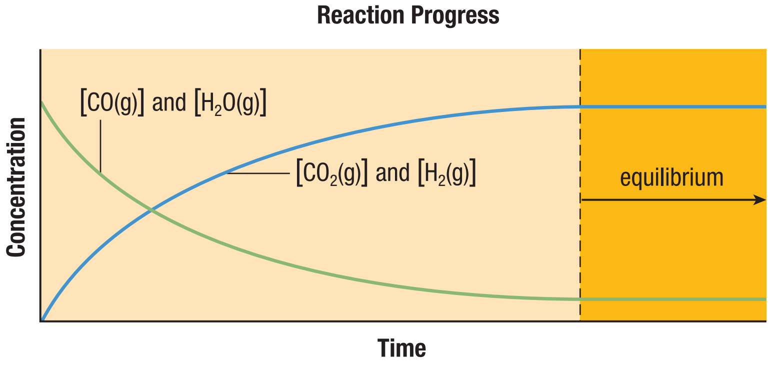


Figure 2 Changes in concentrations over time, when equal amounts of carbon monoxide gas and water vapour are allowed to react in a closed vessel

Scientists call the relative concentration of reactants and products in a chemical reaction system at equilibrium the **equilibrium position**. In the reaction depicted in Figure 2, the equilibrium position is the point at which the relative concentrations of the reactants and products stop changing. By convention, the equilibrium position is communicated in reference to the left-hand side (the reactant side) or the right-hand side (the product side).

equilibrium position the relative concentrations of reactants and products in a system in dynamic equilibrium

The equilibrium position of the reaction between water vapour and carbon monoxide gas lies far to the right. In other words, almost all the reactants are converted to products. However, the concentrations of the reactants never reach zero. If all chemical equilibria are dynamic equilibria, what chemical reactions are occurring?

Reversible reactions are chemical reactions that proceed in both the forward and reverse directions. In a dynamic equilibrium, the reaction rates in the forward and reverse directions of a reversible reaction are equal and so a constant concentration of reactants and products will always be present. Reversible reactions are identified by a double arrow symbol ($\rightleftharpoons$) in a chemical equation. The balanced equation for our example is therefore

reversible reaction a chemical reaction that proceeds in both the forward and reverse directions, setting up an equilibrium in a closed system

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

When the water vapour and carbon monoxide gas were first added to the closed vessel, no hydrogen gas or carbon dioxide gas were present (**Figure 3**). Since there were no reactants available for the reverse reaction, it did not occur. As the forward reaction proceeded, the concentrations of hydrogen gas and carbon dioxide gas increased, providing reactants for the reverse reaction. Consequently, the rate of the reverse reaction increased. The system reached equilibrium once the rate of the forward reaction became equal to the rate of the reverse reaction.

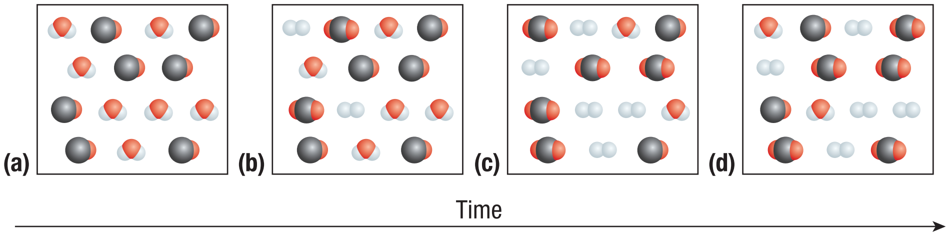


Figure 3 (a) Water vapour and carbon monoxide gas are mixed in equal amounts and (b) begin to react to form gaseous carbon dioxide and hydrogen. After some time, (c) equilibrium is reached and from that point on (d) the numbers of reactant and product molecules then remain constant over time.

Mini **Investigation**

The Water Exchange

Skills: Predicting, Performing, Observing, Evaluating

SKILLS HANDBOOK **A2.1, A3.2, A6.5**

When a reversible chemical reaction occurs in a closed system, the system eventually reaches dynamic equilibrium. In this investigation, you and a partner will use volumes of water to model the development of a system at equilibrium.

Equipment and Materials: marker; two 50 mL graduated cylinders; 2 large straws; water

1. Work in pairs. With the marker, label one 50 mL graduated cylinder "A" and the other "B."
2. Measure 50 mL of water into cylinder A only. Then, place one large straw in cylinder A and another in cylinder B.
3. Create a table to record the volume of water in cylinders A and B. You will need room to record about 20 volumes for each.
4. Working simultaneously, one partner must trap the water in the straw in cylinder A and transfer it to cylinder B while the other partner must trap any water in the straw in cylinder B and transfer it to cylinder A. To trap and transfer the water, first hold the straw flat against the cylinder bottom with one hand. Then, wet one finger on the other hand and use that finger to cover the top of the straw. Lift the straw with both hands and transfer it to the other cylinder.
5. Once you and your partner have transferred your straw to the other cylinder, release the straw and let the water flow out. Then, measure and record the volume in each cylinder.
6. Return each empty straw to its original cylinder.
7. Repeat Steps 4 to 6 until the volumes stop changing.
8. Clean up your area.

A. Using the data in your table, create a graph of the data by plotting volume over the number of transfers. Place the data from both cylinder A and cylinder B on the same graph. T/I C

B. How did the volumes of water in each of the cylinders change over the course of this activity? T/I

C. Describe how you can tell from your graph when equilibrium was established. T/I

D. Consider that the straws, cylinders, and water comprise a system. Is the system open or closed? Why? K/U T/I

E. Explain how this investigation modelled a dynamic equilibrium. T/I A

Forward and Reverse Reactions

In an equilibrium system, an equilibrium position can be reached starting from the forward reaction or from the reverse reaction. Is the equilibrium position the same starting from either side? Consider the chemical reaction system between dinitrogen tetroxide gas, $N_2O_4(g)$, and nitrogen dioxide gas, $NO_2(g)$, that was depicted in Figure 1. In a sealed vessel at SATP, the reaction will progress to chemical equilibrium, according to the balanced chemical equation

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

Table 1 shows the initial concentrations and the final concentrations reached at equilibrium for two different experiments. In the first, a sealed 1 L vessel was filled with only nitrogen dioxide gas. In the second, the vessel initially contained only dinitrogen tetroxide.

Table 1 Changes in Concentrations of $NO_2(g)$ and $N_2O_4(g)$ by the Forward or Reverse Reactions

	Initial concentrations (mol/L)		**Final concentrations (mol/L)**	
	$N_2O_4(g)$	$NO_2(g)$	$N_2O_4(g)$	$NO_2(g)$
Experiment 1	0.750	0	0.721	0.0580
Experiment 2	0	1.50	0.721	0.0580

UNIT TASK BOOKMARK

As you work on the Unit Task described on page 582, you might apply what you learned about forward and reverse reactions in equilibrium systems.

Notice that the initial concentration of dinitrogen tetroxide gas in experiment 1 is half that of the nitrogen dioxide gas in experiment 2. As shown in **Figure 4**, when one molecule of dinitrogen tetroxide gas reacts, two molecules of nitrogen dioxide gas form. The initial concentrations of gases were chosen to reflect this 1:2 ratio. Regardless of which substance was the reactant and which was the product, the final concentrations of the gases at equilibrium are the same (**Figure 5**). WEB LINK

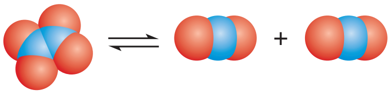


Figure 4 Molecular model of decomposition of dinitrogen tetroxide gas to nitrogen dioxide gas

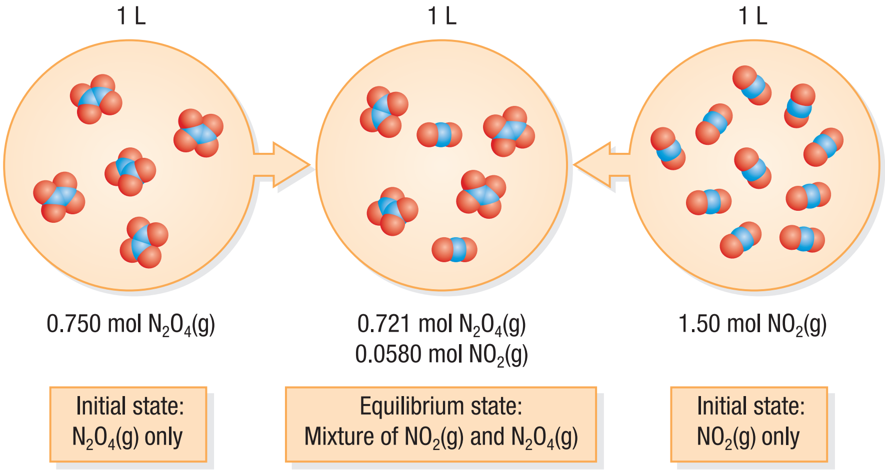


Figure 5 The composition of the mixture at dynamic equilibrium is the same regardless of whether the system started with gaseous nitrogen dioxide or with gaseous dinitrogen tetroxide.

From experiments like this, chemists have made the following generalization:

> For a closed chemical equilibrium system in constant environmental conditions, the same equilibrium concentrations are reached regardless of the direction by which equilibrium was reached.

Investigation 7.1.1

The Extent of a Chemical Reaction (page 472)

In this investigation you will combine various quantities of two solutions that react to form a precipitate. You will then test the precipitate to discover whether any or both of the reactants remain in solution to see if the reaction went to completion or formed an equilibrium.

Stoichiometry and Chemical Equilibria

When the concentrations of reactants and products do not change, is the reaction always at equilibrium? To answer this, consider the synthesis of ammonia gas, $NH_3(g)$. Ammonia gas is an important compound used in the production of plant fertilizers. Canada alone produces over 4000 million t of ammonia every year. Ammonia gas can be synthesized from nitrogen gas and hydrogen gas by the chemical reaction system given by the equation

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

If you were a manufacturer of ammonia, you would want to maximize the quantity of ammonia gas produced under particular conditions. Manufacturing needs such as yield are one reason that drives chemists to explore the characteristics of chemical equilibria. CAREER LINK

In experiments, when gaseous nitrogen, hydrogen, and ammonia are mixed in a closed vessel at 25 °C, the reaction is very slow. The concentrations of these gases change very little over time, regardless of the initial amounts. Chemists think that lack of reactivity is due to the strength of the bonds in the reactants—substances with high bond energies are less reactive. The bond energy of the N–N bond is 941 kJ/mol and the bond energy of the H–H bond is 432 kJ/mol. Both of these bonds are very strong and so both the reactants in ammonia gas synthesis are very unreactive. Manufacturers of ammonia gas use an iron catalyst to increase the rate of ammonia synthesis. In turn, the rate of the reverse reaction increases with the quantity of ammonia produced until equilibrium is reached.

LEARNING TIP

Concentrations of Gases

Concentrations provided to you in this chapter are given in moles per litre. A concentration of 1.00 mol/L of hydrogen gas, $H_2(g)$, means there is one mole of $H_2(g)$ per litre of space occupied.

You can predict the changes in concentration of reactants and products as a system approaches equilibrium from the coefficients of a balanced chemical equation (the stoichiometry). For the ammonia reaction system, the molar ratio of nitrogen gas to hydrogen gas to ammonia gas is 1:3:2. From this ratio, you can predict that, for every 1 mol of nitrogen gas that reacts, 3 mol of hydrogen gas will be consumed and 2 mol of ammonia gas will form. Experiments have confirmed these predictions (**Figure 6**). The decrease in hydrogen gas concentration is 3 times the decrease in nitrogen gas concentration. The increase of ammonia concentration is 2 times the decrease of the nitrogen concentration. You can also use the 1:3:2 molar ratio to predict concentration changes in reactants and products when equilibrium is reached from the opposite direction.

In fact, for many years chemists were unable to find conditions under which this reaction system would reach equilibrium at a rate that converted the reactants to ammonia gas quickly enough to be useful. As you will see in Section 7.3, the scientist who eventually solved this puzzle was given a Nobel prize to honour the achievement.

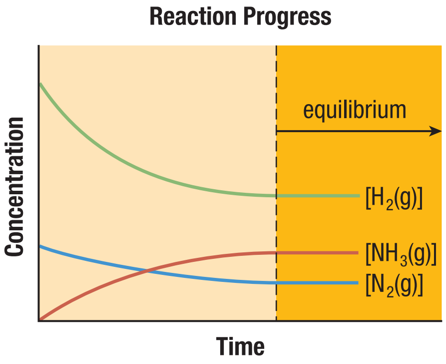


Figure 6 Concentration changes over time for the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ when only nitrogen gas and hydrogen gas are mixed initially.

Determining Concentrations for Chemical Equilibria

For chemical equilibrium systems composed of aqueous solutions or gases, one strategy to perform stoichiometric calculations is to use an ICE table. In an ICE table, I stands for "initial" concentrations of reactants and products before the reaction, C for "change" in the concentrations of reactants and products from the start of the reaction to when equilibrium is achieved, and E for "equilibrium" concentrations of reactants and products.

Tutorial 1 Calculating Equilibrium Concentrations

In this tutorial, you will use an ICE table to find concentrations in chemical equilibrium systems. Although stoichiometric calculations use either concentrations or the amount in moles because the volume of the system remains the same, we will always use concentration values in ICE tables and in calculations involving equilibrium. Keep in mind that the values in ICE tables must be in mol/L.

Sample Problem 1: Calculating Equilibrium Concentrations from Initial Reactant Concentrations

Hydrogen fluoride gas, HF(g), is used in the production of many important substances, such as medicines. Hydrogen fluoride may be synthesized from gaseous hydrogen, $H_2(g)$, and fluorine, $F_2(g)$. The balanced chemical equation for this reaction is

$$H_2(g) + F_2(g) \rightleftharpoons 2\ HF(g)$$

When a chemist starts this chemical reaction in a sealed container at SATP, the initial concentration of gaseous hydrogen and of gaseous fluorine is 2.00 mol/L. No hydrogen fluoride gas is present initially. What are the equilibrium concentrations of hydrogen gas and hydrogen fluorine gas, if the equilibrium concentration of floride gas is 0.48 mol/L?

Given: $[H_2(g)]_{\text{initial}} = 2.00$ mol/L; $[F_2(g)]_{\text{initial}} = 2.00$ mol/L; $[HF(g)]_{\text{initial}} = 0$ mol/L; $[F_2(g)]_{\text{equilibrium}} = 0.48$ mol/L

Required: $[H_2(g)]_{\text{equilibrium}}$; $[HF(g)]_{\text{equilibrium}}$

Analysis: Set up an ICE table. Your table should have two columns and three rows. Put the letters I, C, and E in the cells of the first column. Then, write the balanced chemical equation above the second column. Add the initial concentrations to the I row, under the corresponding symbol in the chemical equation.

Use a variable, such as *x*, to represent the changes in the concentrations of reactants and products. Then add coefficients to *x* that correspond to the coefficients in the balanced equation.

From the balanced equation, you know that $H_2(g)$ and $F_2(g)$ are converted to HF(g) in a 1:1:2 molar ratio. During the reaction, the concentrations of $H_2(g)$ and $F_2(g)$ decrease as the concentration of HF(g) increases. Since $H_2(g)$ and $F_2(g)$ are consumed in a 1:1 molar ratio, the decrease in their concentrations is $-x$ mol/L. Since 2 mol of HF(g) are produced per 1 mol of $H_2(g)$ and of $F_2(g)$, the increase in concentration of HF(g) is $+2x$. The equilibrium concentrations of $H_2(g)$ and $F_2(g)$ will be their initial concentrations, 2.00 mol/L, minus the decrease in their concentrations (*x* mol/L).

In the E row of your ICE table, place the expression $2.00 - x$ under both $H_2(g)$ and $F_2(g)$. Since there was initially no HF(g), the equilibrium concentration of HF(g) will be $0 + 2x$, or $2x$, (the increase in its concentration). Your ICE table should now look similar to **Table 2**. Remember that the units of all values are mol/L.

Table 2 ICE Table for Calculating Equilibrium Concentrations

	$H_2(g)$	+	$F_2(g)$	$\rightleftharpoons$	2 HF(g)
I	2.00		2.00		0
C	$-x$		$-x$		$+2x$
E	$2.00 - x$		$2.00 - x$		$2x$

Solution

Step 1. Write and solve the equation for *x*, using the values in the ICE table.

$[F_2(g)]_{\text{equilibrium}}$ was given as 0.48 mol/L. By your analysis, you also know that $[F_2(g)]_{\text{equilibrium}}$ is represented by the expression $2.00 - x$.

$$\begin{aligned} 2.00\ \text{mol/L} - x &= 0.48\ \text{mol/L} \\ -x &= 0.48\ \text{mol/L} - 2.00\ \text{mol/L} \\ &= -1.52\ \text{mol/L} \\ x &= 1.52\ \text{mol/L} \end{aligned}$$

Step 2. Use the value of *x* to calculate the equilibrium concentrations of the other two entities.

$$\begin{aligned} [H_2(g)] &= 2.00\ \text{mol/L} - x \\ &= 2.00\ \text{mol/L} - 1.52\ \text{mol/L} \\ [H_2(g)] &= 0.48\ \text{mol/L} \\ [HF(g)] &= 2x \\ &= 2(1.52\ \text{mol/L}) \\ [HF(g)] &= 3.04\ \text{mol/L} \end{aligned}$$

Statement: The equilibrium concentrations of hydrogen gas and hydrogen fluoride gas are 0.48 mol/L and 3.04 mol/L, respectively.

Sample Problem 2: Equilibrium Concentrations from a Graph of Reaction Progress

When ammonia gas, $NH_3(g)$, is heated, it decomposes to form nitrogen gas, $N_2(g)$, and hydrogen gas, $H_2(g)$. A chemist adds 4.0 mol of ammonia gas to a 2.0 L sealed, rigid container and heats it. **Figure 7** shows the changes in the amount of ammonia gas she observed over time.

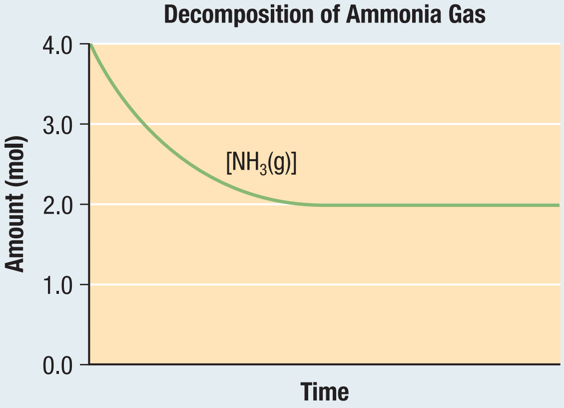


Figure 7

The balanced equation for this chemical reaction system is

$$2\ NH_3(g) \rightleftharpoons N_2(g) + 3\ H_2(g)$$

Determine the equilibrium concentrations of $N_2(g)$ and $H_2(g)$.

Given: initial quantity of $NH_3 = 4.0$ mol; volume $= 2.0$ L

Required: $[N_2(g)]_{\text{equilibrium}}$; $[H_2(g)]_{\text{equilibrium}}$

Solution:

Step 1. Calculate the initial concentration of ammonia gas.

$$[NH_3(g)]_{\text{initial}} = \frac{4.0\text{ mol}}{2.0\text{ L}}$$

$$[NH_3(g)]_{\text{initial}} = 2.0\text{ mol/L}$$

Step 2. Using Figure 7, determine the amount of ammonia gas at equilibrium, once the amount remains stable

Since the amount is stable at the last time point, this is the amount of ammonia gas at equilibrium.

$$[NH_3(g)]_{\text{equilibrium}} = \frac{2.0\text{ mol}}{2.0\text{ L}}$$

$$[NH_3(g)]_{\text{equilibrium}} = 1.0\text{ mol/L}$$

Step 3. Use an ICE table to determine the equilibrium concentrations of $N_2(g)$ and $H_2(g)$.

First, list the initial concentrations of reactants and products in the I row. Then, indicate changes in concentrations in the C row by letting multiples of x represent changes in the concentrations of reactants and products. Remember that the multiples of x always correspond to the coefficients in the balanced equation. Then, where appropriate in the E row, use positive x expressions to indicate that a reactant or product increases in concentration as the reaction proceeds, and negative x expressions to indicate that a reactant or product decreases in concentration as the reaction proceeds. Your ICE table should be similar to **Table 3**.

Table 3 ICE Table for Calculating Equilibrium Concentrations

	$2\ NH_3(g)$	$\rightleftharpoons$	$N_2(g)$	$+$	$3\ H_2(g)$
I	2.0		0		0
C	$-2x$		$+x$		$+3x$
E	$2.0 - 2x$		x		$3x$

Step 4. Calculate the value of x, using the initial, change, and equilibrium concentrations of ammonia gas.

$$\begin{aligned} 2.0\text{ mol/L} - 2x &= 1.0\text{ mol/L} \\ -2x &= -1.0\text{ mol/L} \\ 2x &= 1.0\text{ mol/L} \\ x &= 0.50\text{ mol/L} \end{aligned}$$

Step 5. Use the value of x to calculate the equilibrium concentrations of nitrogen gas and hydrogen gas.

$$\begin{aligned} [N_2(g)]_{\text{equilibrium}} &= x \\ [N_2(g)]_{\text{equilibrium}} &= 0.50\text{ mol/L} \\ [H_2(g)]_{\text{equilibrium}} &= 3x \\ &= 3(0.50\text{ mol/L}) \\ [H_2(g)]_{\text{equilibrium}} &= 1.5\text{ mol/L} \end{aligned}$$

Statement: The equilibrium concentration of nitrogen gas is 0.50 mol/L and the equilibrium concentration of hydrogen gas is 1.5 mol/L.

Practice

1. When dinitrogen tetroxide gas, $N_2O_4(g)$, is placed in a sealed container at 100 °C, it decomposes into nitrogen dioxide gas, $NO_2(g)$, according to the following balanced equation:

   $$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

   A laboratory technician places 0.25 mol of dinitrogen tetroxide gas in a 1.0 L closed container. At equilibrium, the concentration of nitrogen dioxide gas is 0.25 mol/L. Use an ICE table to determine the equilibrium concentration of dinitrogen tetroxide gas. T/I [ans: $[N_2O_4(g)]_{\text{equilibrium}} = 0.12$ mol/L]

2. At 35 °C, 3.00 mol of pure nitrosyl chloride gas, $NOCl(g)$, is contained in a sealed 3.00 L flask. The nitrosyl chloride gas decomposes to nitric oxide gas, $NO(g)$, and chlorine gas, $Cl_2(g)$ until equilibrium is reached.

   $$2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$$

   At equilibrium, the concentration of nitric oxide gas is 0.043 mol/L. Use an ICE table to determine the equilibrium concentrations of nitrosyl chloride gas and chlorine gas under the conditions used. T/I [ans: $[NOCl(g)]_{\text{equilibrium}} = 0.96$ mol/L; $[Cl_2(g)]_{\text{equilibrium}} = 0.022$ mol/L]

3. A chemist places 2.00 mol of ethene gas, $C_2H_4(g)$, and 1.25 mol of bromine gas, $Br_2(g)$, in a sealed 0.500 L container. **Figure 8** shows the concentration of ethene gas over time. The temperature of the vessel and its contents are kept constant. The balanced chemical equation for the reaction is

   $$C_2H_4(g) + Br_2(g) \rightleftharpoons C_2H_4Br_2(g)$$

   Determine the equilibrium concentration of ethene, bromine, and 1,2-dibromoethane gases. T/I

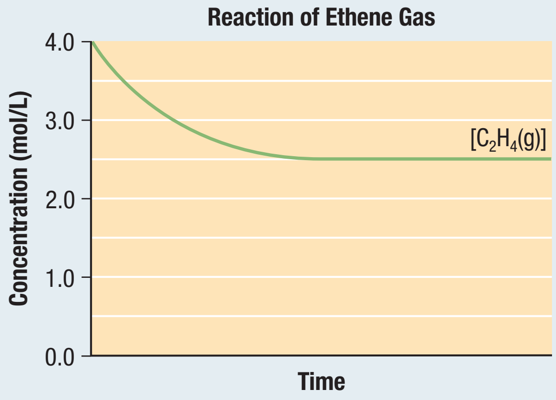


Figure 8

[ans: $[C_2H_4(g)]_{\text{equilibrium}} = 2.5$ mol/L; $[Br_2(g)]_{\text{equilibrium}} = 1.0$ mol/L; $[C_2H_4Br_2(g)]_{\text{equilibrium}} = 1.5$ mol/L]

7.1 Review

Summary

- Some chemical reactions do not go to completion, but to a chemical equilibrium, which is a dynamic equilibrium in a closed system in which the forward and reverse reactions occur at equal rates.
- In an equilibrium system, an equilibrium position can be reached starting from the forward reaction or from the reverse reaction.

Questions

1. In carbonated pop, the bubbles come from carbonic acid, $H_2CO_3(aq)$, in the liquid decomposing to carbon dioxide gas, $CO_2(g)$, and water. K/U A
   (a) Explain how the sealed bottle of pop is an example of a dynamic equilibrium.
   (b) What happens when you open the pop bottle?
2. The following balanced chemical equation represents a chemical system at equilibrium: K/U

$$\underset{\text{colourless}}{C_2H_4(g)} + \underset{\text{brown}}{Br_2(g)} \rightleftharpoons \underset{\text{colourless}}{C_2H_4Br_2(g)}$$

   (a) What visual changes will you see at equilibrium?
   (b) What is occurring at the molecular level?
   (c) Is the equilibrium static or dynamic?
3. When combined in a closed vessel, hydrogen gas and iodine gas will form hydrogen iodide gas until an equilibrium position is reached. K/U T/I C
   (a) Write a balanced equation for this chemical reaction system.
   (b) Suppose you carry out an investigation starting with a 2.0 L flask containing 0.45 mol of hydrogen iodide. Predict how the concentrations of the gases will change as the system reaches equilibrium.
   (c) In a second experiment, the concentration of each of the gases was monitored (**Figure 9**). Complete an ICE table for the reaction.

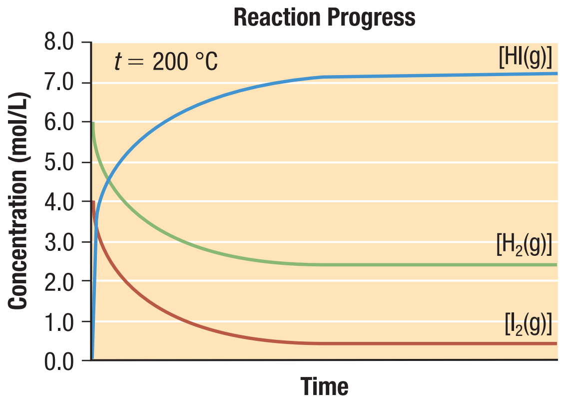


Figure 9

4. Sulfuric acid is an important industrial chemical that is usually produced by a series of reactions. One of these involves an equilibrium between gaseous sulfur dioxide, oxygen, and sulfur trioxide.

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

   If 2.5 mol of sulfur dioxide gas and 2.0 mol of oxygen gas are placed in a sealed 1.0 L container and allowed to reach equilibrium, 0.75 mol of sulfur dioxide remains. Use an ICE table to determine the concentration of the other gases at equilibrium. T/I
5. Phosphorus pentachloride gas, $PCl_5(g)$, will decompose to phosphorous trichloride, $PCl_3(g)$, and chlorine, $Cl_2(g)$, at 160 °C. In a sealed vessel, the reaction will proceed to equilibrium:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

   A chemist places 3.00 mol of phosphorous pentachloride gas into a sealed 1.50 L flask at 160 °C. At equilibrium, he observes there is 0.300 mol of phosphorous trichloride gas and some chlorine gas. Calculate the equilibrium concentrations of gaseous phosphorous pentachloride and chlorine. T/I
6. Fructose is a carbohydrate found in many foods, especially sweet fruits. If you eat a meal that is rich in fructose, the concentration of fructose in solution inside the intestinal tract of the small intestine (i.e., the concentration outside the cells) will be higher than the fructose concentration inside the cells making up the intestine. This causes fructose to diffuse into the cells. A
   (a) Will diffusion result in the absorption of all fructose molecules from the digesting food travelling through the intestine? Explain.
   (b) Conduct research to determine why cells are able to absorb the maximum possible amount of nutrients from their surroundings.

WEB LINK

Equilibrium Law and the Equilibrium Constant

7.2

In the mid-1800s, two Norwegian chemists, Cato Maximilian Guldberg and Peter Waage (**Figure 1**), conducted detailed studies of chemical equilibrium systems. Based on their observations, they were able to describe a chemical equilibrium in a closed system in mathematical terms. The mathematical description is known as the **equilibrium law**. The equilibrium law is sometimes called the law of mass action.

What is the equilibrium law and why is it useful? To start our discussion, suppose that A, B, C, and D are chemical entities in gas or aqueous states, and that *a*, *b*, *c*, and *d* are the coefficients in a balanced chemical equation. We can now represent a chemical equilibrium system by this general chemical equation:

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium law for this general reaction may be represented quantitatively by the following mathematical equation:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The square brackets in the equation indicate the concentrations of the chemical entities at equilibrium. *K* is the symbol for the **equilibrium constant**, a constant numerical value that defines the equilibrium law for a given system. Since the units of the equilibrium constant vary according to the values of *a*, *b*, *c*, and *d*, equilibrium constant values are usually reported without units.

Figure 1 Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900) first proposed the equilibrium law in 1864.

equilibrium law the mathematical description of a chemical system at equilibrium

equilibrium constant (*K*) a constant numerical value defining the equilibrium law for a given system; units are not included when giving the value of *K*

Analyzing the Equilibrium Law

To see how the equilibrium law is useful, consider the formation of hydrogen iodide gas, HI(g), from its elements. The balanced chemical equation for this reaction is

$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$$

Table 1 shows the results from an investigation to observe how changing the initial concentration of the reactants and products affected the equilibrium. The reaction was allowed to proceed to equilibrium in a sealed 2.00 L flask at 485 °C.

Table 1 Equilibria for Formation of Hydrogen Iodide from Its Elements at 485 °C

Trial	Initial concentration (mol/L)			Equilibrium concentration (mol/L)		
	$[H_2(g)]$	$[I_2(g)]$	$[HI(g)]$	$[H_2(g)]$	$[I_2(g)]$	$[HI(g)]$
1	2.00	2.00	0	0.442	0.442	3.119
2	0	0	2.000	0.221	0.221	1.560
3	0	0.010	0.350	0.035	0.045	0.280

In **Table 2**, the data from each trial were entered into the equilibrium law equation. What do you notice about the value of the equilibrium constants?

Table 2 Calculation of *K* from Experimental Results in Table 1

Trial 1	Trial 2	Trial 3
$K = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$ $K = \frac{(3.119)^2}{(0.442)(0.442)}$ $K = 49.8$	$K = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$ $K = \frac{(1.560)^2}{(0.221)(0.221)}$ $K = 49.8$	$K = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$ $K = \frac{(0.280)^2}{(0.035)(0.045)}$ $K = 49.8$

Investigation 7.2.1

The Equilibrium Law (page 473)
This activity provides an opportunity for you to use experimental data to find the mathematical relationship for the equilibrium law.

Table 3 Equilibrium Constant for the Production of Ammonia Gas from Elemental Nitrogen and Hydrogen at Various Temperatures

Temperature (°C)	*K*
25	4.26×10^{8}
300	1.02×10^{-5}
400	8.00×10^{-7}

The equilibrium constant value is the same, 49.8, for all three trials. The equilibrium constant will always have the same value of 49.8 regardless of the initial concentrations, providing that all other variables are kept the same. Chemists have found that this holds true for any specific chemical reaction at equilibrium at a given temperature: the value of the equilibrium constant remains the same, regardless of initial concentrations.

However, the value of the equilibrium constant depends on the reaction temperature. In **Table 3**, notice how the equilibrium constant value changes with temperature when gaseous nitrogen and hydrogen are combined in a closed vessel and react to form ammonia gas, $NH_3(g)$. The chemical equation for this reaction is

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Writing Equilibrium Law Equations and Calculating *K*

In Section 7.1, you saw that the equilibrium position of a reaction describes the relative concentration of reactants and products in a chemical reaction system. By convention, the equilibrium position is expressed as being far to the right (toward products) or far to the left (toward reactants). The equilibrium constant, *K*, can be used to determine the equilibrium position of a chemical reaction system. You will calculate the equilibrium constant from the equilibrium law equation in Tutorial 1. Always use amount concentrations of the reactants and products at equilibrium in the equilibrium law expression calculation. Remember that, in this textbook, the concentrations of aqueous solutions and gaseous substances are provided in mol/L.

Tutorial 1 Writing Equilibrium Law Equations and Calculating *K*

In this tutorial, you will first see how to write an equilibrium equation from balanced chemical equations. Then, you will use equilibrium law equations to calculate the equilibrium constant, *K*, for several chemical reaction systems.

Sample Problem 1: Writing an Equilibrium Law Equation from a Balanced Chemical Equation

Write the equilibrium equation for the reaction described by the following balanced equation:

$$4\,NH_3(g) + 7\,O_2(g) \rightleftharpoons 4\,NO_2(g) + 6\,H_2O(g)$$

Solution

Step 1. Identify the reactants and products and their coefficients.

Reactants: $4\,NH_3(g)$; $7\,O_2(g)$

Products: $4\,NO_2(g)$; $6\,H_2O(g)$

Step 2. Apply the equilibrium law equation.

Place the products in the numerator and the reactants in the denominator. Use the coefficients from the balanced equation as exponents.

$$K = \frac{[NO_2(g)]^4[H_2O(g)]^6}{[NH_3(g)]^4[O_2(g)]^7}$$

Sample Problem 2: Calculating *K* for a Synthesis Reaction

In a closed vessel at 500 °C, gaseous nitrogen, $N_2(g)$, and hydrogen, $H_2(g)$, combine in an equilibrium reaction to form ammonia gas, $NH_3(g)$:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

The equilibrium concentrations of gaseous nitrogen, hydrogen, and ammonia, respectively, are 1.50×10^{-5} mol/L, 3.45×10^{-1} mol/L, and 2.00×10^{-4} mol/L.

Calculate the equilibrium constant, *K*, for this chemical reaction under these conditions.

Given: $[N_2(g)]_{\text{equilibrium}} = 1.50 \times 10^{-5}$ mol/L;
$[H_2(g)]_{\text{equilibrium}} = 3.45 \times 10^{-1}$ mol/L;
$[NH_3(g)]_{\text{equilibrium}} = 2.00 \times 10^{-4}$ mol/L

Required: *K*

Solution: Write the equilibrium law equation using the balanced chemical equation. Then, substitute the equilibrium concentrations into the equilibrium law equation and solve for *K*. Remember that *K* is reported without units.

$$K = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

$$= \frac{(2.00 \times 10^{-4})^2}{(1.50 \times 10^{-5})(3.45 \times 10^{-1})^3}$$

$$K = 6.49 \times 10^{-2}$$

Statement: The equilibrium constant, *K*, is 6.49×10^{-2} for the chemical reaction system at 500 °C.

Sample Problem 3: Calculating *K* for a Decomposition Reaction

In a closed vessel at 500 °C, ammonia gas, $NH_3(g)$, will decompose into its elements:

$$2\ NH_3(g) \rightleftharpoons N_2(g) + 3\ H_2(g)$$

Calculate the equilibrium constant, *K*, for the decomposition of ammonia gas into its elements under these conditions. This reaction is the reverse of that in Sample Problem 2, so use the same equilibrium concentrations.

Given: $[N_2(g)]_{\text{equilibrium}} = 1.50 \times 10^{-5}$ mol/L;
$[H_2(g)]_{\text{equilibrium}} = 3.45 \times 10^{-1}$ mol/L;
$[NH_3(g)]_{\text{equilibrium}} = 2.00 \times 10^{-4}$ mol/L

Required: *K*

Solution:

$$K = \frac{[N_2(g)][H_2(g)]^3}{[NH_3(g)]^2}$$

$$= \frac{(1.50 \times 10^{-5})(3.45 \times 10^{-1})^3}{(2.00 \times 10^{-4})^2}$$

$$K = 15.4$$

Statement: The equilibrium constant, *K*, for the decomposition of ammonia at 500 °C is 15.4.

If you compare the two equilibrium constants that you calculated in Sample Problems 2 and 3, you can see that they are very different. However, these values are mathematically related.

Allow *K* to represent the equilibrium constant of the forward reaction or the formation of ammonia gas (Sample Problem 2). Then, let *K′* represent the equilibrium constant of the reverse reaction or the decomposition of ammonia gas (Sample Problem 3). The equilibrium law equations for the reactions are

$$K = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} = 6.49 \times 10^{-2}$$

$$K' = \frac{[N_2(g)][H_2(g)]^3}{[NH_3(g)]^2} = 15.4$$

If you compare the concentrations in these two equations, you will see that *K* is the mathematical reciprocal of *K′*. To check this, you can calculate the reciprocal of *K′*:

$$K' = 15.4, \text{ so}$$

$$\frac{1}{K'} = \frac{1}{15.4}$$

$$= 6.49 \times 10^{-2}$$

Practice

1. Write the equilibrium law equation for the reactions represented by the following balanced chemical equations:
   (a) $2\ CO_2(g) \rightleftharpoons 2\ CO(g) + O_2(g)$
   (b) $2\ Cl_2(g) + 2\ H_2O(g) \rightleftharpoons 4\ HCl(g) + O_2(g)$
   (c) $2\ O_3(g) \rightleftharpoons 3\ O_2(g)$
   (d) $4\ NH_3(g) + 3\ O_2(g) \rightleftharpoons 2\ N_2(g) + 6\ H_2O(g)$ T/I

2. In a closed vessel at 327 °C, methanol gas, $CH_3OH(g)$, is formed by reacting gaseous carbon monoxide with hydrogen gas. When the reaction reaches equilibrium, the concentration of carbon monoxide gas is 0.079 mol/L, of hydrogen gas is 0.158 mol/L, and of methanol gas is 0.021 mol/L. The balanced chemical equation for the chemical reaction system is

   $$CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g)$$

   Calculate the equilibrium constant for this reaction. **T/I** [ans: $K = 11$]

3. Write the balanced chemical equation for the reaction with the following equilibrium law equation:

   $$K = \frac{[NO(g)]^2[Br_2(g)]}{[NOBr(g)]^2}$$

   T/I [ans: $2\ NOBr(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$]

Equilibrium Constant and Reaction Rate

When a reversible chemical reaction is at equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. We can show why this is true. Consider a hypothetical reversible reaction in which reactants A and B form products C and D.

$$A + B \rightleftharpoons C + D$$

Since it is a reversible chemical reaction, dynamic equilibrium is achieved when the forward reaction proceeds at the same rate as the reverse reaction. The chemical equation for the forward reaction of the chemical equilibrium system is

$$A + B \rightarrow C + D$$

Assume that this reaction is an elementary process, which is a chemical process that is completed in a single step. Recall from Chapter 6 that, in a dilute solution, the rate of a chemical reaction is proportional to the amount concentrations of the reactants. If k_f is the rate constant for the forward reaction, the rate of the forward reaction is

$$\text{Forward reaction rate} = k_f[A][B]$$

Similarly, for the reverse reaction given by the chemical equation

$$C + D \rightarrow A + B$$

if k_r is the rate constant, then this equation represents the reverse reaction rate:

$$\text{Reverse reaction rate} = k_r[C][D]$$

At equilibrium, the forward reaction rate must equal the reverse reaction rate.

$$k_f[A][B] = k_r[C][D]$$

Rearranging this equation as a ratio gives

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

This ratio is the same as the equilibrium law equation for our hypothetical equilibrium system. Therefore, the ratio of the rate constants of the forward and reverse reactions is equal to the equilibrium constant, K.

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]} = K$$

For simple reversible reactions in which all the coefficients are 1, we would also arrive at this equation by placing the coefficients of 1 in the equation originally proposed by the chemists Guldberg and Waage:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

However, this mathematical relationship is true only for elementary processes. Most chemical reactions are not elementary processes.

Heterogeneous Equilibria

The chemical equilibrium systems that we have discussed so far have been examples of a **homogeneous equilibrium**, in which all reactants and products in the systems were in the same state of matter. When the reactants and products in a chemical equilibrium system are present in more than one state, the system is a **heterogeneous equilibrium**.

homogeneous equilibrium a chemical equilibrium system in which all reactants and products are in the same state of matter, such as the gas state

heterogeneous equilibrium a chemical equilibrium system in which the reactants and products are present in at least two different states, such as gases and solids

For example, calcium carbonate, $CaCO_3(s)$, can undergo a reversible decomposition reaction to form solid calcium oxide, $CaO(s)$, and carbon dioxide gas:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

This reaction is used in the commercial preparation of calcium oxide (also known as lime) from calcium carbonate sources, such as limestone. Lime has many uses, such as in the manufacture of steel and plastics. Straightforward application of the equilibrium law leads to the equation

$$K = \frac{[CO_2(g)][CaO(s)]}{[CaCO_3(s)]}$$

However, the equilibrium position of a heterogeneous equilibrium does not depend on the quantities of pure solids or liquids. The fundamental reason for this behaviour is that the concentrations of pure solids and liquids cannot change. In the reversible decomposition reaction of calcium carbonate, the concentrations of solid calcium carbonate and solid calcium oxide remain constant (**Figure 2**). CAREER LINK

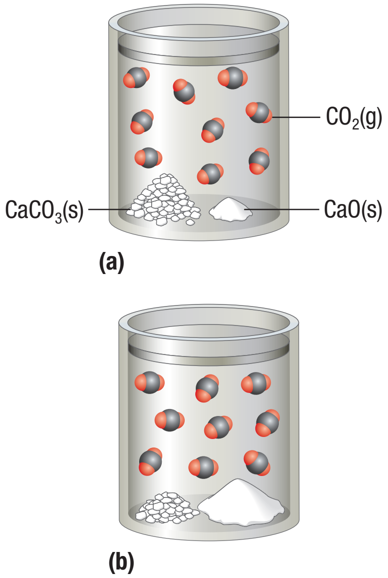


Figure 2 The position of the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ does not depend on the quantities of solid calcium carbonate and calcium oxide that are present, but only on the concentration of carbon dioxide gas.

If we represent these constant concentrations by the symbols C_1 and C_2 respectively, we can write the equilibrium law equation as

$$K = \frac{[CO_2(g)]C_1}{C_2}$$

Since C_1 and C_2 are constants, and K is also a constant, we can simplify the equilibrium law equation by including all the constants together. We can then write the equilibrium law equation for this reaction as

$$K = [CO_2(g)]$$

We can write the following generalization from this analysis:

> If pure solids or pure liquids are involved in a chemical equilibrium system, their concentrations are not included in the equilibrium law equation for the reaction system.

We cannot simplify the equilibrium law expression for solutions or gases, since the concentrations of substances in these states can vary. Therefore, carefully note the states of all substances in a reaction system. For example, consider the decomposition of liquid water to gaseous hydrogen and oxygen:

$$2\,H_2O(l) \rightleftharpoons 2\,H_2(g) + O_2(g)$$

The equilibrium law equation for this reaction is

$$K = [H_2(g)]^2[O_2(g)]$$

We did not include water in the equation, because it is a pure liquid. However, we could instead carry out the reaction under conditions where water is in the gas state.

$$2\,H_2O(g) \rightleftharpoons 2\,H_2(g) + O_2(g)$$

Since the concentration of water vapour can change, we must now include it the equilibrium law equation:

$$K = \frac{[H_2(g)]^2[O_2(g)]}{[H_2O(g)]^2}$$

Tutorial 2 Equilibrium Expressions for Heterogeneous Equilibria

In this tutorial, you will write the equilibrium law equations for heterogeneous equilibrium reaction systems. Remember to simplify the equation by omitting the concentrations of any pure solids or liquids.

Sample Problem 1: A Reaction System with a Pure Solid and a Pure Liquid

Solid phosphorous pentachloride, $PCl_5(s)$, can undergo a reversible reaction to form liquid phosphorous trichloride, $PCl_3(l)$, and chlorine gas, $Cl_2(g)$. Write the equilibrium law expression for this heterogeneous equilibrium.

Solution

Write the balanced chemical equation for the reaction. Then, write the equilibrium law equation. Omit the concentrations of the pure solid, $PCl_5(s)$, and the pure liquid, $PCl_3(l)$.

$$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$$

$$K = [Cl_2(g)]$$

Sample Problem 2: A Reaction System with Two Pure Solids

When deep blue solid copper(II) sulfate pentahydrate, $CuSO_4{\cdot}5H_2O(s)$, is heated to drive off water vapour, $H_2O(g)$, white solid anhydrous copper(II) sulfate, $CuSO_4(s)$, is formed. The reaction is reversible. Write the balanced chemical equation and the equilibrium law equation for this reaction system.

Solution

$$CuSO_4{\cdot}5H_2O(s) \rightleftharpoons CuSO_4(s) + 5\ H_2O(g)$$

$$K = [H_2O(g)]^5$$

Practice

1. Write the equilibrium law equation for the following heterogeneous equilibrium reaction systems:
   (a) the decomposition of solid ammonium chloride, $NH_4Cl(s)$, to gaseous ammonia, $NH_3(g)$, and hydrogen chloride gas, $HCl(g)$, which is represented by the balanced chemical equation

   $$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$ [ans: $K = [NH_3(g)][HCl(g)]$]

   (b) the production of solid sodium carbonate, $Na_2CO_3(s)$; carbon dioxide gas; and water vapour by heating solid sodium hydrogen carbonate, $NaHCO_3(s)$ [ans: $K = [CO_2(g)][H_2O(g)]$]

   (c) the reaction of elemental zinc, $Zn(s)$, in an aqueous solution of copper(II) chloride, $CuCl_2(aq)$ (**Figure 3**) T/I $\left[\text{ans: } K = \dfrac{[ZnCl_2(aq)]}{[CuCl_2(aq)]}\right]$

Figure 3 Stages in the reaction progress of elemental zinc in copper(II) chloride solution

The Magnitude of the Equilibrium Constant, *K*

We have seen that the magnitude of the equilibrium constant, *K*, can vary significantly. What does the magnitude of the equilibrium constant tell us about an equilibrium system? To answer this question, consider the reaction of carbon monoxide gas, $CO(g)$, with oxygen gas, $O_2(g)$, to produce carbon dioxide gas, $CO_2(g)$. This reaction contributes some of the carbon dioxide gas released into the atmosphere by internal combustion engines (**Figure 4**). The balanced equation for this reaction is

$$2\,CO(g) + O_2(g) \rightleftharpoons 2\,CO_2(g)$$

When this reaction is conducted in a sealed vessel at 25 °C, the equilibrium constant is 3.3×10^{91}. Therefore, the equilibrium law equation can be written as

$$K = \frac{[CO_2(g)]^2}{[CO(g)]^2[O_2(g)]} = 3.3 \times 10^{91}$$

Figure 4 In the open system of this tailpipe, oxygen gas present in the air will react with any carbon monoxide gas emitted by the engine, converting it into carbon dioxide gas that enters the atmosphere.

Looking at the equilibrium law equation, the numerator includes the equilibrium concentration of the product, and the denominator includes the equilibrium concentrations of the reactants. The very large value of the equilibrium constant indicates that the equilibrium position is significantly toward the right. We can therefore predict that, at equilibrium, the concentration of carbon dioxide gas (the product) will be much greater than the concentrations of carbon monoxide gas and oxygen gas (the reactants).

In contrast, the reversible reaction of nitrogen dioxide gas, $NO_2(g)$, with nitric oxide gas, $NO(g)$, to form gaseous dinitrogen monoxide, $N_2O(g)$, and oxygen,

$$NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$$

has an equilibrium constant that is close to being equal to 1.

$$K = \frac{[N_2O(g)][O_2(g)]}{[NO_2(g)][NO(g)]} = 0.915$$

Since this equilibrium constant is close to 1, the concentration of the products at equilibrium is approximately equal to the concentration of the reactants.

Finally, let us look at the equilibrium constant for the reversible thermal decomposition of water at 1000 °C. The balanced chemical equation and the equilibrium law equation for this reaction are as follows:

$$2\,H_2O(g) \rightleftharpoons 2\,H_2(g) + O_2(g)$$

$$K = \frac{[H_2(g)]^2[O_2(g)]}{[H_2O(g)]^2} = 7.3 \times 10^{-10}$$

The value of the equilibrium constant for this chemical reaction system is extremely small. This means that the concentration of water vapour is much larger than the concentrations of hydrogen gas and oxygen gas at equilibrium. At this temperature, the equilibrium position is toward the left and highly favours the reactants.

Table 4 summarizes the relationship between the magnitude of the equilibrium constant value and the equilibrium position.

Table 4 Relationship between the Magnitude of the Equilibrium Constant, *K*, and Equilibrium Position

Magnitude of *K*	Equilibrium position
$K >>> 1$	far to the right (favours products)
$K \approx 1$	equilibrium concentration of the products similar to that of the reactants
$K <<< 1$	far to the left (favours reactants)

7.2 Review

Summary

- An equilibrium law equation is a mathematical representation of a reversible chemical reaction.
- The equilibrium constant, *K*, is the ratio of the concentrations of the products to the concentrations of the reactants at equilibrium. It is independent of initial concentration, but varies with the temperature at which the reaction occurs.
- In a homogeneous equilibrium, all substances have the same state. In a heterogeneous equilibrium, the substances are in at least two different states.
- The concentrations of solids and pure liquids are not included in the equilibrium expression because they are constant.
- The magnitude of the equilibrium constant, *K*, reflects the equilibrium position.

Questions

1. Write the equilibrium law equation, *K*, for the chemical reaction systems represented by each of the following chemical equations: T/I
   (a) $SiH_2(g) + 2\ Cl_2(g) \rightleftharpoons SiCl_4(g) + H_2(g)$
   (b) $2\ PBr_3(g) + 3\ Cl_2(g) \rightleftharpoons 2\ PCl_3(g) + 3\ Br_2(g)$
   (c) $H_2O(l) \rightleftharpoons H_2O(g)$
   (d) $2\ NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO2(g) + H_2O(g)$
2. At a particular temperature, a 3.0 L flask contains 2.4 mol of chlorine, $Cl_2(g)$; 1.0 mol of nitrosyl chloride, NOCl(g); and 4.5×10^{-3} mol of nitric oxide, NO(g). Calculate the equilibrium constant, given the balanced chemical equation

   $$2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$$ T/I
3. An equilibrium mixture contains 1.0 mol of iron metal, Fe(s); 1.0×10^{-3} mol of oxygen gas; and 2.0 mol of solid iron(III) oxide, $Fe_2O_3(s)$, in a 2.0 L container. The reaction is represented by the balanced chemical equation

   $$4\ Fe(s) + 3\ O_2(g) \rightleftharpoons 2\ Fe_2O_3(s)$$

   Calculate the value of *K* for this reaction. T/I
4. Use a graphic organizer to summarize what you have learned about homogeneous and heterogeneous equilibria and how their equilibrium law equations are written. K/U C
5. Liquid methanol, $CH_3OH(l)$, is an important solvent in industry and can also be used as a fuel. Methanol may be synthesized in the gas state from carbon monoxide gas, CO(g), and hydrogen gas, $H_2(g)$, in a chemical reaction system that comes to equilibrium in a closed vessel at 225 °C. T/I A C
   (a) Write the balanced chemical equation for the formation of methanol gas from carbon monoxide gas and hydrogen gas at 225 °C.
   (b) The equilibrium constant, *K*, for this reaction at 225 °C is 6.3×10^{-3}. Predict the relative concentration of the methanol gas when equilibrium is established.
   (c) Based on your answer for (b), predict whether this equilibrium system could generate large quantities of methanol. Explain your answer.
   (d) What would be the equilibrium constant for the reverse reaction?
6. Coal, C(s), can be burned directly as a source of energy or can be converted to carbon monoxide gas, CO(g), which can also be used as a fuel. The conversion process involves reacting coal with carbon dioxide gas to produce carbon monoxide gas. T/I C A
   (a) Write the balanced chemical equation for the reaction.
   (b) Write the equilibrium constant equation.
   (c) The value of the equilibrium constant for this chemical reaction system is 1.6×10^{-2} at 25 °C and 1.7×10^{2} at 1000 °C. At which temperature will more carbon monoxide gas be produced? Explain your reasoning.
   (d) What are some advantages of a gaseous fuel over a solid fuel?
   (e) What safety issues are involved in working with carbon monoxide gas at high temperatures?

7.3

Chemistry JOURNAL

Fritz Haber: Explore an Equilibrium, Feed the World

SKILLS HANDBOOK A4, A5.1

ABSTRACT

Ammonia gas is produced from elemental nitrogen and oxygen in a reversible reaction, but the equilibrium position heavily favours the reactants at SATP. Fritz Haber conducted basic research on this chemical equilibrium system and fundamentally changed our understanding of equilibria. In a body of investigative work that won him the Nobel Prize in Chemistry in 1916, Haber showed how temperature, pressure, and the addition of a catalyst affected equilibrium position. This work laid the foundation for the chemical engineer Carl Bosch to invent the Haber-Bosch process for industrial-scale ammonia synthesis.

Introduction

The late nineteenth century brought rapid population growth in North America and in Europe, which strained the food supply. To meet the demand, farmers turned to nitrogen-based fertilizers to raise their yields. However, the main sources were naturally occurring and limited: guano (bird droppings), and sodium nitrate from mines. It was known that ammonia and ammonia-containing substances could be used as a fertilizer, but ammonia supplies were also limited. The chemist Fritz Haber (**Figure 1**) was working on improving the energy efficiency of another useful chemical reaction. Impressed by his work, in 1909 the German chemical company BASF hired Haber to investigate the production of ammonia gas from atmospheric nitrogen.

Figure 1 Fritz Haber (1868–1934) made fundamental contributions to the understanding of chemical equilibria.

Investigating Temperature and Pressure

The balanced chemical equation for the production of ammonia gas from its elements is

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

When Haber began his investigations, it was known that this chemical reaction produced very little ammonia gas and that the quantity produced decreased as temperature was increased. Haber's investigations led him to conclude that, when temperature was increased, although the reaction rate increased, the equilibrium position shifted to favour the reactants even more. In his Nobel lecture, Haber explained his next step in his investigations.

> *"To begin with, it was clear that a change to the use of maximum pressure would be advantageous. It would improve the point of equilibrium and probably the rate of reaction as well."*

Unfortunately, Haber found that the temperature of the reaction must be 700 °C to shift the equilibrium position enough to produce greater quantities of ammonia, even at the maximum pressure he could produce with his equipment. The energy needed to create these conditions made this approach uneconomical and so not useful. **Figure 2** shows some of Haber's original data from his work on the effects of temperature and pressure on ammonia production.

t (°C)	T (K)	$\frac{P_{NH_3}}{P_{N_2}{}^{0.5}P_{H2}{}^{0.5}}$	$-\log \frac{P_{NH_3}}{P_{N_2}{}^{0.5}P_{H2}{}^{0.5}}$	Percentage of NH_3 at equilibrium at 1 atm	at 30 atm	at 100 atm	at 200 atm
200	473	0.1807	0.660	15.3	67.6	80.6	85.8
300	573	1.1543	0.070	2.18	31.8	52.1	62.8
400	673	1.8608	0.0138	0.44	10.7	25.1	36.3
500	773	2.3983	0.0040	0.129	3.62	10.4	17.6
600	873	2.8211	0.00151	0.049	1.43	4.47	8.25
700	973	3.1621	0.00069	0.0223	0.66	2.14	4.11
800	1073	3.4417	0.00036	0.0117	0.35	1.15	2.24
900	1173	3.6736	0.000212	0.0069	0.21	0.68	1.34
1000	1273	3.8679	0.000136	0.0044	0.13	0.44	0.87

Figure 2 Data contained in a table prepared by Haber and presented during his Nobel lecture in 1916

An Energy-Efficient Solution

Inspired by the work of other scientists, Haber decided to look for a catalyst that would affect the equilibrium instead. Catalysts do not change the equilibrium position, but they do affect the rate of both the forward and reverse reactions. After much work, Haber discovered that iron oxide could play this role in this equilibrium system, so he was able to produce ammonia at lower temperatures and pressures.

An Application of Insight

Although Haber had achieved his goal and found a way to synthesize ammonia gas from its elements, this did not address the economic and social problems associated with the limited supply of ammonia. Haber discussed this issue during his Nobel lecture:

> *". . . I was never in doubt that my laboratory work would produce no more than a scientific confirmation of basic principles and a criterion of experimental aids, and that much would need to be added to any success of mine to ensure economic success on an industrial scale. On the other hand, I would hardly have concentrated so much on this problem had I not been convinced of the economic necessity of chemical progress in this field . . . while the immediate object of science lies in its own development, its ultimate aim must be bound up in the moulding influence which it exerts at the right time upon life in general and the whole human arrangement of things around us."*

Industrial-scale production of ammonia relied on the work of Carl Bosch, BASF's chief chemical engineer. He modified Haber's process and then designed an industrial chemical plant that eventually began producing 10 000 t of ammonia per year. The process is called the Haber–Bosch process to honour the work of both men (**Figure 3**).

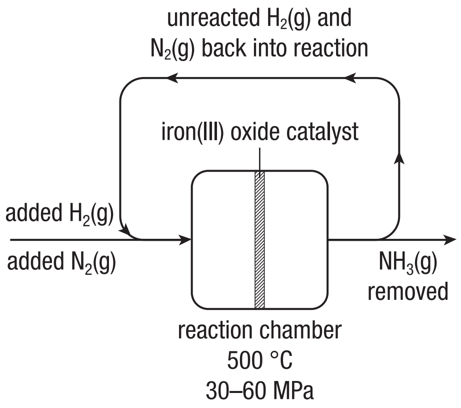


Figure 3 In the Haber–Bosch process, iron(III) oxide is a catalyst and so is not used up. Any reactants present at equilibrium are recycled. The product, ammonia gas, is constantly removed.

Conclusion

Fritz Haber's exploration of the equilibrium system in which ammonia gas is synthesized from its elements was motivated mainly by curiosity. However, the results of his investigations had profound effects on the world outside his laboratory.

Further Reading

Haber, F. (1920). The synthesis of ammonia from its elements. Nobel Lectures, Chemistry 1901–1921. Amsterdam: Elsevier Publishing.

Smil, V. (2004). *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production*. Cambridge, MA: MIT Press.

WEB LINK

7.3 Questions

1. Why did the increase in temperature actually lower the ammonia yield? K/U
2. What was the "economic necessity" that Haber discussed in his lecture that encouraged the investigation into the production of ammonia from its elements? K/U
3. Explain how the addition of a catalyst speeds up the production of ammonia. Does the quantity of ammonia at equilibrium change? K/U
4. How does the pressure inside the reaction vessel affect the equilibrium? K/U
5. Both economics and available technologies place limits on the industrial production of chemicals. Describe how economics and the available technologies affected Haber's final process for synthesizing ammonia. How has the process been modified since then? Choose a creative way to communicate your answer. C A
6. Do you think the focus of scientific research should be on solving real-world problems? Why or why not? Refer to the work of Haber in your answer. A

WEB LINK

Qualitative Changes in Equilibrium Systems

7.4

Imagine that your friend is trying to stay in the same place while walking up an escalator that is moving down. She will be able to maintain her location if the rate at which she walks up equals the rate at which the escalator moves down. As long as the rate your friend walks up is the same as the rate that the escalator moves down, this system is in a state of dynamic equilibrium. However, should the escalator begin to move faster while your friend maintains the same rate of walking up, the dynamic equilibrium will be disturbed and the location of your friend on the escalator will shift down. To re-establish equilibrium, she must increase her stepping rate to match the new rate of motion of the escalator. However, when dynamic equilibrium is re-established, she will be at a new location, lower on the escalator. As we will see, the changes in this dynamic equilibrium are analogous to what happens in a chemical equilibrium system when it is disturbed.

What do we mean when we say a chemical system at equilibrium is disturbed? Previously in this chapter, we saw that changes in temperature can shift the position of an equilibrium in a closed system. These changes are examples of disturbances in a chemical equilibrium system. In general, chemical systems at equilibrium may be disturbed by changes in pressure, temperature, concentration, or a combination of these.

Figure 1 Henry-Louis Le Châtelier (1850–1936), a chemist and engineer, is best known for his generalization about the nature of disturbance to chemical equilibria.

Le Châtelier's Principle

In 1884, the French chemist Henry-Louis Le Châtelier (**Figure 1**) was best known for his work in analyzing chemical reaction systems at equilibrium. Le Châtelier started with a well-defined initial equilibrium state, then changed one property of the system. He observed that there would be a temporary "non-equilibrium" state in the chemical reaction system, and then a new equilibrium state would become established. The goal behind Le Châtelier's investigations was to maximize the yield of products from equilibrium systems, using this systematic process of trial and error. As he gathered data, he saw a pattern emerge. He communicated this pattern to the scientific community as the generalization now known as **Le Châtelier's principle**. WEB LINK

Le Châtelier's principle a generalization that states that chemical systems at equilibrium shift to restore equilibrium when a change occurs that disturbs the equilibrium

> When a chemical system at equilibrium is disturbed by a change in a property, the system adjusts in a way that opposes the change.

Le Châtelier's principle allows chemists to predict the qualitative effects of changes in concentration, pressure, and temperature on a chemical reaction system at equilibrium. Since Le Châtelier's time, this generalization has been supported through extensive evidence. It is regularly applied by chemical engineers who want to maximize the yield of a desired product to make industrial-scale chemical processes more efficient. In fact, Fritz Haber and Carl Bosch used Le Châtelier's principle in their work to devise a process for the economical production of ammonia gas from atmospheric nitrogen (Section 7.3.) CAREER LINK

Le Châtelier's Principle and Changes in Concentration

An adjustment by a system at equilibrium that results in a change in the concentrations of reactants and products is called an **equilibrium shift**. One way to cause an equilibrium shift is to add additional reactant to the reaction vessel. By applying Le Châtelier's principle, we can predict that increasing the concentration of a reactant will shift the equilibrium to the right, to oppose this change. This prediction can be tested by investigation. For example, when a light yellow solution of iron(III) ions, $Fe^{3+}(aq)$, is mixed

equilibrium shift a change in concentrations of reactants and products in order to restore an equilibrium state with a colourless solution of thiocyanate ions, $SCN^-(aq)$, an equilibrium is reached with the product, iron thiocyanate ions, $FeSCN^{2+}(aq)$. The balanced chemical equation for this chemical reaction system is

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

Note that there are two reactants and one product in the forward reaction of this equilibrium system. **Figure 2** shows the concentrations of the reactants and products over time. At the zero time point, the two solutions are mixed. Notice how the concentrations of reactants fall as the concentration of the product increases. When the reaction system reaches equilibrium, all three concentrations remain constant and all three lines on the graph are horizontal. At the point marked by the first dotted vertical line, more thiocyanate ions are added to the equilibrium. This causes the solution to change colour (**Figure 3**). After the addition, the concentration of thiocyanate briefly increases, then it decreases again. The decrease is the result of some of these ions being used to form more product, the iron thiocyanate ions. Similarly, the concentration of aqueous iron(III) ions decreases as some of them are used also in product formation. However, eventually equilibrium is re-established at a new position.

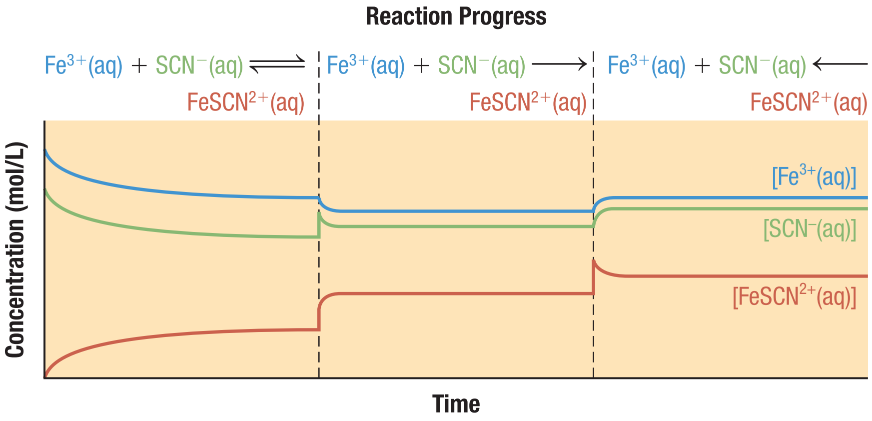


Figure 2 When yellow aqueous iron(III) ions, $Fe^{3+}(aq)$, initially mix with colourless aqueous thiocyanate ions, $SCN^-(aq)$, a portion of the ions combine to form red aqueous iron thiocyanate ions, $FeSCN^{2+}(aq)$. As the reaction progresses, the concentrations of reactants fall as the concentration of the product rises, until equilibrium is reached. When more thiocyanate ions are added at the point indicated by the dashed line, the aqueous thiocyanate ion concentration increases momentarily but then falls off as additional aqueous iron thiocyanate ions are produced. Can you identify what change was made to the system at the second dashed line?

Figure 3 The deep red colour of the equilibrium system changes when more aqueous thiocyanate ions are added, indicating an equilibrium shift.

This experiment verifies the prediction made by Le Châtelier's principle, that increasing the concentration of a reactant will shift the equilibrium to the right. Notice that the concentrations of reactants and products at this new equilibrium position are different from their concentrations in the original equilibrium. When additional reactant is added, the equilibrium concentration of the added reactant in the new equilibrium is usually higher than was its equilibrium concentration in the original equilibrium.

Le Châtelier's principle also predicts that removing some of a reactant in a chemical system at equilibrium will shift the equilibrium to the left (toward reactants), to partially counteract the lower reactant concentration. We will look at these predictions more closely by considering an investigation of the chemical reaction system represented by the following chemical equation:

$$2\,CO_2(g) \rightleftharpoons 2\,CO(g) + O_2(g)$$

When more carbon dioxide gas was added to the system at equilibrium, its concentration first spiked, then immediately started to decrease as the concentrations of the products increased. The concentrations of gaseous carbon dioxide, carbon monoxide, and oxygen at the new equilibrium position are higher than they were in the original equilibrium (**Figure 4(a)**). When one of the products, carbon monoxide gas, was removed from the system at equilibrium, more reactant was converted to products to compensate for the change (**Figure 4(b)**). The equilibrium shifts to the right: the concentration of oxygen gas increases while the concentration of carbon dioxide gas decreases, until a new equilibrium is established.

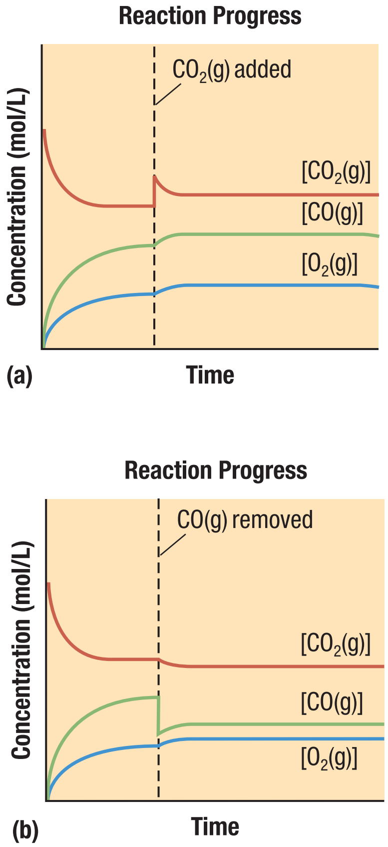


Figure 4 (a) At the dotted line, when the system was at equilibrium, more carbon dioxide gas (reactant) was added to the system. The equilibrium responded by shifting to the right (in the direction of products). The concentration of the reactant at the new equilibrium is also higher. (b) At the dotted line, when the system was at equilibrium, carbon monoxide gas (product) was removed from the system. As in (a), the equilibrium responded by shifting to the right, converting more reactant to products.

Collision Theory and Concentration Changes in an Equilibrium System

According to collision theory, entities in a chemical system must collide to react. When the concentration of an entity in a chemical reaction system is increased, it is more likely that that entity will collide with other entities. There are simply more of them present. However, only collisions between reactant entities can potentially contribute to a chemical reaction. Even so, the more frequently collisions occur overall, the more likely it is that a chemical reaction will take place.

Collision theory explains the response of a chemical reaction system at equilibrium to a change in concentration as the result of random collisions and probability. When we add more reactant entities in an equilibrium system, the equilibrium shifts to the right because the number of successful collisions for the forward reaction increases. If, instead, we add more product entities, then the number of successive collisions for the reverse reaction will increase and the equilibrium will shift to the left. WEB LINK

The rate of a chemical reaction reflects how often reacting entities collide, be they products or reactants. Therefore, when we add a reactant to an equilibrium system, the resulting higher concentration increases the rate of the forward reaction to which it contributes. The higher rate, in turn, decreases the concentration of that substance, so the forward reaction rate then decreases. Conversely, the product(s) of the forward reaction increase in concentration and so become more likely to collide, causing the rate of the reverse reaction to increase. Once the rates of the forward and reverse reactions become equal, a new equilibrium is established. The rates of the forward and reverse reactions will not be the same as in the original equilibrium, however.

Applications of Le Châtelier's Principle and Concentration Changes

Chemical engineers may apply Le Châtelier's principle when designing industrial processes based on reversible reactions. Often the production process involves continuous addition of reactants or removal of products. This prevents the chemical reaction system from ever reaching equilibrium, so that the formation of products will always be favoured. One example of this is in the industrial production of aqueous nitric acid, HNO_3(aq):

$$3\ NO_2(g) + H_2O(l) \rightleftharpoons 2\ HNO_3(aq) + NO(g)$$

Nitric acid has many uses, such as in the synthesis of fertilizers, explosives, dyes, and perfumes. Nitric oxide is not as useful. In the industrial production of aqueous nitric acid, the nitric oxide gas is removed from the chemical reaction system by reacting it with oxygen gas. As the nitric acid product is removed, the equilibrium shifts to the right to compensate, so more reactants form products. This has the desired result of increasing the yield of nitric acid.

Another example is the gasification of carbon. This chemical reaction system is an important part of the conversion of biomass to usable hydrogen gas fuel. At high temperatures, elemental carbon, C(s), reacts with water vapour to produce hydrogen gas and carbon monoxide gas. The balanced equation for the gasification of carbon is

$$C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g)$$

Carbon monoxide gas then reacts with water vapour to produce gaseous carbon dioxide and hydrogen in a reaction known as the water–gas shift reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

As fast as the gasification reaction produces gaseous carbon monoxide (and hydrogen), it is used up as a reactant in the water–gas shift reaction. Thus, the water-gas shift reaction constantly forces the equilibrium position of the gasification reaction to the right, producing more products. This has the effect of increasing the yield of hydrogen.

Le Châtelier's principle also applies to biological processes. For example, hemoglobin in your blood, Hb(aq), binds to dissolved oxygen, $O_2(aq)$, in a reversible reaction represented by this balanced equation:

$$Hb(aq) + O_2(aq) \rightleftharpoons HbO_2(aq)$$

Oxygen is first absorbed into your lungs. The concentration of oxygen (a reactant) in the lungs is high, so the equilibrium position is to the right, toward the product, hemoglobin–oxygen complex, $HbO_2(aq)$. The hemoglobin–oxygen complex in the blood is then pumped to your body cells, where the oxygen concentration is relatively low. In other words, the concentration of this reactant is low in your body cells. To compensate, the equilibrium shifts to the left, in favour of the reactants. As a result, oxygen is released from hemoglobin, and it is then available for use by your body cells. CAREER LINK

Le Châtelier's Principle and Changes in Energy

A system at equilibrium will also shift when it is disturbed by the addition or removal of energy. For example, an equilibrium will shift when the temperature is increased or decreased (a change in thermal energy). To apply Le Châtelier's principle and predict how a change in energy will affect a chemical system at equilibrium, we can think of energy as a reactant or a product. For example, energy is absorbed in an endothermic reaction. If we consider energy to be a reactant, we can write the word equation

$$\text{reactants} + \text{energy} \rightleftharpoons \text{products}$$

Similarly, since energy is released during an exothermic reaction, we can consider energy to be a reactant and write

$$\text{reactants} \rightleftharpoons \text{products} + \text{energy}$$

To use Le Châtelier's principle to predict how an equilibrium will shift in response to a change in energy, consider how the system can counteract this shift.

Figure 5 The room-temperature sample in the centre contains a mix of both gases. Changing the temperature shifts the endothermic reaction equilibrium. The sample on the left, at 0 °C, is shifted toward the formation of colourless dinitrogen tetroxide gas. The darker colour of the sample sample on the right, at 85 °C, is due to a shift toward the formation of reddish brown nitrogen dioxide gas.

Endothermic Reactions

If an endothermic reaction is cooled (thermal energy removed), we can consider that the quantity of one of the reactants has been decreased. We can therefore predict that the equilibrium will shift to the left (toward the reactants), and energy will be released. For example, the decomposition of dinitrogen tetroxide gas, $N_2O_4(g)$, to nitrogen dioxide gas, $NO_2(g)$, is an endothermic process. We can represent the reaction by this balanced equation:

$$\underset{\text{colourless}}{N_2O_4(g)} + \text{energy} \rightleftharpoons \underset{\text{reddish brown}}{2\,NO_2(g)}$$

If thermal energy were added to this equilibrium system by heating, the equilibrium would likely shift to the right. The additional energy would be absorbed to create more product, nitrogen dioxide gas. Since dinitrogen tetroxide gas is colourless and nitrogen dioxide gas is reddish brown, such a shift would make the gas mixture a darker colour. **Figure 5** shows the visible changes in this chemical reaction system when the temperature was changed from room temperature to 0 °C or to 85 °C.

Exothermic Reactions

If thermal energy is removed from an exothermic reaction—where energy is a product—then the equilibrium will shift to the right (toward the products), and energy will be released to counteract the change. If energy is added to an exothermic reaction, the equilibrium will shift to the left to compensate for the change, and the energy will be used as products are converted to reactants. An example of an exothermic reaction is the forward reaction in the reversible reaction in which sulfur trioxide gas, $SO_3(g)$, is produced from gaseous oxygen and sulfur dioxide, $SO_2(g)$. The balanced chemical equation for this reaction, including energy, is

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) + \text{energy}$$

From Le Châtelier's principle, we can predict that removing energy will shift the equilibrium to the right. When the reaction vessel is cooled, more energy will be released and more sulfur trioxide gas will be produced (**Figure 6**).

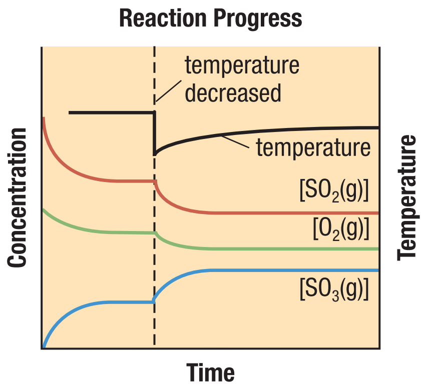


Figure 6 Cooling this system after it has reached equilibrium results in a new equilibrium being established at a lower temperature.

UNIT TASK BOOKMARK

How could you use information about Le Châtelier's principle as you work on the Unit Task on page 582?

In summary, if energy is added to or removed from a chemical reaction system at equilibrium, the equilibrium shifts in the direction that will compensate for the change in energy.

Le Châtelier's Principle and Changes in Gas Volume

If you have ever used a manual bicycle pump, you know that changing the volume of a sealed container of gas changes the pressure of the gas in the container. Changing the volume of a container of gas also changes the concentrations of the gases in the container. To understand how pressure relates to concentration in gases, first consider what happens to pressure when the volume of a gas changes. We will assume that our gas behaves as an **ideal gas**, which is a hypothetical gas that obeys all gas laws. According to Boyle's law, the pressure exerted on a container by a certain amount of an ideal gas held at a constant temperature varies inversely with the volume of the gas. This means that, as the volume of a gas changes, its pressure changes too. In the case of a bicycle pump, decreasing the volume of the cylinder to one-third its original volume would increase the pressure threefold.

Boyle's law holds true whether the container holds a pure gas or a mixture of gases. However, when a container holds a gas mixture, each gas exerts its own partial pressure. The **partial pressure** of a gas is the pressure exerted by any one gas in a mixture, and is the same pressure as it would exert alone. The total pressure is simply the sum of all the partial pressures. When the volume of a container is changed, each gas in the mixture contributes its new partial pressure to the new total pressure. When the volume of a gas mixture decreases, the concentration (number of entities per unit volume) increases proportionally to the increase of their partial pressures.

ideal gas a hypothetical gas composed of entities that have no size, travel in straight lines, and have no attraction to each other (no intermolecular forces); a gas that obeys all gas laws

partial pressure the pressure that a gas, in a mixture of gases, would exert if it alone occupied the whole volume occupied by the mixture

Figure 7 illustrates the changes that take place in a container of gas when the volume decreases by half. The container is holding a mixture of gases that react according to the equation

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

By Boyle's law, we know that reducing the volume of the container by one-half will double the total pressure of the gases in the container. Since the partial pressure of each gas will double, the number of molecules of each gas per unit volume will also double. According to the balanced chemical equation, there are 4 reactant entities—1 $N_2(g)$ and 3 $H_2(g)$—per unit volume for every 2 product entities—2 $NH_3(g)$ (**Figure 7(a)**). The total partial pressure of the reactants is twice that of the products, so, when the volume of the container is reduced, the change in concentrations of the reactants will be greater than the change in concentration of the product (**Figure 7(b)**). Le Châtelier's principle predicts that the equilibrium reaction will shift to the right to reduce the total number of entities per unit volume in the container from 4 entities—1 $N_2(g)$ and 3 $H_2(g)$—to 2 entities—2 $NH_3(g)$, which reduces the total pressure of the system (**Figure 7(c)**).

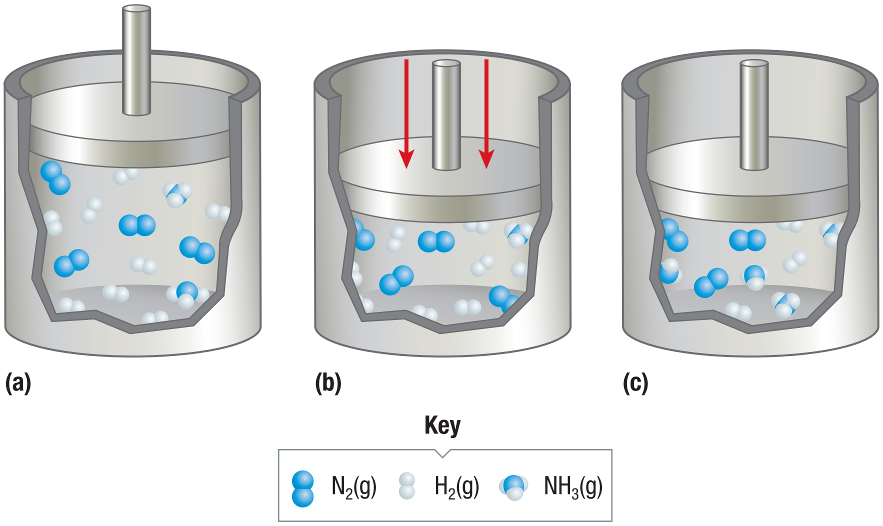


Figure 7 (a) The container holds the equilibrium reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$.
(b) The volume of the container is decreased by half, which doubles the total pressure of the system.
(c) The reaction shifts to the right, which decreases the total number of particles in the container and the total pressure by producing more ammonia, $NH_3(g)$.

Investigation **7.4.1**

Testing Le Châtelier's Principle (page 474)

In this investigation, you will use Le Châtelier's principle to make predictions about how some chemical equilibrium systems will respond to particular chemical and physical changes, and then make observations to see if your predictions are correct.

Changing an Equilibrium System without Affecting Equilibrium Position

As chemists and chemical engineers strive for ever higher efficiency and productivity in equilibrium systems, they may be limited by how much they can change concentration, pressure, and temperature. However, it is possible to modify the amount of reactants and products using methods that do not change the equilibrium position. These methods include using a catalyst, adding an inert gas, and changing the state of the reactants. We will take a brief look at some examples of these methods and see how they work.

Catalysts

Earlier in your studies, you learned that a catalyst provides an alternative path for a chemical reaction that has a lower activation energy barrier (**Figure 8**). In a reversible reaction, catalysts increase the reaction rates of the forward and reverse reactions equally, since both reactants and products can form by the lower-energy path.

Therefore, a catalyst does not change the equilibrium position, and the final equilibrium concentrations of reactants and products are not altered. However, the reaction reaches equilibrium much faster, which can be very useful.

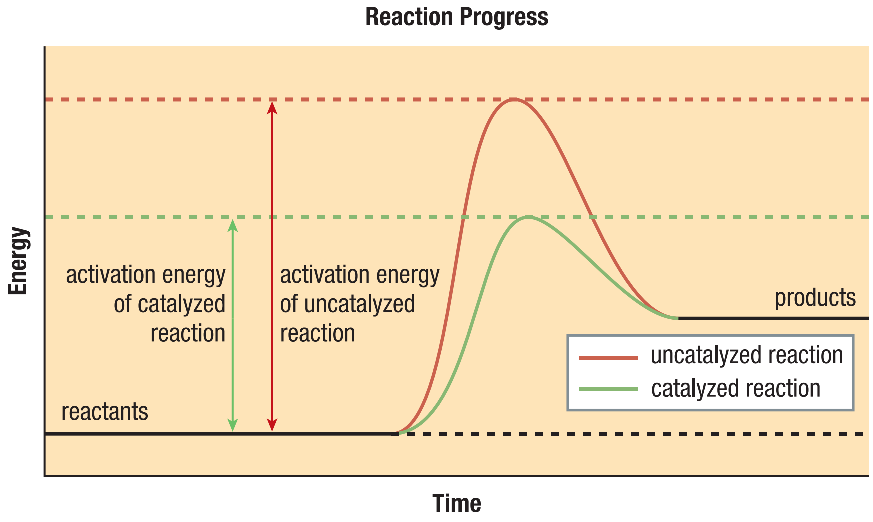


Figure 8 The effect of a catalyst is to lower the activation energy of a reaction. It does not change the energy levels of the reactants and products, so the overall energy change is not affected. As a result, the position of the equilibrium is not affected.

Inert Gas

An inert gas is a gas that is not reactive, and so will not enter into a chemical reaction. If an inert gas is added to an equilibrium system involving a gas mixture and the volume of the container is kept constant, the total number of entities in the volume and therefore the total pressure will increase. However, the partial pressures of the reactant and product entities remain the same. Since there are more entities there are more collisions, but collisions involving the inert gas will not result in a chemical reaction. These collisions can, however, redirect the movement of any entity involved. Imagine that the inert gas entities are fixed obstacles placed randomly in the container, like bumpers in a pinball game. The number and frequency of collisions between reactants and products remain the same. The obstacles redirect reactant and product entities when hit, but do not change the frequency with which reactants and/or product entities collide with each other. As long as the collision frequency for both forward and reverse reactions is unchanged, equilibrium will not shift (**Figure 9**).

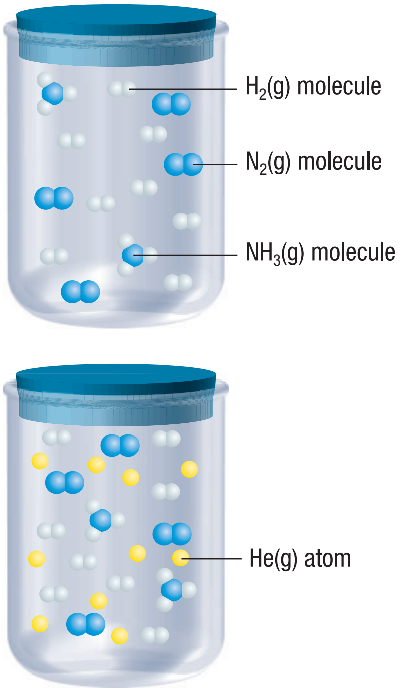


Figure 9 Adding an inert gas, He(g), to a container increases the total pressure of the system but has no effect on the equilibrium concentrations of reactants and products since their partial pressures did not change.

State of Reactants

When a chemical system involves entities in more than one state of matter, equilibrium is affected only by changes in concentration of entities that are in the same state of matter as the substances involved in the chemical reaction system. For example, consider the reaction of solid iodine vapour with hydrogen gas:

$$H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g)$$

Solid iodine is placed in the reaction vessel with hydrogen gas. The solid iodine sublimes (passes directly to gas from the solid phase) before reacting with hydrogen. Once the system has come to equilibrium, the reaction vessel holds a mixture of hydrogen gas, iodine gas, hydrogen iodide gas, and solid iodine. Provided there is some solid iodine present at equilibrium, the gas phase will be saturated with iodine (that is, a second equilibrium will have been established between the solid and gaseous forms of iodine). Adding more solid iodine at that point cannot change the amount of gaseous iodine and, consequently, changing the amount of solid iodine does not affect equilibrium.

7.4 Review

Summary

- Le Châtelier's principle states that any system at equilibrium will respond to a disturbance by shifting to oppose the disturbance.
- Equilibrium position can be affected in predictable ways by changes in concentration of reactants or products, energy, or pressure.
- A catalyst may increase the rate at which a chemical reaction system comes to equilibrium but does not affect the equilibrium position.
- A chemical system at equilibrium will not be disturbed by adding an inert gas or a substance in a different state of matter from that in which the chemical reaction is occurring.

Questions

1. The following balanced chemical equation represents a reaction at equilibrium:

$$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g) + \text{energy}$$

Predict how the equilibrium might respond to the following changes. Explain your answers. K/U T/I

(a) The volume of the container is decreased.
(b) The temperature of the container is increased.
(c) The concentration of $C_2H_6(g)$ is decreased by removing the product.
(d) More hydrogen gas is added.

2. A pair of students conducted an investigation using the equilibrium system represented by the balanced chemical equation below. So far, their notes include the testable question, the experimental design, and the evidence. Answer the questions in parts (a) to (c) to complete the prediction, analysis, and evaluation for this investigation.

$$\underset{\text{blue}}{Cu^{2+}(aq)} + 4\,Cl^-(aq) \rightleftharpoons \underset{\text{green}}{CuCl_4{}^{2-}(aq)}$$

Testable Question

What effect does the addition of chloride ions have on the equilibrium position of the system?

Experimental Design

Test tubes containing 10 mL each of copper(II) chloride solution, $CuCl_2(aq)$, were combined with 1.0, 2.0, and 5.0 mol/L hydrochloric acid, HCl(aq), in a total volume of 15 mL. All test tubes were stoppered, shaken, and allowed to reach equilibrium. The colour at equilibrium was observed and recorded.

Evidence

Table 1 Observations K/U T/I

Test tube number	Concentration of HCl(aq) added (mol/L)	Colour at equilibrium
1	1.0	blue
2	2.0	blue-green
3	5.0	green

(a) Write a prediction for this investigation.
(b) Analyze the evidence to answer the testable question.
(c) Identify the independent variable, the dependent variable, and the controls used.

3. Old-fashioned "smelling salts" consist of solid ammonium carbonate, $(NH_4)_2CO_3(s)$. Smelling salts could bring a person out of a faint by undergoing the following reaction. The released ammonia gas has a distinct smell.

$$(NH_4)_2CO_3(s) \rightleftharpoons 2\,NH_3(g) + CO_2(g) + H_2O(g)$$

This decomposition reaction is endothermic. Would the smell of ammonia increase or decrease as the temperature is increased? K/U

4. The only "stress" (change) that changes the value of the equilibrium constant, *K*, is a change in temperature. K/U

(a) For an exothermic reaction, in what direction will the equilibrium position shift as temperature increases? What happens to the value of *K*?
(b) Answer Part (a) for an endothermic reaction.
(c) If the value of *K* increases with a decrease in temperature, is the reaction exothermic or endothermic? Explain.

Quantitative Changes in Equilibrium Systems

Carbon dioxide gas can dissolve in liquid water, $H_2O(l)$, to form a solution of carbonic acid, $H_2CO_3(aq)$, in a reversible reaction. This equilibrium system is involved in maintaining the pH of your blood. If your blood pH falls outside a narrow range of values—lower than 7.35 or higher than 7.45—you can suffer life-threatening symptoms. Cellular respiration produces aqueous carbon dioxide and liquid water. When these products are transferred from the cells to the blood, they can combine to produce aqueous carbonic acid, which lowers blood pH. This chemical reaction system can be represented by this equation:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

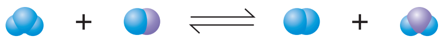
In critical cases of low blood pH, a doctor may administer a solution of hydrogen carbonate ions, HCO_3^- (aq), intravenously to raise the pH to normal range (**Figure 1**). We can think of carbonic acid as an ionic compound that decomposes readily to aqueous hydrogen carbonate ions and hydrogen ions, $H^+(aq)$. Administering aqueous hydrogen carbonate will cause the equilibrium system in the equation above to shift away from carbonic acid to the left, toward the reactants. This reduces the acid concentration and so raises blood pH. Knowing how much hydrogen carbonate produces the desired shift can have life-or-death implications. Fortunately, the equilibrium law equation allows us to predict equilibrium shifts quantitatively.

Figure 1 People with type 1 diabetes that is not well controlled are at higher risk for low blood pH.

We know that the equilibrium constant does not change with concentration. However, adjusting any concentration of an entity in this expression will disturb the equilibrium. This will force the equilibrium to shift through changes in the concentrations of other entities until the equilibrium constant is re-established at its original value, indicating that the system is again at equilibrium.

What happens at the level of the chemical entities to restore the equilibrium constant in a disturbed equilibrium? To answer this, imagine a reaction involving entities composed of two different hypothetical atoms, which we will represent as ● and ●.

The chemical reaction between these entities is reversible and the chemical reaction system has an equilibrium constant, *K*, of 25. We can represent this chemical reaction system as



Now, assume we place 12 ● and 12 ● in a closed reaction chamber and allow them to react. **Figure 2** depicts the entities in the reaction vessel before any chemical reactions have occurred.

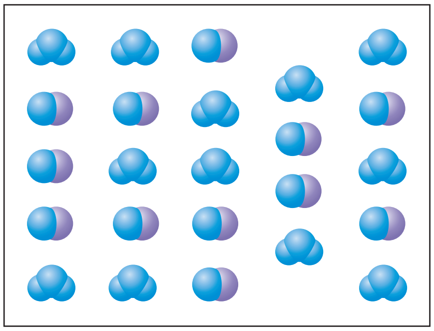
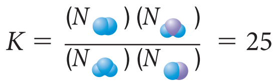


Figure 2 At the start of the reaction, 24 reactant molecules are mixed together in a reaction chamber in a 1:1 ratio.

Suppose that we allow the chemical reaction to reach equilibrium. Since we know the value of the equilibrium constant is 25, the equilibrium law equation for this reaction can be represented graphically as



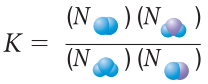
In this equation, N represents the number of each entity. Since the equilibrium constant is not reported with units, the ratio of numbers (of entities) to numbers will yield the same value as the ratio of concentrations to concentrations. Therefore, we can use actual numbers of entities in the equilibrium law equation. We want to determine how many  and  entities will be present when this chemical system reaches equilibrium. How can we do this?

One strategy we can try is trial and error. Suppose we start by guessing that 5  will have reacted when the system reaches equilibrium. Since we know from the balanced equation that equal numbers of  and  react, then 5  must also have reacted and produced 5  and 5  (see **Table 1**).

Table 1 Number of Entities at Initial and New Conditions for a Reaction where K is 25; Numbers Determined by Trial and Error

				
Initial number of entities	12	12	0	0
Guessed change in number of entities	12 − 5 = 7	12 − 5 = 7	0 + 5 = 5	0 + 5 = 5
Equilibrium number of entities	?	?	?	?

We can check if the distribution in Table 1 forms a valid equilibrium for this chemical reaction system by substituting the numbers in the table into the equilibrium expression to see if we get a value of 25 (the given equilibrium constant value).



$$= \frac{(5)(5)}{(7)(7)}$$

$$K = 0.51$$

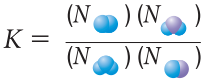
Since the calculated value using the numbers from Table 1 is not 25, we know that our guess was incorrect. The value that we calculated is less than 25, so we also know that the correct distribution must have a larger numerator (products) relative to the denominator (reactants).

Clearly, we underestimated by guessing that only 5 of the original reactants would need to react to reach equilibrium. How can we find the correct number? We might instead use a variable, such as x, to represent the number of entities that react and then analyze the distribution using an ICE table, as shown in **Table 2**.

Table 2 Initial, Change, Equilibrium Table for Hypothetical Equilibrium System

	 +	 $\rightleftharpoons$	 +	
Initial number of entities	12	12	0	0
Change in number of entities	$-x$	$-x$	$+x$	$+x$
Equilibrium number of entities	$12-x$	$12-x$	$+x$	$+x$

Rewriting the equilibrium expression for this algebraic representation gives



$$K = \frac{(x)(x)}{(12 - x)(12 - x)}$$

Since we know that the equilibrium constant, K, is equal to 25, we can solve this equation for x.

$$\frac{(x)(x)}{(12 - x)(12 - x)} = 25$$

$$\frac{x^2}{(12 - x)^2} = 25$$

$$\frac{\sqrt{x^2}}{\sqrt{(12 - x)^2}} = \sqrt{25}$$

$$\frac{x}{12 - x} = \pm 5$$

$$x = (\pm 5)(12 - x)$$

The square root of a number may be positive or negative. If $\sqrt{25} = +5$, then

$$\begin{aligned} x &= (5)(12 - x) \\ x &= 60 - 5x \\ 6x &= 60 \\ x &= 10 \end{aligned}$$

If $\sqrt{25} = -5$, then

$$\begin{aligned} x &= (-5)(12 - x) \\ x &= -60 + 5x \\ 4x &= 60 \\ x &= 15 \end{aligned}$$

We started with 12 entities of each reactant, so a value of 15 for x would give us a negative number of atoms, which is not possible. Therefore, the solution is that x is equal to 10. To check this, we substitute 10 for x in our algebraic equation for the equilibrium constant:

$$\begin{aligned} K &= \frac{(x)(x)}{(12 - x)(12 - x)} \\ &= \frac{(10)(10)}{(12 - 10)(12 - 10)} \\ K &= 25 \end{aligned}$$

Figure 3 depicts this distribution of entities at equilibrium.

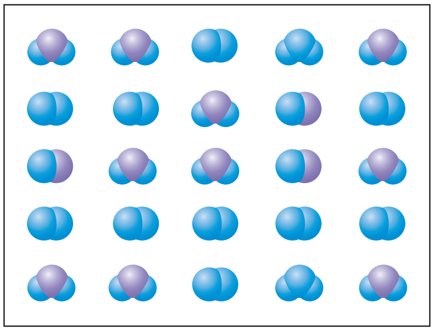


Figure 3 At equilibrium, the system contains 10 , 10 , 2 , and 2 .

The Reaction Quotient (Q)

reaction quotient (*Q*) the product of the concentrations of the products, divided by the product of the concentrations of the reactants, for a chemical reaction that is not necessarily at equilibrium

The **reaction quotient (*Q*)** is the ratio of the product of the concentrations of the products to the product of the concentrations of the reactants. Like the equilibrium constant, this ratio can be used to analyze an equilibrium system. However, the

instantaneous concentrations concentrations that occur together at a particular instant in time in the progress of a chemical reaction

reaction quotient can be calculated for a chemical reaction that is not at equilibrium. To obtain the reaction quotient, the equilibrium law equation is applied using instantaneous concentrations. **Instantaneous concentrations** are a set of concentrations that correspond to a particular instant in time. The specific instant in time does not matter, as long as the concentrations of all reactants and products are measured at the same instant. If the concentrations of reactants and products are measured when a system is at equilibrium, then the reaction quotient, Q, will have the same value as the equilibrium constant, K. CAREER LINK

It is often convenient to measure concentrations at the beginning of a reaction, when all product concentrations are zero. For example, consider the synthesis of ammonia gas, $NH_3(g)$, from gaseous nitrogen, $N_2(g)$, and hydrogen, $H_2(g)$. You may recall that Fritz Haber's explorations of this reaction system won him the Nobel Prize in Chemistry (Section 7.3). The balanced chemical equation for this reaction is

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

The reaction quotient equation for this reaction system at any time is

$$Q = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

When the concentration of any reactant or product is zero, the chemical equilibrium system will shift in the direction that produces the missing substance. What happens at a point when none of the concentrations are zero? To predict the direction in which the chemical equilibrium system will shift, we can compare the values of the reaction quotient, Q, to the equilibrium constant, K. The relative sizes of Q and K can give three possible predictions:

1. Q is less than K. The ratio of the concentrations of products to the concentrations of reactants is smaller than when the chemical system is at equilibrium. To move Q toward K, the concentrations of products must increase while the concentration of the reactants decreases. The chemical equilibrium system shifts to the right, consuming reactants and forming products until equilibrium is reached and Q equals K.
2. Q is equal to K. The chemical system is at equilibrium, so no shift will occur.
3. Q is greater than K. The ratio of the concentrations of products to the concentrations of reactants is larger than when the chemical system is at equilibrium. To move Q toward K, the concentrations of products must decrease and that of reactants must increase. The chemical equilibrium system shifts to the left and converts products into reactants until it achieves equilibrium and Q equals K.

These predictions are summarized graphically in **Figure 4**. WEB LINK

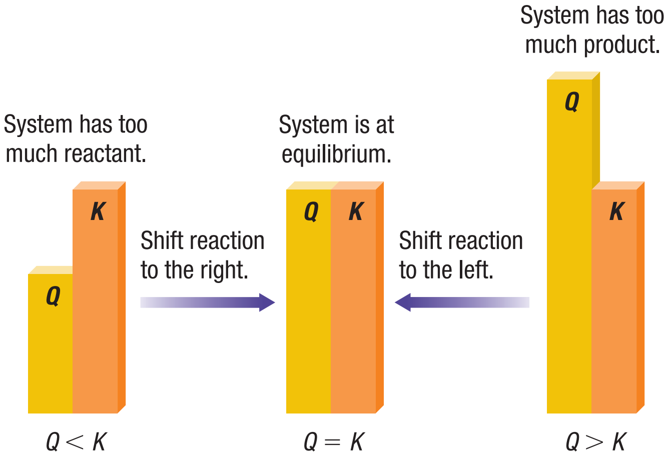


Figure 4 The relationship between reaction quotient, Q, and the equilibrium constant, K.

Tutorial 1 Using the Reaction Quotient

It is useful to think of the reaction quotient as just that—a quotient (i.e., the result of a mathematical division) of the products over the reactants. If the reaction quotient is larger than *K*, then the concentrations of the products are high and the concentrations of the reactants are low compared to their equilibrium values. If the quotient is less than *K*, then products are low and reactants are high. Once we know which of these cases applies, it is clear in which direction a reaction will proceed to reach equilibrium.

Sample Problem 1: Using *Q* to Determine if a Chemical Reaction System Is at Equilibrium

For the synthesis of ammonia gas at 500 °C in a closed vessel from gaseous nitrogen and hydrogen, the equilibrium constant, *K*, is 6.01×10^{-2}. The balanced chemical equation for this reaction is

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

For each of the following initial conditions, determine if the given concentrations represent an equilibrium. If not, predict the direction in which the reaction will proceed to reach equilibrium.

(a) $[NH_3(g)]_{initial} = 1.00 \times 10^{-3}$ mol/L;
$[N_2(g)]_{initial} = 1.00 \times 10^{-5}$ mol/L;
$[H_2(g)]_{initial} = 2.00 \times 10^{-3}$ mol/L

(b) $[NH_3(g)]_{initial} = 2.00 \times 10^{-4}$ mol/L;
$[N_2(g)]_{initial} = 1.50 \times 10^{-5}$ mol/L;
$[H_2(g)]_{initial} = 3.54 \times 10^{-1}$ mol/L

(c) $[NH_3(g)]_{initial} = 1.00 \times 10^{-4}$ mol/L;
$[N_2(g)]_{initial} = 5.00$ mol/L;
$[H_2(g)]_{initial} = 1.00 \times 10^{-2}$ mol/L

(a) **Given:** $[NH_3(g)]_{initial} = 1.00 \times 10^{-3}$ mol/L;
$[N_2(g)]_{initial} = 1.00 \times 10^{-5}$ mol/L;
$[H_2(g)]_{initial} = 2.00 \times 10^{-3}$ mol/L; $K = 6.01 \times 10^{-2}$

Required: *Q*

Solution:

Step 1. Write the equilibrium constant equation for the reaction system and calculate *Q* from the given concentrations:

$$Q = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$
$$= \frac{(1.00 \times 10^{-3})^2}{(1.00 \times 10^{-5})(2.00 \times 10^{-3})^3}$$
$$Q = 1.25 \times 10^7$$

Since $K = 6.01 \times 10^{-2}$, *Q* is greater than *K*, and the system is not at equilibrium.

Step 2. Since *Q* is greater than *K*, the system has more of the product now than it would have at equilibrium. To reach equilibrium, the equilibrium system must shift to the left (toward the reactants).

Statement: At the given initial conditions, this chemical reaction system must shift to the left, toward reactants, to reach equilibrium.

(b) **Given:** $[NH_3(g)]_{initial} = 2.00 \times 10^{-4}$ mol/L;
$[N_2(g)]_{initial} = 1.50 \times 10^{-5}$ mol/L;
$[H_2(g)]_{initial} = 3.54 \times 10^{-1}$ mol/L; $K = 6.01 \times 10^{-2}$

Required: *Q*

Solution: Calculate *Q*, and compare its value to the value of *K*.

$$Q = \frac{(2.00 \times 10^{-4})^2}{(1.50 \times 10^{-5})(3.54 \times 10^{-1})^3}$$
$$Q = 6.01 \times 10^{-2}$$

Since $K = 6.01 \times 10^{-2}$, *Q* is equal to *K* and the system is at equilibrium.

Statement: Since the chemical reaction system is at equilibrium at the given initial conditions, it will not shift.

(c) **Given:** $[NH_3(g)]_{initial} = 1.00 \times 10^{-4}$ mol/L;
$[N_2(g)]_{initial} = 5.00$ mol/L;
$[H_2(g)]_{initial} = 1.00 \times 10^{-2}$ mol/L; $K = 6.01 \times 10^{-2}$

Required: *Q*

Solution:

Step 1. Calculate *Q*, and compare its value to the value of *K*.

$$Q = \frac{(1.00 \times 10^{-4})^2}{(5.00)(1.00 \times 10^{-2})^3}$$
$$Q = 2.00 \times 10^{-3}$$

Step 2. *Q* is less than *K*, so the system is not at equilibrium. To reach equilibrium, the equilibrium system must shift to the right, toward the product.

Statement: At the given initial conditions, this chemical equilibrium system will shift to the right (toward the product) to achieve equilibrium.

Practice

1. The equilibrium constant, *K*, is 0.020 when the chemical reaction system given by the following balanced chemical equation is carried out in a closed container at 445 °C:

   $2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$

   Determine the value of *Q* to establish whether this chemical reaction system is at equilibrium when reactants and products have the following concentrations. If the system is not at equilibrium, predict the direction in which the reaction will proceed to reach equilibrium. T/I
   (a) $[HI(g)] = 0.14$ mol/L, $[H_2(g)] = 0.040$ mol/L, and $[I_2(g)] = 0.010$ mol/L. [ans: $Q = 0.020$]
   (b) $[HI(g)] = 0.20$ mol/L, $[H_2(g)] = 0.15$ mol/L, and $[I_2(g)] = 0.090$ mol/L. [ans: $Q = 0.34$; left]
2. In a closed container, dinitrogen tetroxide gas, $N_2O_4(g)$, decomposes to nitrogen dioxide gas, $NO_2(g)$. The equilibrium constant, *K*, for this reaction is 0.87 at 55 °C. A chemist fills a vessel with dinitrogen tetroxide gas at 55 °C. He then analyzes the contents twice as the reaction is proceeding, and finds that it contains the following concentrations:
   Time 1: $[N_2O_4(g)] = 0.80$ mol/L, $[NO_2(g)] = 1.55$ mol/L
   Time 2: $[N_2O_4(g)] = 1.66$ mol/L, $[NO_2(g)] = 1.2$ mol/L

   For each time, determine whether the system was in equilibrium. If it was not, predict the direction in which the reaction would proceed to achieve equilibrium. [ans: Time 1: no, left; Time 2: yes] T/I
3. When heated, solid silver oxide, $Ag_2O(s)$, will decompose into silver metal, Ag(s), and oxygen gas, $O_2(g)$. In a sealed vessel, the chemical system will form an equilibrium with an equilibrium constant, *K*, of 2.5×10^{-3}.

   $2\ Ag_2O(s) \rightleftharpoons 4\ Ag(s) + O_2(g)$

   (a) Write the equilibrium constant equation. K/U
   (b) When the instantaneous concentration of oxygen gas is 5.0×10^{-2} mol/L, is the chemical system at equilibrium? If not, in what direction will it shift to reach equilibrium? [ans: no; left] T/I

Calculating Equilibrium Concentrations

We can calculate the value of the equilibrium constant if we are given the initial concentrations of all reactants and products and at least one equilibrium concentration. We can also calculate the equilibrium concentrations from the equilibrium constant and the initial concentrations.

Tutorial 2 Calculating Equilibrium Concentrations

One strategy to find equilibrium concentrations of reactants and products is to work with the initial concentrations. You can then modify these initial concentrations appropriately to find the equilibrium concentrations.

Sample Problem 1: Determining Equilibrium Concentrations and *K* from All Initial Concentrations and One Equilibrium Concentration

Phosphorus pentachloride gas, $PCl_5(g)$, decomposes to form phosphorus trichloride gas, $PCl_3(g)$, and chlorine gas, $Cl_2(g)$:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

A 2.00 L sealed flask at 30 °C initially contains 0.298 mol of phosphorus trichloride gas, 8.70×10^{-3} mol of phosphorus pentachloride gas, and no chlorine gas. At equilibrium, the flask contains 2.00×10^{-3} mol of chlorine gas. Calculate the equilibrium concentrations of all entities and the value of *K*.

Given: Volume, $V = 2.00$ L;
$n_{\text{initial } PCl_5(g)} = 8.70 \times 10^{-3}$ mol;
$n_{\text{initial } PCl_3(g)} = 0.298$ mol; $n_{\text{initial } Cl_2(g)} = 0$ mol;
$n_{\text{equilibrium } Cl_2(g)} = 2.00 \times 10^{-3}$ mol

Required: $[PCl_5(g)]_{\text{equilibrium}}$; $[PCl_3(g)]_{\text{equilibrium}}$; *K*

Analysis: $c = \dfrac{n}{V}$

Solution:

Step 1. Calculate concentrations, c, in mol/L from the given amounts of all entities.

$$[PCl_5(g)]_{initial}; \; c = \frac{n_{initial}}{V}$$
$$= \frac{8.70 \times 10^{-3}\text{ mol}}{2.00\text{ L}}$$
$$[PCl_5(g)]_{initial} = 4.35 \times 10^{-3}\text{ mol/L}$$

Using the same formula,

$$[PCl_3(g)]_{initial} = 0.149\text{ mol/L}$$

Since there is no chlorine gas initially, $[Cl_2(g)]_{initial}$ is 0 mol/L. The equilibrium concentration of $Cl_2(g)$ is

$$[Cl_2(g)]_{equilibrium}; \; c = \frac{n_{equilibrium}}{V}$$
$$= \frac{2.00 \times 10^{-3}\text{ mol}}{2.00\text{ L}}$$
$$[Cl_2(g)]_{equilibrium} = 1.00 \times 10^{-3}\text{ mol/L}$$

Step 2. Use an ICE table to determine the required equilibrium concentrations.

According to the balanced chemical equation for the chemical reaction system, the mole ratio is 1:1:1. The initial concentration of $Cl_2(g)$ was 0 mol/L, and 1.00×10^{-3} mol/L of $Cl_2(g)$ is present at equilibrium, so there is a decrease in the concentration of $PCl_5(g)$ and an increase $PCl_3(g)$ of 1.00×10^{-3} mol/L.

Since all the coefficients in the balanced equation are 1, the magnitude of the change is the same for all entities. Organize this information in an ICE table, similar to **Table 3**.

Table 3 ICE Table for Calculating Equilibrium Concentrations

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
I	4.35×10^{-3}		0.149		0
C	$-(1.00 \times 10^{-3})$		$+(1.00 \times 10^{-3})$		$+(1.00 \times 10^{-3})$
E	3.35×10^{-3}		0.150		1.00×10^{-3}

Step 3. Calculate the equilibrium constant, K, by substituting the equilibrium concentrations into the equilibrium constant equation.

$$K = \frac{[Cl_2(g)][PCl_3(g)]}{[PCl_5(g)]}$$
$$= \frac{(1.00 \times 10^{-3})(0.150)}{(3.35 \times 10^{-3})}$$
$$K = 4.48 \times 10^{-2}$$

Statement: The equilibrium concentration of the reactant, phosphorus pentachloride gas, $PCl_5(g)$, is 3.35×10^{-3} mol/L. The equilibrium concentrations of the products are 0.150 mol/L for phosphorus trichloride gas, $PCl_3(g)$, and 1.00×10^{-3} mol/L for chlorine gas, $Cl_2(g)$. The equilibrium constant for the equilibrium system is 4.48×10^{-2}.

Sample Problem 2: Determining Equilibrium Concentrations from *K* and Initial Concentrations Only

Carbon monoxide gas, $CO(g)$, reacts with steam, $H_2O(g)$, to produce carbon dioxide, $CO_2(g)$, and hydrogen, $H_2(g)$. At 700 K, the equilibrium constant is 5.10. Calculate all equilibrium concentrations if 1.250 mol of each entity is initially placed in a 500.0 mL sealed flask.

Given: $V = 500.0$ mL; $n_{initial\ CO(g)} = 1.250$ mol; $n_{initial\ H_2O(g)} = 1.250$ mol; $n_{initial\ H_2(g)} = 1.250$ mol; $n_{initial\ CO_2(g)} = 1.250$ mol; $K = 5.10$

Required: $[CO(g)]_{equilibrium}$; $[H_2O(g)]_{equilibrium}$; $[H_2(g)]_{equilibrium}$; $[CO_2(g)]_{equilibrium}$

Solution:

Step 1. Convert the given amounts to concentrations in mol/L by dividing by the volume.

$$[CO(g)]_{initial} = \frac{1.250\text{ mol}}{0.5000\text{ L}}$$
$$[CO(g)]_{initial} = 2.500\text{ mol/L}$$

Since $n_{initial}$ is the same for all products and reactants, and $[CO(g)]_{initial} = 2.500$ mol/L, you know that $[H_2O(g)]_{initial} = 2.500$ mol/L, $[CO_2(g)]_{initial} = 2.500$ mol/L, and $[H_2(g)]_{initial} = 2.500$ mol/L.

Step 2. Write the balanced equation for the equilibrium reaction system.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Step 3. Calculate the reaction quotient, Q, for the initial concentrations and compare its value with the given value of K.

$$Q = \frac{[CO_2(g)][H_2(g)]}{[CO(g)][H_2O(g)]}$$
$$= \frac{(2.500)(2.500)}{(2.500)(2.500)}$$
$$Q = 1.000$$

Since this Q is less than the given value of 5.10 for K, the system is not at equilibrium. For Q to be equal to K (5.10), the chemical reaction system must shift to the right (toward products).

Step 4. Use an ICE table to determine the required changes to the equilibrium concentrations. Use a variable for unknowns. Your table should look similar to **Table 4**.

Table 4 ICE Table for Calculating Equilibrium Concentrations

	$CO(g)$ +	$H_2O(g)$ $\rightleftharpoons$	$CO_2(g)$ +	$H_2(g)$
I	2.500	2.500	2.500	2.500
C	$-x$	$-x$	$+x$	$+x$
E	$2.500-x$	$2.500-x$	$2.500+x$	$2.500+x$

Step 5. Calculate the value of x by substituting the given value of K and the concentrations from the ICE table into the equilibrium constant equation. Note that all concentrations have units of mol/L, but we have omitted the units to simplify the calculation.

$$\frac{[CO_2(g)][H_2(g)]}{[CO(g)][H_2O(g)]} = 5.10$$

$$\frac{(2.500 + x)(2.500 + x)}{(2.500 - x)(2.500 - x)} = 5.10$$

$$\frac{\sqrt{(2.500 + x)^2}}{\sqrt{(2.500 - x)^2}} = \sqrt{5.10}$$

$$\frac{2.500 + x}{2.500 - x} = \pm 2.258$$

$$2.500 + x = (\pm 2.258)(2.500 - x)$$

$$x = \pm 2.258(2.500 - x) - 2.500$$

Solve for x for the positive root.

$$x = 2.258(2.500 - x) - 2.500$$

$$x = 5.645 - 2.258x - 2.500$$

$$3.258x = 3.145$$

$$x = 0.965$$

Solve for x for the negative root.

$$x = -2.258(2.500 - x) - 2.500$$

$$x = -5.645 + 2.258x - 2.500$$

$$8.145 = 1.258x$$

$$x = 6.475$$

Substituting this value of x into the expressions for equilibrium concentrations in the ICE table results in negative concentration values, which are not possible in the real world. Therefore, use $x = 0.965$ mol/L in the equilibrium concentration calculations.

Step 6. Calculate the equilibrium concentrations.

Reactants:

$$[CO(g)]_{\text{equilibrium}} \text{ and } [H_2O(g)]_{\text{equilibrium}} = 2.500 - x$$

$$= 2.500 - 0.965$$

$$[CO(g)]_{\text{equilibrium}} \text{ and } [H_2O(g)]_{\text{equilibrium}} = 1.535 \text{ mol/L}$$

Products:

$$[CO_2(g)]_{\text{equilibrium}} \text{ and } [H_2(g)]_{\text{equilibrium}} = 2.500 + x$$

$$= 2.500 + 0.965$$

$$[CO_2(g)]_{\text{equilibrium}} \text{ and } [H_2(g)]_{\text{equilibrium}} = 3.465 \text{ mol/L}$$

Check these values by substituting them into the equilibrium law equation.

$$K = \frac{[CO_2(g)][H_2(g)]}{[CO(g)][H_2O(g)]}$$

$$= \frac{(3.465)^2}{(1.535)^2}$$

$$K = 5.096$$

This result is the same as the given value of K (5.10), within rounding error.

Statement: The equilibrium concentration for both carbon monoxide gas and steam is 3.47 mol/L. The equilibrium concentration for both carbon dioxide gas and hydrogen gas is 1.54 mol/L.

Practice

1. In a 250 mL sealed container at 150 °C, 0.50 mol of both iodine gas, $I_2(g)$, and bromine gas, $Br_2(g)$, are mixed and allowed to react until they form an equilibrium with iodine monobromide gas, IBr(g). The equilibrium constant for this reaction is 1.2×10^2. What are the equilibrium concentrations for iodine gas and bromine gas? T/I [ans: $[I_2] = 0.3$ mol/L; $[Br_2] = 0.3$ mol/L]
2. In a 2.00 L reaction vessel at 440 °C, hydrogen gas and iodine vapour form gaseous hydrogen iodide. The equilibrium constant, K, is 49.7. Determine the equilibrium concentrations for all entities if 4.00 mol of hydrogen gas and 1.99 mol of iodine vapour are combined and the equilibrium concentration of hydrogen gas is 1.07 mol/L. T/I [ans: $[H_2(g)] = 1.07$ mol/L; $[I_2(g)] = 0.06$ mol/L; and $[HI(g)] = 1.86$ mol/L.]
3. At a temperature of 500 K, carbon dioxide gas, $CO_2(g)$, and solid carbon, C(s), will react to form an equilibrium.

   $$CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)$$

   When 0.250 mol of carbon dioxide gas was placed in a 0.500 L flask with carbon powder and reacted until equilibrium was reached, the concentration of carbon monoxide gas at equilibrium was 0.0157 mol/L. Determine the value of the equilibrium constant, K, and the concentration of carbon dioxide gas at equilibrium. T/I [ans: $K = 5.01 \times 10^{-4}$, $[CO_2(g)]_{\text{equilibrium}} = 0.492$ mol/L]

Solving More Complex Equilibrium Problems

So far, we have worked only with problems in which the initial concentrations and stoichiometry gave us polynomials that were easily reduced to simple linear equations. Concentrations, temperatures, and equilibrium constants were carefully chosen so that you could follow the logic of the solutions more easily. However, in the real world, problem-solving for chemical equilibria will rarely involve linear equations. Instead, equilibrium problems often require working with higher-order polynomials. In Tutorial 3, you will see how and when to use the same strategy we have used thus far to solve these more complex problems.

Tutorial 3 Solving More Complex Equilibrium Problems

The general strategy to solve more complex equilibrium problems is the same as for the simpler problems. You will either be given or be expected to know the following: the balanced equation for the reaction, the equilibrium law equation for the reaction, the equilibrium constant for the equilibrium system, and the initial concentrations of the entities in the reaction.

Sample Problem 1: Using Assumptions about the Magnitude of *x*

Carbon monoxide gas, $CO(g)$, is a primary starting material in the synthesis of many organic compounds, including methanol, $CH_3OH(l)$. At 2000 °C, K is 6.40×10^{-7} for the decomposition of carbon dioxide gas, $CO_2(g)$, into carbon monoxide and oxygen, $O_2(g)$. Calculate the concentrations of all entities at equilibrium if 0.250 mol of $CO_2(g)$ is placed in a 1.000 L closed container and heated to 2000 °C.

Given: $V = 1.000$ L; $n_{CO_2(g)} = 0.250$ mol; $K = 6.40 \times 10^{-7}$

Required: $[CO_2(g)]_{[equilibrium]}$; $[O_2(g)]_{equilibrium}$; $[CO(g)]_{equilibrium}$

Solution:

Step 1. Determine initial concentrations of substances in mol/L, using any given amounts and volumes.

Since the reaction has not yet started, the initial concentration of $CO_2(g)$ and $O_2(g)$ is 0 mol/L. Since V is 1.000 L,

$$[CO_2(g)]_{initial};\ c = \frac{n}{V}$$

$$[CO_2(g)]_{initial} = 0.250\ \text{mol/L}$$

Step 2. Calculate Q and compare it to K.

Since there are initially no products, you also know that Q is 0. Q is therefore less than K and the equilibrium system will shift to the right, toward the products.

Step 3. Use an ICE table to determine the equilibrium concentrations.

Write the balanced chemical equation for the reaction

$$2\ CO_2(g) \rightleftharpoons 2\ CO(g) + O_2(g)$$

Use a variable for unknowns, using coefficients according to the stoichiometry of the balanced equation. Your table should look similar to **Table 5**.

Table 5 ICE Table for Calculating Equilibrium Concentrations

	$2\ CO_2(g) \rightleftharpoons$	$2\ CO(g)\ +$	$O_2(g)$
I	0.250	0.00	0.00
C	$-2x$	$+2x$	$+x$
E	$0.250 - 2x$	$2x$	x

Step 4. Substitute the equilibrium concentrations into the equilibrium constant equation, and solve for the unknown.

$$K = \frac{[CO(g)]^2[O_2(g)]}{[CO_2(g)]^2} = 6.40 \times 10^{-7}$$

$$\frac{(2x)^2(x)}{(0.250 - 2x)^2} = 6.40 \times 10^{-7}$$

$$\frac{4x^3}{(0.250 - 2x)^2} = 6.40 \times 10^{-7}$$

There is not an easy way to solve a cubic equation. However, you can simplify it by making some reasonable assumptions. Notice that the equilibrium constant value is very small compared to the initial concentration of carbon dioxide gas. Therefore, very little carbon dioxide gas will decompose at this temperature. From this, you can assume that the value of x will also be so small as to be negligible.

If x is negligible, then $2x$ will be a very small number. Therefore,

$$[CO_2(g)]_{equilibrium} = [CO_2(g)]_{initial} - 2x$$

$$= 0.250\ \text{mol/L} - (\text{very small number})$$

$$[CO_2(g)]_{equilibrium} \approx 0.250\ \text{mol/L}$$

At equilibrium, then, the cubic equation for K can be simplified and solved.

$$\frac{4x^3}{(0.250 - 2x)^2} = 6.40 \times 10^{-7}$$

$$\frac{4x^3}{(0.250)^2} \approx 6.40 \times 10^{-7}$$

$$4x^3 \approx (6.40 \times 10^{-7})(0.250)^2$$

$$x^3 \approx \frac{4.00 \times 10^{-8}}{4}$$

$$x \approx \sqrt[3]{1.00 \times 10^{-8}}$$

$$x \approx 2.15 \times 10^{-3}$$

Now, use this value to test the validity of your earlier assumption.

$$\begin{aligned}[\text{CO}_2(\text{g})]_{\text{equilibrium}} &= [\text{CO}_2(\text{g})]_{\text{initial}} - 2x \\ &= 0.250 \text{ mol/L} - 2(2.15 \text{ mol/L} \times 10^{-3}) \\ &= 0.250 \text{ mol/L} - 0.00430 \text{ mol/L} \\ [\text{CO}_2(\text{g})]_{\text{equilibrium}} &= 0.246 \text{ mol/L}\end{aligned}$$

The difference between 0.250 mol/L and 0.246 mol/L is 0.004, or 1.6 %. This very small discrepancy will have little effect on calculations of equilibrium concentrations. In general, a difference of less than 5 % justifies the simplifying assumption. It can be shown that, if the concentration to which x is added or subtracted is at least 100 times the value of K, the simplifying assumption will give an error of less than 5 %. We will call this the "hundred rule." The hundred rule can determine if a simplifying assumption is warranted in a complex calculation and so should be used before the calculation is made.

$$\frac{[\text{CO}_2(\text{g})]_{\text{initial}}}{K} = \frac{0.250}{6.40 \times 10^{-7}}$$

$$\frac{[\text{CO}_2(\text{g})]_{\text{initial}}}{K} = 3.91 \times 10^{5}$$

The ratio of 3.91×10^5 is much greater than 100, which shows that the assumption $0.250 - 2x = 0.250$ was warranted.

Now that you have a good approximation of x, you can use it to solve for the equilibrium concentrations by substituting it in the expressions in the ICE table. This will give you the following concentrations:

$[\text{CO}_2(\text{g})]_{\text{equilibrium}} = 0.246$ mol/L

$[\text{CO}(\text{g})]_{\text{equilibrium}} = 4.30 \times 10^{-3}$ mol/L

$[\text{O}_2(\text{g})]_{\text{equilibrium}} = 2.15 \times 10^{-3}$ mol/L

Step 5. Check your work by determining K from the equilibrium concentrations you calculated, and comparing the value to the standard value of K. If they are within 5 %, you can be confident that your calculations are correct.

$$K = \frac{[\text{CO}(\text{g})]^2[\text{O}_2(\text{g})]}{[\text{CO}_2(\text{g})]^2}$$

$$= \frac{(4.30 \times 10^{-3})^2(2.15 \times 10^{-3})}{(0.246)^2}$$

$$K = 6.57 \times 10^{-7}$$

The calculated value of K (6.57×10^{-7}) is within 3 % of the given value (6.40×10^{-7}).

Statement: The equilibrium concentrations for gaseous carbon dioxide, carbon monoxide, and oxygen are 0.246 mol/L, 4.30×10^{-3} mol/L, and 2.15×10^{-3} mol/L, respectively.

Sample Problem 2: Rejecting an Assumption about the Magnitude of x

If 0.500 mol of dinitrogen tetroxide gas, $N_2O_4(g)$, is placed in a 1.00 L closed container at 150 °C, what will be the concentrations of dinitrogen tetroxide gas and nitrogen dioxide gas, $NO_2(g)$, at equilibrium? The equilibrium constant, K, is 4.50 under these conditions.

Given: $V = 1.00$ L; $n_{N_2O_4} = 0.500$ mol; $K = 4.50$

Required: all equilibrium concentrations in mol/L

Solution:

Step 1. Since initially there are no products, Q is 0, which is smaller than K. The equilibrium system will shift to the right, in the direction of products.

Step 2. Using the balanced chemical equation, construct an ICE table similar to **Table 6**.

Table 6 ICE Table for Calculating Equilibrium Concentrations

	$N_2O_4(g)$ $\rightleftharpoons$	$2\ NO_2(g)$
I	0.500	0.00
C	$-x$	$+2x$
E	$0.500 - x$	$2x$

Step 3. Substitute the expressions from the ICE table into the equilibrium constant equation. The equilibrium law for this reaction is

$$\frac{[\text{NO}_2(\text{g})]^2}{[\text{N}_2\text{O}_4(\text{g})]} = 4.50$$

$$\frac{(2x)^2}{(0.500 - x)} = 4.50$$

This equation cannot be solved by taking the square root of both sides. Apply the hundred rule to see if x can be assumed to be negligible.

$$\frac{[N_2O_4(g)]_{initial}}{K} = \frac{0.500}{4.50}$$

$$\frac{[N_2O_4(g)]_{initial}}{K} = 0.111$$

Since 0.111 is much less than 100, the assumption that $0.500 + x \approx 0.500$ is not warranted. Therefore, you must solve the equation.

Step 4. Solve the equation.

$$\frac{(2x)^2}{(0.500 - x)} = 4.50$$

$$(2x)^2 = (0.500 - x)4.50$$

$$4x^2 = 2.250 - 4.50x$$

$$4x^2 + 4.50x - 2.250 = 0$$

You can see that this is a quadratic equation of the general form

$$ax^2 + bx + c = 0$$

You can get the root of a quadratic equation by using the quadratic formula.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-4.50 \pm \sqrt{(4.50)^2 - 4(4)(-2.250)}}{2(4)}$$

$$= \frac{-4.50 \pm 7.50}{8}$$

$$x = -1.50$$

or

$$x = 0.375$$

The negative root would result in a negative concentration for $NO_2(g)$, so $x = 0.375$ is the only acceptable solution to the quadratic equation. Use this value to calculate the equilibrium concentrations for $NO_2(g)$ and $N_2O_4(g)$ from the expressions in your ICE table.

$$[N_2O_4(g)]_{equilibrium} = 0.125\ mol/L$$

$$[NO_2(g)]_{equilibrium} = 0.750\ mol/L$$

Step 5. Check your results by calculating K to see if it equals the given value of 4.50.

The calculated value of 4.50 for K is equal to the given value of 4.50.

Statement: The solution is at equilibrium when the concentration of dinitrogen tetroxide is 0.125 mol/L and the concentration of nitrogen dioxide is 0.750 mol/L.

Sample Problem 3: Rejecting an Assumption about the Magnitude of x

Suppose that hydrogen fluoride gas, HF(g), is synthesized by combining 3.000 mol of hydrogen gas, $H_2(g)$, and 6.000 mol of fluorine gas, $F_2(g)$, in a 3.000 L sealed flask. Assume that the equilibrium constant for the synthesis reaction at this temperature is 1.15×10^2. What are the concentrations for each gas at equilibrium?

Given: $V = 3.000\ L$; $n_{H_2(g)} = 3.000\ mol$; $n_{F_2(g)} = 6.000\ mol$;
$K = 1.15 \times 10^2$

Required: $[H_2(g)]_{equilibrium}$; $[F_2(g)]_{equilibrium}$; and $[HF(g)]_{equilibrium}$

Solution:

Step 1. Convert the given amounts to concentrations in mol/L.

$$[H_2(g)]_{initial} = 1.000\ mol/L$$

$$[F_2(g)]_{initial} = 2.000\ mol/L$$

$$[HF(g)]_{initial} = 0\ mol/L$$

Step 2. Calculate Q and compare it to K.

At the start of the reaction Q is 0, which is less than K. The chemical reaction system must shift to the right, toward the products.

Step 3. Use an ICE table to determine the required equilibrium concentrations, similar to **Table 7**.

Table 7 ICE Table for Calculating Equilibrium Concentrations

	$H_2(g)$	+	$F_2(g)$	$\rightleftharpoons$	$2\ HF(g)$
I	1.000		2.000		0
C	$-x$		$-x$		$+2x$
E	$1.000 - x$		$2.000 - x$		$2x$

Step 4. Write the equilibrium constant equation.

$$K = \frac{[HF(g)]^2}{[H_2(g)][F_2(g)]} = 1.15 \times 10^2$$

$$\frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 1.15 \times 10^2$$

Step 5. Apply the hundred rule to see if x can be assumed to be negligible.

$$\frac{[F_2(g)]_{initial}}{K} = \frac{2.00}{1.15 \times 10^2}$$

$$\frac{[F_2(g)]_{initial}}{K} = 0.017$$

Since 0.017 is much less than 100, the simplification assumption that $2.00 - x \approx 2.00$ is not warranted.

Therefore, you must solve the equation. Rearrange the equation into the form of a quadratic equation, $ax^2 + bx + c = 0$.

$$\frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 1.15 \times 10^2$$

$$(2x)^2 = (1.15 \times 10^2)(1.000 - x)(2.000 - x)$$

$$4x^2 = (1.15 \times 10^2)(2.000 - 2.000x - 1.000x + x^2)$$

$$4x^2 = 2.30 \times 10^2 - (4.45 \times 10^2)x + (1.15 \times 10^2)x^2$$

$$(1.11 \times 10^2)x^2 - (4.45 \times 10^2)x + 2.30 \times 10^2 = 0$$

Solve the quadratic equation.

$$x = \frac{4.45 \times 10^2 \pm \sqrt{(-4.45 \times 10^2)^2 - 4(1.11 \times 10^2)(2.30 \times 10^2)}}{2(1.11 \times 10^2)}$$

$x = 2.14$ mol/L or $x = 0.968$ mol/L

Since the value of 2.14 for x would give a negative value for the equilibrium concentration of hydrogen gas ($[H_2(g)] = 1.000$ mol/L $- x$), this value is not valid. The correct value for x therefore is 0.968 mol/L. Substituting this value in the expressions in the ICE table gives the following concentrations:

$[H_2(g)]_{\text{equilibrium}} = 3.20 \times 10^{-2}$ mol/L

$[F_2(g)]_{\text{equilibrium}} = 1.03$ mol/L

$[HF(g)]_{\text{equilibrium}} = 1.94$ mol/L

Step 6. Check these concentrations by substituting them into the equilibrium expression.

The calculated value of 1.14×10^2 is in close agreement with the given value for K (1.15×10^2).

Statement: The equilibrium concentrations for this chemical reaction system are 3.20×10^{-2} mol/L for hydrogen, 1.03 mol/L for fluorine, and 1.94 mol/L for hydrogen fluoride.

Practice

1. Cyclopropane gas will spontaneously undergo isomerization to form propene gas. If 2.50 mol of cyclopropane is placed in a sealed 0.500 L container, it will come to equilibrium with its isomer, propene. The value of the equilibrium constant, K, for this chemical system is 5.6. Determine the concentration of each of gas at equilibrium. T/I

   [ans: [cyclopropane] = 0.76 mol/L, [propene] = 4.24 mol/L]

2. If 0.200 mol of hydrogen gas, $H_2(g)$, and 0.200 mol of iodine gas, $I_2(g)$, are placed in a 1.00 L sealed flask, an equilibrium system will be established with hydrogen iodide gas, HI(g). Determine the concentration of all gases at SATP, given that the equilibrium constant, K, is 49.5. T/I

   [ans: [HI(g)] = 0.311 mol/L, $[H_2(g)]$ = 0.044 mol/L, $[I_2(g)]$=0.044 mol/L]

3. In a sealed vessel, a chemist allowed the decomposition of hydrogen chloride gas, HCl(g), to hydrogen gas, $H_2(g)$, and chlorine gas, $Cl_2(g)$, until equilibrium was reached. The balanced equation for this chemical reaction system is

   $$2\,HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

   If the chemist started the reaction with 0.500 mol of hydrogen chloride gas at 25 °C in a sealed 250.0 mL vessel, what was the concentration of all the gases at equilibrium, given that the equilibrium constant has a value of 3.2×10^{-34} at this temperature? T/I

   [ans: [HCl(g)] = 2.00 mol/L; $[H_2(g)] = 3.6 \times 10^{-17}$ mol/L; $[Cl_2\,(g)] = 3.6 \times 10^{-17}$ mol/L]

7.5 Review

Summary

- The magnitude of the equilibrium constant for a reaction, *K*, is directly proportional to the extent of that reaction.
- The reaction quotient, *Q*, is the product of the concentrations of the products, divided by the product of the concentrations of the reactants, for a chemical reaction that is not necessarily at equilibrium.
- Comparing the values of *Q* and *K* indicates whether a chemical reaction system is at equilibrium and, if not, the direction it will shift.

Questions

1. A chemist places a mixture of 2.00 mol of hydrogen gas, $H_2(g)$; 1.00 mol of nitrogen gas, $N_2(g)$; and 2.00 mol of ammonia gas, $NH_3(g)$, in a sealed, rigid 1.00 L flask at 750 K.

   The equilibrium constant for this reaction is 1.05×10^{21} at 750 K. T/I C
   (a) Write the balanced chemical equation for the synthesis of ammonia gas.
   (b) Calculate *Q* from the initial amounts of gases.
   (c) Determine whether the chemical system is at equilibrium. If the system is not at equilibrium, in which direction will the equilibrium shift?
2. The equilibrium constant is 0.0900 at 25 °C for the chemical reaction system represented by

   $$H_2O(g) + Cl_2O(g) \rightleftharpoons 2\ HOCl(g)$$

   For which sets of conditions below is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift? All flasks are rigid and sealed. T/I
   (a) A 1.0 L flask contains 1.0 mol $HOCl(g)$, 0.10 mol $Cl_2O(g)$, and 0.10 mol $H_2O(g)$.
   (b) A 2.0 L flask contains 0.084 mol $HOCl(g)$, 0.080 mol $Cl_2O(g)$, and 0.98 mol $H_2O(g)$.
   (c) A 3.0 L flask contains 0.25 mol $HOCl(g)$, 0.0010 mol $Cl_2O(g)$, and 0.56 mol $H_2O(g)$.
3. In a sealed, rigid container, nitrogen dioxide gas, $NO_2(g)$, is in equilibrium with dinitrogen tetroxide gas, $N_2O_4(g)$:

   $$2\ NO_2(g) \rightleftharpoons N_2O_4(g) \quad K = 1.15 \text{ at } 55\ °C$$

   Find the equilibrium concentration of gaseous nitrogen dioxide and dinitrogen tetroxide if the initial concentration of nitrogen dioxide gas is 0.850 mol/L. T/I
4. A rigid, sealed 1.00 L flask was filled with 2.00 mol carbon monoxide and 2.00 mol water vapour. After equilibrium was reached, it was found that 1.30 mol of each of carbon dioxide and hydrogen was present. Calculate the value of the equilibrium constant, *K*, for this reaction, assuming all substances are in the gas phase. T/I
5. A lab technician places 12.0 mol of sulfur trioxide gas, $SO_3(g)$, into a 3.0 L sealed, rigid container. The sulfur trioxide gas dissociates into gaseous sulfur dioxide, $SO_2(g)$, and oxygen, $O_2(g)$, until equilibrium is reached and 3.0 mol of sulfur dioxide is present. Calculate the equilibrium constant, *K*.

   $$2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$$ T/I
6. At a particular temperature, the gases sulfur dioxide, $SO_2(g)$, and nitrogen dioxide, $NO_2(g)$, react in a closed vessel to form the gases sulfur trioxide, $SO_3(g)$ and nitric oxide, $NO(g)$:

   $$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

   If the equilibrium constant, *K*, is 3.75 and the initial concentration of all four gases was 0.800 mol/L, calculate the equilibrium concentrations of all these gases. T/I
7. The equilibrium constant, *K*, has a value of 2.4×10^{-3} at a given temperature, for the reaction represented by the balanced equation

   $$2\ H_2O(g) \rightleftharpoons 2\ H_2(g) + O_2(g)$$

   At equilibrium, the concentrations of water vapour and hydrogen gas were 1.1×10^{-1} mol/L and 1.2×10^{-2}, respectively. What was the equilibrium concentration of oxygen gas? T/I
8. The creation of shells by mollusc species is a fascinating process. By using calcium from their food and aqueous environment and some complex equilibrium processes, these animals produce a hard calcium carbonate shell. One important equilibrium reaction in this process is

   $$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

   $$K = 5.6 \times 10^{-11}$$

   If 0.16 mol of HCO_3^- is placed into 1.00 L of solution, what will the equilibrium concentration of CO_3^{2-} be? T/I

7.6

Solubility Equilibria and the Solubility Product Constant

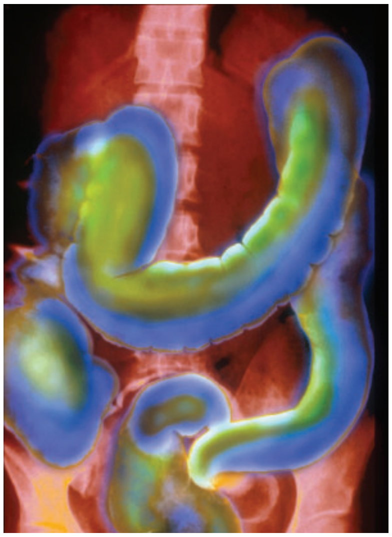


Figure 1 Barium sulfate makes the large intestine more visible in this X-ray image. Barium ions are toxic to humans, so the low solubility of barium sulfate also protects the patient from any toxic side effects.

Before undergoing an X-ray of the digestive tract, patients may be asked to consume a room-temperature (27 °C) barium "meal" composed of barium sulfate and water. At either 27 °C or body temperature (37 °C), the barium meal is mainly water and solid barium sulfate crystals, with a very small quantity of dissolved barium ions, $Ba^{2+}(aq)$, and sulfate ions, $SO_4^{\ 2-}(aq)$. The undissolved crystals of barium sulfate block the transmission of X-rays through the digestive tract, creating a clear image of the structures of the digestive tract (**Figure 1**).

The low solubility of barium sulfate, $BaSO_4$, is one reason this compound is used in the diagnosis of gastrointestinal disorders. **Solubility** is the quantity of a solute that dissolves in a solvent under specific conditions, such as the amount of sugar that can dissolve in water at 100 °C. For example, calcium sulfate, $CaSO_4(s)$, is more soluble in cold water than in hot water. This can have significant effects on plumbing. In pipes carrying cold water, any calcium sulfate remains dissolved and is harmless. In hot water, such as in a water heater, the calcium sulfate is less soluble and so may precipitate out of solution along with other compounds, such as calcium carbonate. The resulting solid can harm parts of the plumbing system.

solubility the quantity of solute that dissolves in a given quantity of solvent at a particular temperature; the concentration of a saturated solution at a particular temperature

Solubility Equilibria of Ionic Compounds

Recall that ionic compounds are composed of ions joined by ionic bonds. In water, ionic compounds form a dynamic equilibrium. For example, silver iodide, AgI(s), is an ionic compound that is slightly soluble in water. Immediately after solid silver iodide is placed in water, all the silver ions, Ag^+, and iodide ions, I^-, are still tightly packed in a crystal lattice structure, as shown in **Figure 2**. The charged ends of polar water molecules, $H_2O(l)$, are attracted to the ions and pull some of them into solution. The oxygen atoms in the water molecules, which have a partial negative charge, orient to surround the positively charged silver ions. Similarly, the positively charged parts of the water molecules orient to surround the negatively charged iodide ions.

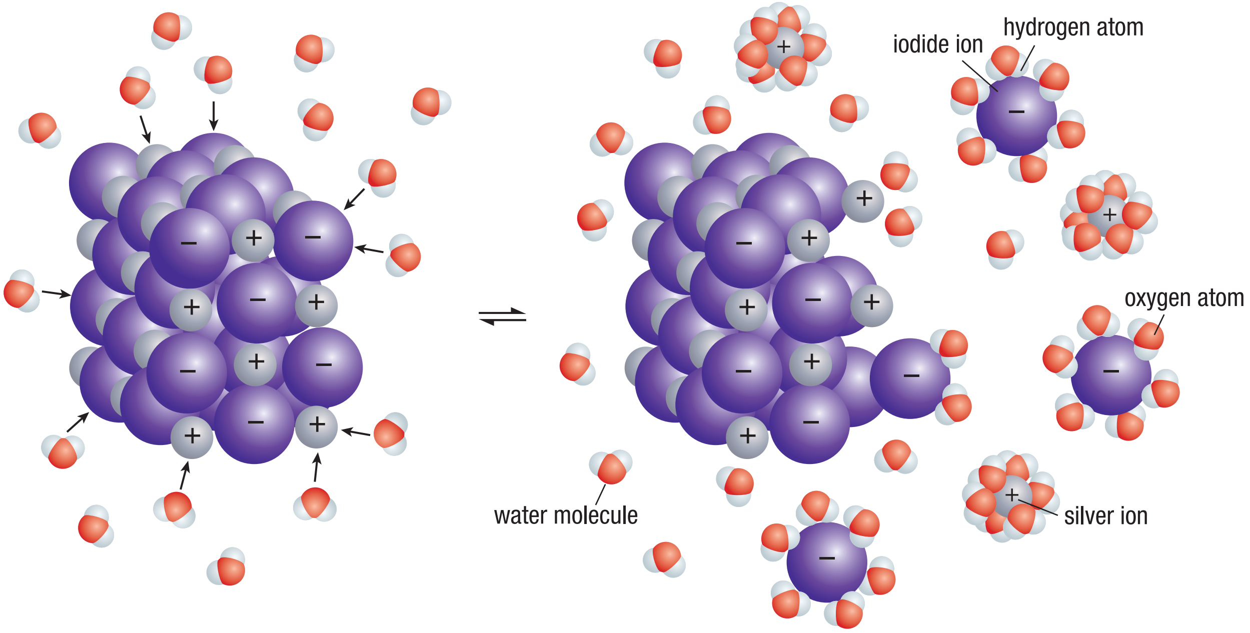


Figure 2 When a solid ionic compound, such as silver iodide, dissolves in water, ions are removed from the crystal lattice as they become surrounded by water molecules. The reverse reaction also takes place, eventually reaching equilibrium.

How does a dynamic equilibrium form? First, consider the chemical equation for the dissolving of silver iodide in water.

$$AgI(s) \rightarrow Ag^{+}(aq) + I^{-}(aq)$$

Once they have entered into solution, the aqueous silver and iodide ions can collide with each other, which can cause them to re-form solid silver iodide. When this happens, a precipitate will form or existing crystals might become larger. The chemical equation for the precipitation of silver iodide from an aqueous solution is

$$Ag^{+}(aq) + I^{-}(aq) \rightarrow AgI(s)$$

Notice how two opposing processes are occurring in the silver iodide solution: dissolution (dissolving) and precipitation. Eventually, these two opposing processes will reach a dynamic equilibrium. At this point the rate at which ions in the solid silver iodide dissolve is equal to the rate at which aqueous silver and iodide ions precipitate. At equilibrium, the solution is saturated: it contains the maximum quantity of solute at a given temperature and pressure. Therefore, the concentrations of aqueous silver ions and aqueous iodide ions remain constant in a saturated solution. This is an example of a **solubility equilibrium**, which is a dynamic equilibrium between a solute and a solvent that occurs in a saturated solution. It can be represented by this equation:

$$AgI(s) \rightleftharpoons Ag^{+}(aq) + I^{-}(aq)$$

solubility equilibrium a dynamic equilibrium between a solute and a solvent in a saturated solution in a closed system

The Solubility Product Constant (K_{sp})

A solubility equilibrium is a heterogeneous equilibrium system between a solid ionic compound and its ions dissolved in a saturated aqueous solution. The equilibrium law equation for the solubility equilibrium between solid silver iodide and its aqueous ions can be written as

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$K = \frac{[Ag^{+}(aq)][I^{-}(aq)]}{[AgI(s)]}$$

The concentration of silver and iodide ions may vary from one saturated solution to the next at the same temperature. However, the concentration of solid silver iodide remains constant. Therefore, we can ignore the concentration of the solid silver iodide in the equilibrium law equation for the solubility equilibrium. The equilibrium constant equation for silver iodide therefore becomes

$$K_{sp} = [Ag^{+}(aq)][I^{-}(aq)]$$

This equation gives us the **solubility product constant (K_{sp}),** which is the value of the equilibrium law equation for a solubility equilibrium. The subscript “sp” distinguishes this constant from the general equilibrium constant, K. As with K, K_{sp} is calculated using concentrations in mol/L, and K_{sp} values are not given units. A table of solubility product constants is provided in Appendix B4.

The K_{sp} of AgI(s) at 25 °C is 8.5×10^{-17}. Temperature is always included when reporting values for the solubility product constant. K_{sp} values vary with temperature because the solubility of substances varies with temperature. We most commonly talk about the K_{sp} value for substances with low solubilities. However, even highly soluble substances, such as sodium chloride, have K_{sp} values. Therefore, any calculation you can perform for a low-solubility substance you can also perform for a highly soluble substance.

solubility product constant (K_{sp}) the value obtained from the equilibrium law applied to a saturated solution

LEARNING **TIP**

Subscripts for K

The general equilibrium constant, K, is sometimes written as K_c or K_{eq} to distinguish it from other equilibrium constants, such as K_{sp}.

Tutorial 1 Writing Solubility Product Constant Equations and Calculating K_{sp} Values

When writing a solubility product constant equation or calculating the value of a solubility product constant, remember that the concentration of the solid can be ignored because it does not vary in a saturated solution.

Sample Problem 1: Writing a Solubility Product Constant Equation from a Balanced Equation

Write a solubility product constant equation for the solubility equilibrium at 25 °C given by the following balanced equation:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

Solution: Since the concentration of $CaF_2(s)$ is constant, do not include it in the denominator of the equilibrium law equation.

Therefore,

$$K_{sp} = [Ca^{2+}(aq)][F^-(aq)]^2$$

Statement: The solubility product constant equation for the solubility equilibrium is

$$K_{sp} = [Ca^{2+}(aq)][F^-(aq)]^2$$

Sample Problem 2: Writing a Solubility Product Constant Equation from a Chemical Formula

Write the solubility product constant equation for a saturated solution of aluminum sulfate, $Al_2(SO_4)_3(aq)$, at 25 °C.

Solution:

Step 1. Write a balanced equation for the aluminum oxide solution equilibrium.

The saturated solution contains an equilibrium between $Al_2(SO_4)_3(s)$ and the dissolved ions, $Al^{3+}(aq)$ and $SO_4^{2-}(aq)$.

$$Al_2(SO_4)_3(s) \rightleftharpoons 2\,Al^{3+}(aq) + 3\,SO_4^{2-}(aq)$$

Step 2. Write the K_{sp} equation, omitting any solids.

$$K_{sp} = [Al^{3+}(aq)]^2[SO_4^{2-}(aq)]^3$$

Statement: The solubility product constant equation for a saturated solution of $Al_2(SO_4)_3(aq)$ is

$$K_{sp} = [Al^{3+}(aq)]^2[SO_4^{2-}(aq)]^3$$

Sample Problem 3: Calculating the K_{sp} Value from Ion Concentrations

A chemist has a closed vessel containing a chunk of solid zinc hydroxide, $Zn(OH)_2(s)$, surrounded by a saturated solution at 25 °C. He determines the concentrations of aqueous zinc ions, $Zn^{2+}(aq)$, and aqueous hydroxide ions, $OH^-(aq)$, to be 2.7×10^{-6} mol/L and 5.4×10^{-6} mol/L, respectively. Calculate the solubility product constant.

Given: $[Zn^{2+}(aq)] = 2.7 \times 10^{-6}$ mol/L; $[OH^-(aq)] = 5.4 \times 10^{-6}$ mol/L

Required: K_{sp}

Solution:

Step 1. Write the balanced equation for the solution equilibrium.

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2\,OH^-(aq)$$

Step 2. Write the K_{sp} equation for the equilibrium, omitting any solids.

$$K_{sp} = [Zn^{2+}(aq)][OH^-(aq)]^2$$

Step 3. Substitute the given ion concentrations into the K_{sp} equation and solve.

$$\begin{aligned} K_{sp} &= [Zn^{2+}(aq)][OH^-(aq)]^2 \\ &= (2.7 \times 10^{-6})(5.4 \times 10^{-6})^2 \\ K_{sp} &= 7.9 \times 10^{-17} \end{aligned}$$

Statement: The K_{sp} of zinc chloride in a saturated solution at 25 °C is 7.9×10^{-17}.

Practice

1. Write a solubility product constant equation for the following equilibrium: K/U

   $$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$$

2. Write the solubility product constant equation for iron(III) hydroxide, $Fe(OH)_3(s)$. K/U
3. In a saturated solution of calcium phosphate, $Ca_3(PO_4)_2$, at 25 °C, the concentrations of the calcium ions and phosphate ions are 4.53×10^{-7} mol/L and 3.02×10^{-7} mol/L, respectively. Calculate the K_{sp} of calcium phosphate. T/I [ans: $K_{sp} = 8.48 \times 10^{-33}$]

Solubility and the Solubility Product Constant

The solubility of an ionic compound varies with the ions it contains. In general, the more highly charged the anions and cations are, the less soluble the ionic compound will be, because it takes more energy for a solvent to break the ionic bonds in the crystal lattice. Therefore, ionic compounds containing divalent ions, such as calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}), are generally less soluble than ionic compounds containing monovalent ions, such as sodium ions (Na^+) and nitrate ions (NO_3^-).

Keep in mind that the solubility of a given ionic compound is different from its solubility product constant. The solubility of an ionic compound tells us the maximum quantity that will dissolve in a given volume of solvent at a particular temperature to form a saturated solution. For example, the molar solubility of lithium carbonate, $Li_2CO_3(s)$, in water at 25 °C is 1.8×10^{-2} mol/L. Therefore, we could prepare a saturated solution of lithium carbonate by dissolving 1.3 g of solid lithium carbonate in 1000 mL of solution or 0.65 g in 500 mL of solution at 25 °C. Nevertheless, the solubility product constant of lithium carbonate at 25 °C is always 8.2×10^{-4}.

Investigation **7.6.1**

The K_{sp} of Calcium Hydroxide (page 476)

Calcium hydroxide, a compound used in the preparation of plaster and mortar, is only slightly soluble in water. In this investigation, you will prepare several solutions of calcium hydroxide, identify the one that is saturated, and use the concentrations of ions in this solution to determine the K_{sp} of calcium hydroxide.

Tutorial 2 Converting between K_{sp} and Solubility Values

Molar solubility and K_{sp} both describe the solubility of a substance, although in different ways. Therefore, it is possible to calculate the value of one if you know the value of the other.

Sample Problem 1: Calculating K_{sp} from Molar Solubility

A technician places a quantity of solid copper(I) bromide, CuBr(s), in a beaker of distilled water. The measured molar solubility of copper(I) bromide is 2.0×10^{-4} mol/L at 25 °C. Calculate the K_{sp} of copper(I) bromide at 25 °C.

Given: Molar solubility of copper(I) bromide: 2.0×10^{-4} mol/L

Required: K_{sp}

Solution:

Step 1. Write the balanced equation for the solubility equilibrium.

$$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$$

Step 2. Write the solubility product constant equation.

$$K_{sp} = [Cu^+(aq)][Br^-(aq)]$$

Step 3. Determine the equilibrium concentrations of the dissolved ions.

From the balanced equation, you know that the molar ratio is 1:1:1, so the concentrations of these ions are equal at any point in time. Since the solubility of solid copper(I) bromide is 2.0×10^{-4} mol/L, then a maximum of 2.0×10^{-4} mol of solid copper(I) bromide can dissolve in water to produce 1.0 L of solution at 25 °C. This will form 2.0×10^{-4} mol of copper(I) ions and 2.0×10^{-4} mol of bromide ions. Therefore, the equilibrium concentrations of these ions are also equal to 2.0×10^{-4} mol/L.

Step 4. Substitute the equilibrium concentrations into the K_{sp} equation and solve for K_{sp}.

$$\begin{aligned} K_{sp} &= [Cu^+(aq)][Br^-(aq)] \\ &= (2.0 \times 10^{-4})(2.0 \times 10^{-4}) \\ K_{sp} &= 4.0 \times 10^{-8} \end{aligned}$$

Statement: The solubility product constant of copper(I) bromide at 25 °C is 4.0×10^{-8}.

Sample Problem 2: Calculating K_{sp} from Solubility Expressed in Mass per Volume

Calculate the K_{sp} value for bismuth sulfide, $Bi_2S_3(s)$, which has a solubility of 4.68×10^{-14} g/100 mL at 25 °C.

Given: Solubility of Bi_2S_3: 4.68×10^{-14} g/100 mL

Required: K_{sp} of Bi_2S_3

Solution:

Step 1. Write the balanced equation.

$$Bi_2S_3(s) \rightleftharpoons 2\,Bi^{3+}(aq) + 3\,S^{2-}(aq)$$

Step 2. Write the solubility product constant equation.

$$K_{sp} = [Bi^{3+}(aq)]^2[S^{2-}(aq)]^3$$

Step 3. Determine the equilibrium concentrations in mol/L of the dissolved ions. Use an ICE table (**Table 1**). Since the concentration of solid Bi_2S_3 remains constant, it is not included.

Table 1 ICE Table for Calculating Equilibrium Concentrations

	$Bi_2S_3(s)$	$\rightleftharpoons$ $2\ Bi^{3+}(aq)$	+ $3\ S^{2-}(aq)$
I	—	0	0
C	—	$+2x$	$+3x$
E	—	$2x$	$3x$

Step 4. Calculate all concentrations in mol/L.

To convert given mass solubility of solid bismuth sulfide to molar solubility, first calculate the molar mass of bismuth sulfide. Then, use the molar mass to convert mass solubility to molar solubility.

$$\text{molar mass of } Bi_2S_3 = (2)\left(208.98\ \frac{g}{mol}\right) + (3)\left(32.07\ \frac{g}{mol}\right)$$

$$\text{molar mass of } Bi_2S_3 = 514.17\ g/mol$$

$$\text{molar solubility of } Bi_2S_3 = \frac{4.68 \times 10^{-14}\ \cancel{g}}{100\ \cancel{mL}} \times \frac{1\ mol}{514.17\ \cancel{g}} \times \frac{1000\ \cancel{mL}}{1\ L}$$

$$\text{molar solubility of } Bi_2S_3 = 9.10 \times 10^{-16}\ mol/L$$

Step 5. Write the K_{sp} equation using the expressions in the ICE table, and then substitute the molar solubility of solid bismuth sulfide for x.

$$\begin{aligned} K_{sp} &= [Bi^{3+}(aq)]^2[S^{2-}(aq)]^3 \\ &= (2x)^2(3x)^3 \\ &= 2^2 3^3 x^5 \\ &= 108(9.10 \times 10^{-16})^5 \\ K_{sp} &= 6.74 \times 10^{-74} \end{aligned}$$

Statement: The solubility product constant of solid bismuth sulfide is 6.74×10^{-74}.

Sample Problem 3: Calculating Molar Solubility from K_{sp}

The solubility product constant of solid copper(II) iodate, $Cu(IO_3)_2(s)$, is 6.9×10^{-8} at 25 °C. Calculate the molar solubility of solid copper(II) iodate at 25 °C.

Given: K_{sp} of $Cu(IO_3)_2(s) = 6.9 \times 10^{-8}$

Required: molar solubility of $Cu(IO_3)_2(s)$ at 25 °C

Solution:

Step 1. Write the balanced chemical equation.

$$Cu(IO_3)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\ IO_3^-(aq)$$

Step 2. Write the solubility product constant equation.

$$K_{sp} = [Cu^{2+}(aq)][IO_3^-(aq)]^2$$

Step 3. Determine the equilibrium concentrations in mol/L of the dissolved ions.

Use an ICE table (**Table 2**).

Table 2 ICE Table for Calculating Equilibrium Concentrations

	$Cu(IO_3)_2(s)$	$\rightleftharpoons$ $Cu^{2+}(aq)$	+ $2\ IO_3^-(aq)$
I	—	0	0
C	—	$+x$	$+2x$
E	—	x	$2x$

Step 4. Substitute the equilibrium concentration expressions from the ICE table into the K_{sp} equation and solve for x.

$x = 2.5 \times 10^{-3}$

Statement: The molar solubility of copper(II) iodate at 25 °C is 2.5×10^{-3} mol/L.

Practice

1. The solubility of magnesium fluoride, $MgF_2(s)$, is 1.72×10^{-3} g/100 mL at 25 °C. What is the K_{sp} value for magnesium fluoride at 25 °C? T/I [ans: 8.41×10^{-11}]
2. Calculate the molar solubility of silver iodide, $AgI(s)$, at 25 °C. Its K_{sp} value at this temperature is 8.5×10^{-17}. T/I [ans: 9.2×10^{-9} mol/L]
3. The K_{sp} of zinc hydroxide, $Zn(OH)_2(s)$, is 7.7×10^{-17} at 25 °C. What is its molar solubility at this temperature? T/I [ans: 2.7×10^{-6} mol/L]
4. Which has a greater solubility, mercury(I) chloride or copper(I) chloride? (Refer to Table 1 in Appendix B4.) Support your answer with calculations. T/I

Predicting Precipitation

What happens when two aqueous solutions containing dissolved ions are mixed? In some cases, ions will combine and form an ionic compound with low solubility, which then precipitates from the solution. For example, **Figure 3** shows what happens when a solution of potassium chromate, $K_2CrO_4(aq)$, is mixed with a solution of silver nitrate, $AgNO_3(aq)$. The reddish-brown precipitate is silver chromate, $Ag_2CrO_4(s)$. Could we have predicted if a precipitate of silver chromate would form before mixing these solutions? Solubility is a complex property and difficult to predict. The only reliable way to know if an ionic compound is soluble is to do the experiment. Solubility tables, such as **Table 3**, summarize the results of many such experiments.

Figure 3 A yellow solution of potassium chromate, $K_2CrO_4(aq)$, mixes with a colourless solution of silver nitrate, $AgNO_3(aq)$. A reddish-brown precipitate of silver chromate, $Ag_2CrO_4(s)$, forms as the solutions mix.

Table 3 Solubility of Some Ionic Compounds at SATP

	Cations	
Anions	**high solubility ≥ 0.1 mol/L at SATP**	**low solubility < 0.1 mol/L at SATP**
F^-	most	Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Fe^{2+}, $Hg_2{}^{2+}$, Pb^{2+}
Cl^-, Br^-, I^-	most	Ag^+, Pb^{2+}, Tl^+, $Hg_2{}^{2+}$, Hg^+, Cu^+
S^{2-}	Group 1, Group 2, $NH_4{}^+$	most
OH^-	Group 1, $NH_4{}^+$, Sr^{2+}, Ba^{2+}, Tl^+	most
$SO_4{}^{2-}$	most	Ag^+, Pb^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Ra^{2+}
$CO_3{}^{2-}$, $PO_4{}^{3-}$, $SO_3{}^{2-}$	Group 1, $NH_4{}^+$	most
$C_2H_3O_2{}^-$	most	Ag^+
$NO_3{}^-$	all	none
$IO_3{}^-$	$NH_4{}^+$, K^+, Na^+	most

It should also come as no surprise that a given cation may be quite soluble when paired with a particular anion, but be insoluble when paired with another. Even though Table 3 does not show all possible ion combinations, we can see important solubility trends and exceptions. For example, only the nitrate ion, $NO_3{}^-$, always forms a soluble compound. All other ions will form a highly soluble compound when combined with some ions but a compound of low solubility when paired with others.

To predict if a precipitate will form when two aqueous solutions are mixed, we can first use a solubility table to predict if any ionic compounds will form that will be of low solubility. For example, suppose you intend to mix an aqueous solution of sodium chloride, $NaCl(aq)$, with an aqueous solution of silver nitrate, $AgNO_3(aq)$. From Table 3, you see that these two ionic compounds are both highly soluble in water. They will dissolve in water according to the following net ionic equations:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$
$$AgNO_3(s) \rightarrow Ag^+(aq) + NO_3{}^-(aq)$$

When you mix these two solutions, the combined solution therefore will contain aqueous sodium ions, chloride ions, silver ions, and nitrate ions. Table 3 shows that sodium chloride and all salts containing the nitrate ion are highly soluble in water. Therefore, dissolved sodium ions will not react with dissolved nitrate ions to produce a solid sodium nitrate precipitate. Silver chloride, however, has a low solubility in water. Therefore, when you mix sodium chloride solution and silver nitrate solution, a precipitate of silver chloride may form while the sodium and nitrate ions remain in solution (**Figure 4**). Whether a precipitate actually forms depends on the concentrations of the silver ions and the chloride ions in the solution.

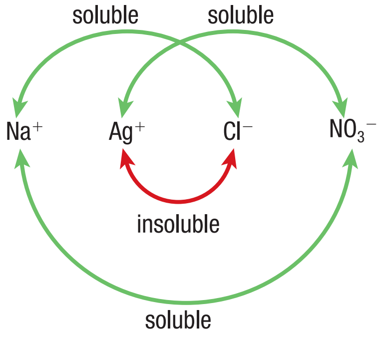


Figure 4 In a solution containing aqueous sodium, silver, chloride, and nitrate ions, only the combination of silver and chloride ions is likely to form a precipitate.

When we know the concentrations of ions in aqueous solution, we can use a quantitative method to predict whether a precipitate will form. The **trial ion product (Q)** is the reaction quotient applied to the initial ion concentrations of a slightly soluble ionic compound. We get a value for the trial ion product by multiplying the concentrations of ions in a specific solution raised to powers equal to their coefficients in a balanced chemical equation. For example, the dissolution equilibrium system of solid calcium fluoride, $CaF_2(s)$, is represented by the following balanced equation:

trial ion product (Q) the product of the concentrations of ions in a specific solution raised to powers equal to their coefficients in the balanced chemical equation; can be used to predict the formation of a precipitate

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

Note that we always write the equilibrium reaction equation so that the dissolution reaction occurs to the right. The trial ion product equation for the dissolution of solid calcium fluoride is

$$Q = [Ca^{2+}(aq)][F^-(aq)]^2$$

If we add a solution containing $Ca^{2+}(aq)$ ions to a solution containing $F^-(aq)$ ions, whether a precipitate will form depends on the concentrations of these ions in the combined solution. To calculate the trial ion product, we substitute the initial concentrations of $Ca^{2+}(aq)$ and $F^-(aq)$ ions into the trial ion product equation. Then, we compare the value of the trial ion product, Q, with the solubility product constant, K_{sp}. The following rules are used to predict whether precipitation will occur:

- If Q is greater than K_{sp}, the dissolution equilibrium system shifts to the left. Precipitation occurs and will continue until the solution reaches a new equilibrium.
- If Q is less than K_{sp}, the dissolution equilibrium system will shift to the right, and no precipitation occurs. The solution is unsaturated, so more solid can dissolve.
- If Q is equal to K_{sp}, the solution is at equilibrium. No precipitation or overall change in concentration will occur.

UNIT TASK **BOOKMARK**

How could you use information about predicting whether a precipitate will form as you work on the Unit Task on page 582?

Tutorial 3 Predicting whether a Precipitate Will Form

You can use a solubility table, such as Table 3, as a qualitative tool to predict if a precipitate is likely to form when aqueous solutions of ions are mixed. Comparing the trial ion product with the solubility product constant allows you to predict quantitatively if a precipitate will form when solutions of known concentrations of ions are mixed.

Sample Problem 1: Predicting Precipitation when Mixing Aqueous Solutions

A student is planning to combine a 1.0×10^{-3} mol/L aqueous solution of silver nitrate, $AgNO_3(aq)$, with a 5.0×10^{-3} mol/L aqueous solution of potassium bromide, $KBr(aq)$ at 25 °C. Will a precipitate form when the solutions are mixed? If so, identify the precipitate.

Given: $[AgNO_3(aq)] = 1.0 \times 10^{-3}$ mol/L; $[KBr(aq)] = 5.0 \times 10^{-3}$ mol/L

Required: To predict if a precipitate will form and identify any predicted precipitate

Solution:

Step 1. Identify all of the ions that will be present in the mixture.

$AgNO_3(aq)$ will contribute aqueous ions of silver, $Ag^+(aq)$, and nitrate, $NO_3^-(aq)$.

$KBr(aq)$ will contribute aqueous ions of potassium, $K^+(aq)$, and bromide, $Br^-(aq)$.

All four ions will be in the mixture: $Ag^+(aq)$, $NO_3^-(aq)$, $K^+(aq)$, and $Br^-(aq)$.

Step 2. Use the solubility rules in Table 3 to predict if a precipitate may form.

Table 3 indicates that $KNO_3(s)$ is highly soluble and that AgBr(s) has low solubility. Therefore, a precipitate of solid silver bromide, AgBr(s), may form.

Step 3. Determine the concentrations of the ions that may react to form a precipitate.

First, write the balanced dissolution equations for $AgNO_3(s)$ and KBr(s):

$AgNO_3(s) \rightarrow Ag^+(aq) + NO_3{}^-(aq)$

$KBr(s) \rightarrow K^+(aq) + Br^-(aq)$

From these balanced equations, you can see that both dissolution reactions have a 1:1:1 molar ratio. Therefore, you know that the concentrations of both ions are equal to the given concentrations of the ionic compounds. Therefore,

$[Ag^+(aq)] = [AgNO_3(aq)]$

$[Ag^+(aq)] = 1.0 \times 10^{-3}$ mol/L

and

$[Br^-(aq)] = [KBr(aq)]$

$[Br^-(aq)] = 5.0 \times 10^{-3}$ mol/L

Step 4. Determine the trial ion product equation of the precipitate that may form.

You have determined that AgBr(s) may precipitate. First, write a balanced equation for the dissolution equilibrium system of AgBr(s).

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

Remember that you must write the balanced equation so that the dissolution reaction occurs to the right. From the balanced equation, the trial ion product equation is

$Q = [Ag^+(aq)][Br^-(aq)]$

Step 5. Calculate Q by substituting the concentrations of the dissolved ions in the mixture into the trial ion product equation.

$$\begin{aligned} Q &= [Ag^+(aq)][Br^-(aq)] \\ &= (1.0 \times 10^{-3}\ \text{mol/L})(5.0 \times 10^{-3}\ \text{mol/L}) \\ Q &= 5.0 \times 10^{-6} \end{aligned}$$

Step 6. Compare the K_{sp} and Q values of the compound that may precipitate, and then predict if the position of this dissolution equilibrium system will shift and whether a precipitate will form.

From Table 1 in Appendix B4,

K_{sp} of AgBr(s) $= 5.4 \times 10^{-13}$

$Q = 5.0 \times 10^{-6}$

Q is greater than K_{sp}, so the dissolution equilibrium system will shift to the left and a precipitate of AgBr(s) will form.

Statement: A precipitate of solid silver bromide, AgBr(s), will form when the two solutions are mixed.

Sample Problem 2: Predicting Precipitation when Mixing Aqueous Solutions

A student mixes 750.0 mL of an aqueous solution of magnesium nitrate, $Mg(NO_3)_2(aq)$, with 300.0 mL of ammonium hydroxide, $NH_4OH(aq)$. The concentration of the initial magnesium nitrate solution is 4.00×10^{-3} mol/L and of the initial ammonium hydroxide solution is 2.00×10^{-2} mol/L. Will a precipitate form? If so, identify the precipitate.

Given: $V_{Mg(NO_3)_2} = 750.0$ mL; $[Mg(NO_3)_2(aq)] = 4.00 \times 10^{-3}$ mol/L; $V_{NH_4OH} = 300.0$ mL; $[NH_4OH(aq)] = 2.00 \times 10^{-2}$ mol/L

Required: Predict if a precipitate will form and identify any predicted precipitate.

Solution:

Step 1. Identify all of the ions in the solution before any reaction occurs.

The initial $Mg(NO_3)_2(aq)$ solution and initial $NH_4OH(aq)$ solution will contribute these four ions to the mixture: $Mg^{2+}(aq)$, $NO_3{}^-(aq)$, $NH_4{}^+(aq)$, and $OH^-(aq)$.

Step 2. Use the solubility rules in Table 3 to predict if a precipitate may form.

Table 3 indicates that solid ammonium nitrate, $NH_4NO_3(s)$, is highly soluble and that solid magnesium hydroxide, $Mg(OH)_2(s)$, has low solubility. Therefore, a precipitate of $Mg(OH)_2(s)$ may form when the two initial solutions are mixed.

Step 3. Determine the concentrations of the ions that may react to form a precipitate.

$Mg(NO_3)_2(s) \rightarrow Mg^{2+}(aq) + 2\ NO_3{}^-(aq)$

$NH_4OH(s) \rightarrow NH_4{}^+(aq) + OH^-(aq)$

Since each dissolution reaction has a 1:1 mole ratio, the initial concentrations of both ions are the same as the given concentrations of the respective ionic compound. Therefore,

$[Mg^{2+}(aq)]_{initial} = 4.00 \times 10^{-3}$ mol/L

$[OH^-(aq)]_{initial} = 2.00 \times 10^{-2}$ mol/L

These concentrations are the concentration of $Mg^{2+}(aq)$ ions in the initial $Mg(NO_3)_2(aq)$ solution and the concentration of $OH^-(aq)$ in the initial $NH_4OH(aq)$ solution *before* these solutions are mixed. When the initial solutions are mixed, the volume of the final mixture, V_f, increases and is the sum of the volumes of the two initial solutions.

$$V_f = V_{Mg(NO_3)_2} + V_{NH_4OH}$$
$$= 750.0 \text{ mL} + 300.0 \text{ mL}$$
$$V_f = 1050.0 \text{ mL}$$

The increase in volume reduces the concentration of the ions. Use the dilution formula to calculate the concentrations of $Mg^{2+}(aq)$ and $OH^-(aq)$ in the final mixture.

$$c_c V_c = c_d V_d$$
$$c_d = \frac{c_c V_c}{V_d}$$

where c_c is the initial, concentrated, ion concentration and c_d is the final, more dilute, ion concentration. V_c and V_d are the corresponding volumes.

Substitute the appropriate values for $Mg^{2+}(aq)$ into the dilution equation.

$$[Mg^{2+}(aq)]_{final} = (4.00 \times 10^{-3} \text{ mol/L})\left(\frac{750.0 \cancel{\text{mL}}}{1050 \cancel{\text{mL}}}\right)$$
$$[Mg^{2+}(aq)]_{final} = 2.86 \times 10^{-3} \text{ mol/L}$$

Then, substitute the appropriate values for $OH^-(aq)$ into the dilution equation.

$$[OH^-(aq)]_{final} = (2.00 \times 10^{-2} \text{ mol/L})\left(\frac{300.0 \cancel{\text{mL}}}{1050 \cancel{\text{mL}}}\right)$$
$$[OH^-(aq)]_{final} = 5.71 \times 10^{-3} \text{ mol/L}$$

Step 4. Determine the trial ion product equation of the precipitate that may form.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)$$
$$Q = [Mg^{2+}(aq)][OH^-(aq)]^2$$

Step 5. Calculate Q.

$$Q = [Mg^{2+}(aq)_{final}][OH^-(aq)_{final}]^2$$
$$= (2.86 \times 10^{-3})(5.71 \times 10^{-3})^2$$
$$Q = 9.32 \times 10^{-8}$$

Step 6. Compare the K_{sp} and Q values of the compound that may precipitate, and then predict if the position of this dissolution equilibrium system will shift and whether a precipitate will form.

From the Table 1 in Appendix B4,

K_{sp} of $Mg(OH)_2 = 5.6 \times 10^{-12}$

$Q = 9.32 \times 10^{-8}$

Since Q is greater than K_{sp}, the dissolution equilibrium system shifts to the left and precipitation occurs.

Statement: A precipitate of $Mg(OH)_2(s)$ will form when these solutions are mixed.

Practice

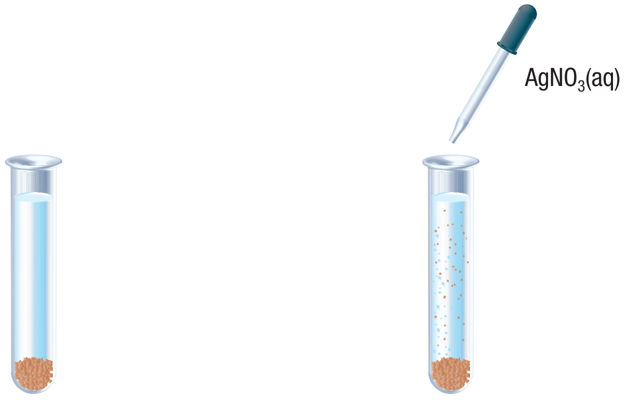
1. Will a precipitate form in an aqueous solution in which the concentration of copper(I) nitrate, $CuNO_3(aq)$, is 0.015 mol/L and the concentration of potassium iodide, KI(aq), is 0.075 mol/L? Explain. T/I
2. A scientist mixes 100.0 mL of a 0.0500 mol/L aqueous solution of lead(II) nitrate, $Pb(NO_3)_2(aq)$, with 200.0 mL of a 0.100 mol/L aqueous solution of sodium iodide, NaI(aq). Will solid lead(II) iodide, $PbI_2(s)$, precipitate? Explain your answer. T/I
3. Predict whether a calcium hydroxide precipitate, $Ca(OH)_2(s)$, will form when 250.0 mL of a 0.0025 mol/L aqueous solution of calcium chloride, $CaCl_2$, is mixed with 300.0 mL of a 0.0015 mol/L aqueous potassium hydroxide solution. Explain your reasoning. T/I
4. Will a precipitate form if a student mixes 100.0 mL of an aqueous solution of 0.100 mol/L calcium chloride, $CaCl_2(aq)$, with 100.0 mL of an aqueous solution of 0.0400 mol/L sodium sulfate, $Na_2SO_4(aq)$? If so, identify the precipitate. T/I

The Common Ion Effect

The position of a solubility equilibrium system can be shifted by changing the temperature, the concentration of the dissolved ions, or both. Now that we can predict if a given set of ion concentrations will produce a precipitate or stay dissolved in solution, we are ready to investigate how we can influence a dissolution equilibrium system. How can a chemist shift a dissolution equilibrium system to favour more precipitate (reactants) or more dissolved ions (products)? A dissolution equilibrium system is just a specific type of a chemical equilibrium, so all the techniques that shift general reaction equilibrium systems can be applied to dissolution equilibrium systems. Consider a saturated solution of silver chromate, $Ag_2CrO_4(aq)$, in equilibrium with a small quantity of undissolved silver chromate, $Ag_2CrO_4(s)$.

$$Ag_2CrO_4(s) \rightleftharpoons 2\ Ag^+(aq) + CrO_4^{2-}(aq)$$

We may use Le Châtelier's principle to predict what will happen if we add a few drops of silver nitrate solution, $AgNO_3(aq)$, to the equilibrium mixture. Silver nitrate solution contains silver ions, $Ag^+(aq)$, and nitrate ions, $NO_3^-(aq)$. Since they are not part of the equilibrium system, the nitrate ions will not affect the equilibrium position. However, the additional silver ions will increase the concentration of silver ions in solution (a product) and shift the equilibrium to the left, toward the reactant. This leftward equilibrium shift may cause solid silver chromate, $Ag_2CrO_4(s)$, to precipitate (**Figure 5**). A precipitate will form only if the new concentrations of aqueous silver ions and chromate ions push the equilibrium system past the solubility limit represented by the solubility product constant, K_{sp}. We can determine if this will happen by comparing the trial ion product, Q, with the solubility product constant. WEB LINK



(a) $Ag_2CrO_4(s) \rightleftharpoons 2\ Ag^+(aq) + CrO_4^{2-}(aq)$ **(b)** $Ag_2CrO_4(s) \xleftarrow{\text{shift}} 2\ Ag^+(aq) + CrO_4^{2-}(aq)$

Figure 5 The common ion effect. (a) A solution of silver chromate is in equilibrium with solid silver chromate. (b) When silver nitrate is added to the solution, the extra silver ion shifts the equilibrium to the left, causing more silver chromate to precipitate.

In this example, the equilibrium shifted to the left because the saturated silver chromate solution and the silver nitrate solution both contained aqueous silver ions. We could expect a similar result if we added a solution that contained chromate ions, $CrO_4^{2-}(aq)$. In general, we can predict that adding a solution that contains a common ion will shift a dissolution equilibrium system toward the solid and may cause some of the ions to precipitate from solution. Lowering the solubility of an ionic compound by the addition of a common ion is called the **common ion effect**.

The common ion effect does not occur only in solutions of substances with low solubility. Highly soluble substances also demonstrate the common ion effect. For example, if you added hydrochloric acid to a saturated solution of sodium chloride, a sodium chloride precipitate might form.

common ion effect a reduction in the solubility of an ionic compound due to the presence of a common ion in solution

Tutorial 4 Calculating the Effect of Common Ions

The amount of an ionic compound that can dissolve in a solution decreases if mixed with a second solution that contains a common ion. You can calculate this effect quantitatively by using the molar solubility values and the solubility product constant, K_{sp}.

Sample Problem 1: Calculating the Molar Solubility of Solid Calcium Fluoride

Calculate the molar solubility of solid calcium fluoride, $CaF_2(s)$, in a 0.025 mol/L solution of sodium fluoride, $NaF(aq)$, at 25 °C. That is, determine the maximum amount of solid calcium fluoride that will dissolve into the aqueous sodium fluoride solution, noting that the two solutions have a common ion.

Solution:

Step 1. Identify the common ion.

The ion present in both $CaF_2(s)$ and NaF(s) is the fluoride ion, $F^-(aq)$.

Step 2. Determine the concentration in mol/L of the common ion in solution before any solid is dissolved.

You need to find the concentration of $F^-(aq)$ in the NaF(aq) solution before $CaF_2(s)$ was added. Table 3 indicates that NaF(s) has high solubility and dissolves completely in water to form $Na^+(aq)$ and $F^-(aq)$ ions.

$$NaF(s) \rightarrow Na^+(aq) + F^-(aq)$$

Since the ions dissolve in a 1:1 molar ratio, the concentrations of sodium and fluoride ions are equal to the concentration of the NaF(aq) solution.

$[Na^+(aq)] = 0.025$ mol/L

$[F^-(aq)] = 0.025$ mol/L

Step 3. Determine the concentration in mol/L of the common ion once the solid has dissolved.

Table 3 indicates that $CaF_2(s)$ has a low solubility in water at 25 °C. Therefore, it will establish a dynamic equilibrium in solution.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

If the $CaF_2(s)$ were dissolving in pure water, you could calculate molar solubility the same way you did in Tutorial 2. However, the $CaF_2(s)$ is being dissolved in solution that already contains some $F^-(aq)$ ions. Therefore, the $CaF_2(s)$ equilibrium will shift to the left relative to its position in pure water and so you should expect less $CaF_2(s)$ to dissolve in the NaF(aq) solution than in pure water. The final concentration of $F^-(aq)$ ions will be equal to the initial concentration (0.025 mol/L) plus the change in concentration caused by adding $CaF_2(s)$ to the solution. **Table 4** is an ICE table summarizing these changes.

Table 4 ICE Table for Calculating Equilibrium Concentrations

	$CaF_2(s)$	$\rightleftharpoons$	**$Ca^{2+}(aq)$**	+	**$2\,F^-(aq)$**
I	—		0		0.025
C	—		$+x$		$+2x$
E	—		x		$0.025 + 2x$

Step 4. Write the equation for the solubility product, K_{sp}, and substitute in the value of K_{sp} for $CaF_2(s)$ from Table 1 in Appendix B4, and the equilibrium concentration expressions from the ICE table. Solve for x.

$$\begin{aligned} K_{sp} &= [Ca^{2+}(aq)][F^-(aq)]^2 \\ 4.0 \times 10^{-11} &= (x)(0.025 + 2x)^2 \\ x &= \frac{4.0 \times 10^{-11}}{(0.025 + 2x)^2} \end{aligned}$$

Since $CaF_2(s)$ has a very low solubility, the amount of $F^-(aq)$ ions that the $CaF_2(s)$ will add to the solution will be very small compared to the 0.025 mol/L provided by the NaF(aq) solution. You can therefore make the simplifying assumption that $0.025 + 2x \approx 0.025$.

$$\begin{aligned} x &\approx \frac{4.0 \times 10^{-11}}{(0.025)^2} \\ &\approx \frac{4.0 \times 10^{-11}}{6.25 \times 10^{-4}} \\ x &\approx 6.4 \times 10^{-8}\ \text{mol/L} \end{aligned}$$

Since x represents the amount of calcium ions that can dissolve in this equilibrium system and there is a 1:1 ratio of calcium ions to solid calcium fluoride, then x is also the solubility of $CaF_2(s)$. Since this value is nearly 5 orders of magnitude smaller than the initial concentration of $F^-(aq)$, you know the simplifying assumption was warranted.

Statement: The molar solubility of calcium fluoride in this solution is 6.4×10^{-8} mol/L.

Practice

1. Make a prediction about the solubility of silver acetate in each of the following: pure water, 0.001 mol/L of silver nitrate, 0.01 mol/L of silver nitrate, 0.001 mol/L of sodium acetate, and 0.01 mol/L of sodium nitrate. Explain your reasoning. T/I
2. The K_{sp} of solid silver chloride, AgCl(s), is 1.8×10^{-10} at 25 °C. T/I A
   (a) What is the molar solubility of solid silver chloride in pure water? [ans: 1.3×10^{-5} mol/L]
   (b) What is the molar solubility of solid silver chloride in a 0.10 mol/L aqueous solution of sodium chloride? [ans: 1.8×10^{-9} mol/L]
   (c) Compare your answers to (a) and (b) and determine if they make sense. Explain.
3. What amount of solid lead (II) chloride, $PbCl_2(s)$, can dissolve in 1.00 L of a 0.200 mol/L aqueous solution of lithium chloride, LiCl(aq)? T/I [ans: 3.0×10^{-4} mol]

7.6 Review

Summary

- A solubility equilibrium is a heterogeneous equilibrium system between a solid ionic compound and its ions dissolved in a saturated aqueous solution.
- The solubility product constant, K_{sp}, is the value of the equilibrium law equation for a solubility equilibrium and does not include the concentration of the solid. K_{sp} varies with temperature and the nature of the ionic solid.
- The trial ion product, Q, is the reaction quotient applied to the ion concentrations of a slightly soluble ionic compound.
- The common ion effect explains why the solubility of an ionic compound may decrease when a common ion is added to the equilibrium system.

Questions

1. What is the difference between molar solubility and the product solubility constant, K_{sp}? K/U
2. What is a common ion? How does its presence affect solubility? Why? K/U
3. (a) Show the balanced equation for the solubility equilibrium that would occur when a solution of barium nitrate, $Ba(NO_3)_2(aq)$, is mixed with a solution of sodium sulfate, $Na_2SO_4(aq)$.
   (b) Write the solubility product constant equation for this equilibrium system. K/U
4. Which is less soluble in water, solid silver chloride, $AgCl(s)$, with a solubility product constant, K_{sp}, of 1.8×10^{-10}, or solid silver bromide, $AgBr(s)$, with a K_{sp} of 5.0×10^{-13}? Explain. K/U
5. Calculate the solubility product constant at 25 °C for silver iodide, $AgI(s)$, given that its solubility at this temperature is 2.14×10^{-7} g/100 mL. T/I
6. Calculate the molar solubility of solid zinc hydroxide, $Zn(OH)_2(s)$, at 25 °C, using the K_{sp} value given in Appendix B4. T/I
7. A student prepares a solution containing 0.01 mol/L calcium nitrate, $Ca(NO_3)_2(aq)$, and 0.025 mol/L sodium phosphate, $Na_3PO_4(aq)$. Will a precipitate form when the student makes this solution? If so, identify the precipitate. T/I
8. A chemist adds 100.0 mL of 4.0×10^{-4} mol/L magnesium nitrate, $Mg(NO_3)_2(aq)$, solution to 100.0 mL of 2.0×10^{-3} mol/L sodium hydroxide, $NaOH(aq)$, solution. Will a precipitate form? Justify your answer. T/I
9. Calculate the molar solubility of solid silver chromate, $Ag_2CrO_4(s)$, in 0.10 mol/L sodium chromate, $Na_2CrO_4(aq)$. T/I
10. Describe the relationship between the solubility product constant, K_{sp}, and the trial ion product, Q. T/I
11. A water treatment plant tests the water and determines that there are high levels of phosphate in the water.
    (a) What are two solutions that could be used to precipitate out the phosphate from the water? A
    (b) Use Le Châtelier's principle to explain how adding these solutions causes a decrease in the phosphate ion concentration. K/U T/I
12. The formation of stalactites and stalagmites in limestone caves (**Figure 6**) is an example of solubility equilibrium in the natural environment. Investigate the formation of stalactites and stalagmites in terms of solubility equilibrium and K_{sp}. Write a short essay to summarize your findings. C A

WEB LINK

Figure 6 Cueva del Vienta in the Guajataca Forest Reserve, Puerto Rico

Investigation 7.1.1 CONTROLLED EXPERIMENT

The Extent of a Chemical Reaction

Solid calcium sulfate, $CaSO_4(s)$, a component of plaster of Paris, is only slightly soluble in water. When solutions of calcium chloride, $CaCl_2(aq)$, and sodium sulfate, $Na_2SO_4(aq)$, are mixed together, they react to form a precipitate of calcium sulfate. In this investigation, you will explore the extent of this chemical reaction by observing if any reactant remains in the final reaction mixture. You will then analyze your observations to decide whether the chemical reaction went to completion or formed an equilibrium system.

Testable Question

In the precipitation reaction between aqueous sodium sulfate, $Na_2SO_4(aq)$, and aqueous calcium chloride, $CaCl_2(aq)$, will all the reactants be converted to products?

Hypothesis

Predict whether any of the aqueous sodium sulfate and aqueous calcium chloride will remain once calcium sulfate stops precipitating from solution. Give a hypothesis to explain your prediction.

Variables

Identify the independent (manipulated) variable and the dependent (responding) variable(s).

Experimental Design

Different volumes of sodium sulfate solution will be added to a solution of calcium chloride and allowed to react. The amounts of sodium sulfate added will be less than, equal to, and more than the stoichiometric amount needed to react completely with the amount of calcium chloride present. The resulting solutions will be filtered. The filtrates will be tested with barium nitrate and with sodium carbonate. If sulfate is present in a filtrate, a precipitate will form when a solution containing barium ions is added. If calcium ions are present in the filtrate, a precipitate will form when a solution containing sodium ions is added.

Equipment and Materials

SKILLS HANDBOOK A1.1, A1.2

- lab apron
- chemical safety goggles
- 250 mL or 100 mL beakers
- 2 small test tubes
- 10 mL or 25 mL graduated cylinder

SKILLS MENU

• Questioning	• Planning	• Analyzing
• Researching	• Controlling Variables	• Evaluating
• Hypothesizing	• Performing	• Communicating
• Predicting	• Observing	

- filtration apparatus
- wash bottle with distilled water
- stirring rod
- filter paper
- 25 mL calcium chloride, $CaCl_2(aq)$ (0.50 mol/L)
- 25 mL sodium sulfate, $Na_2SO_4(aq)$ (0.50 mol/L)
- dropper bottles containing
  - 1.0 mol/L $Na_2CO_3(aq)$
  - saturated solution of $Ba(NO_3)_2(aq)$

Barium compounds are toxic. Solutions containing barium should be collected in a marked disposal container at the end of the investigation. Wash your hands before leaving the laboratory.

Procedure

SKILLS HANDBOOK A2.1, A3.4

1. Write a procedure for performing several trials of the reaction between aqueous sodium sulfate and aqueous calcium chloride. For each trial, calculate the volume of each solution needed so that at least one trial has excess sulfate ions, one has excess calcium ions, and one has the reactants in stoichiometrically equivalent amounts. Describe how to filter the reaction, using an apparatus similar to that in **Figure 1**. Include steps for testing the filtrates for excess ions, recording the results of each trial, and any safety procedures.

Figure 1 Insoluble substances are trapped in the filter paper.

2. Obtain your teacher's approval, then carry out the investigation.

Analyze and Evaluate

(a) Answer the testable question. T/I

(b) Sulfate ions will react with $Ba(NO_3)_2(aq)$ and form a precipitate according to the equation

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Explain what you observed when you added a few drops of $Ba(NO_3)_2(aq)$ to the filtrate, using the chemical names of the reactants and products. T/I

(c) Calcium ions will react with $Na_2CO_3(aq)$ and form a precipitate according to the equation

$$Ca^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow CaCO_3(s)$$

Explain what you observed when you added a few drops of $Na_2CO_3(aq)$ to the filtrate, using the chemical names of the reactants and products. T/I

(d) Did your evidence support or refute your prediction? Explain. T/I

Apply and Extend

(e) How could you determine if the concentrations of the initial reactants affect the formation of a precipitate? T/I

Investigation 7.2.1 ACTIVITY

The Equilibrium Law

The equilibrium law equation was developed from careful measurements of concentrations of reactants and products, which were then tested against mathematical models to see which best reproduced the data. In this activity, you will be given data from a chemical equilibrium system to test against various mathematical models. The balanced chemical equation for the chemical equilibrium is

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

In this chemical equilibrium system, the reactants and products have very different colours (**Figure 1**).

Figure 1 Potassium thiocyanate solution is clear and colourless. When added to a yellow solution of iron(III) nitrate, a deep brownish-red colour is produced, indicating the formation of iron(III) thiocyanate ions. This makes changes in the concentrations of the reactants and products easy to measure with simple equipment.

Purpose

To test various mathematical relationships to see which gives a constant value for all five trials of experimental data

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Procedure

SKILLS HANDBOOK A2.1, A6

Using the data in **Table 1**, test the following mathematical relationships to see which gives a constant value for all five trials (within an experimental error of 5 %):

1. $[Fe^{3+}(aq)][SCN^{-}(aq)][FeSCN^{2+}(aq)]$
2. $[Fe^{3+}(aq)] + [SCN^{-}(aq)] + [FeSCN^{2+}(aq)]$
3. $\dfrac{[FeSCN^{2+}(aq)]}{[Fe^{3+}(aq)][SCN^{-}(aq)]}$
4. $\dfrac{[Fe^{3+}(aq)]}{[FeSCN^{2+}(aq)]}$
5. $\dfrac{[SCN^{-}(aq)]}{[FeSCN^{2+}(aq)]}$

Table 1 Iron(III) Thiocyanate Equilibrium at SATP

Trial	$[Fe^{3+}(aq)]$ (mol/L)	$[SCN^{-}(aq)]$ (mol/L)	$[FeSCN^{2+}(aq)]$ (mol/L)
1	3.91×10^{-2}	8.02×10^{-5}	9.22×10^{-4}
2	1.48×10^{-2}	1.91×10^{-4}	8.28×10^{-4}
3	6.27×10^{-3}	3.65×10^{-4}	6.58×10^{-4}
4	2.22×10^{-3}	5.41×10^{-4}	3.55×10^{-4}
5	1.78×10^{-3}	6.13×10^{-4}	3.23×10^{-4}

Analyze and Evaluate

(a) In a sentence, describe the mathematical relationship you found to be the best fit for the data. T/I

Apply and Extend

(b) In trial 6, the concentration of iron(III) ions is 2.10×10^{-2} and of thiocyanate ions is 2.70×10^{-2}. Use the mathematical relationship you found in question (a) to calculate the concentration of iron(III) thiocyanate ions in this trial. (Hint: Use an average of your calculated constant value.) T/I

(c) Predict the intensity of the colour of the solution in trial 6 (see question (b)) relative to the colour of the solutions in trials 1 to 5. Justify your prediction. T/I

Investigation 7.4.1 CONTROLLED EXPERIMENT

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Testing Le Châtelier's Principle

Le Châtelier's principle helps chemists predict how equilibrium reactions will respond to changes in temperature, pressure, or concentrations. In this investigation, you will predict and then observe the response of a variety of chemical equilibrium systems to chemical and physical changes.

Testable Question

Can Le Châtelier's principle correctly predict the shift in chemical equilibrium caused by changes in concentration, temperature, and pressure?

Hypothesis

Based on the chemical equation for each part of this investigation, write a prediction of how the disturbance that you will be carrying out is likely to affect each of the equilibrium systems. Using Le Châtelier's principle, state the hypothesis on which you based each of your predictions.

Variables

Identify the independent and dependent variables for the equilibrium system in each part of the investigation.

Experimental Design

Changes will be applied to the following four chemical equilibrium systems and evidence gathered to test the predictions made based on Le Châtelier's principle. Control samples will be used in all cases.

Part A: Carbon Dioxide–Carbonic Acid Equilibrium

$$\mathrm{CO_2(g) + H_2O \rightleftharpoons H^+(aq) + HCO_3^-(aq)}$$

You will place a premixed $\mathrm{CO_2(g)}$–$\mathrm{HCO_3^-(aq)}$ equilibrium mixture under increased pressure.

Part B: Thymol Blue Indicator

$$\mathrm{H_2Tb(aq) \rightleftharpoons H^+(aq) + HTb^-(aq)}$$
$$\mathrm{HTb^- \rightleftharpoons H^+(aq) + Tb^{2-}(aq)}$$

You will add aqueous hydrochloric acid and sodium hydroxide solution to different samples of the equilibrium mixture.

Part C: Copper(II) Complexes

$$\mathrm{[Cu(H_2O)_4]^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 4\,H_2O(l)}$$

You will add aqueous ammonia and hydrochloric acid to samples of the equilibrium mixture.

Part D: Iron(III)–Thiocyanate Equilibrium

$$\mathrm{Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)}$$

You will add aqueous iron(III) nitrate, potassium thiocyanate, and sodium hydroxide to samples of the provided equilibrium mixture.

Equipment and Materials

SKILLS HANDBOOK A1.1, A1.2

- lab apron
- gloves
- chemical safety goggles
- 100 mL beaker
- large waste beaker
- 6 to 12 small test tubes
- test-tube rack
- marker or wax pencil
- 25 mL graduated cylinder

- syringe with needle removed (5 to 50 mL)
- Luer lock or solid rubber stopper that fits syringe end
- distilled water
- crushed ice
- hot-water bath
- dropper bottles containing solutions of:
    - carbon dioxide–bicarbonate equilibrium mixture (pH = 7)
    - bromothymol blue indicator
    - silver nitrate, $AgNO_3(aq)$ (0.2 mol/L)
    - thymol blue indicator
    - hydrochloric acid, $HCl(aq)$ (0.1 mol/L)
    - sodium hydroxide, $NaOH(aq)$ (0.1 mol/L)
    - copper(II) sulfate, $CuSO_4(aq)$ (0.1 mol/L)
    - ammonia, $NH_3(aq)$ (1.0 mol/L)
    - sodium hydroxide, $NaOH(aq)$ (1.0 mol/L)
    - iron(III)–thiocyanate equilibrium mixture
    - iron(III) nitrate, $Fe(NO_3)_3(aq)$ (0.2 mol/L)
    - potassium thiocyanate, $KSCN(aq)$ (0.2 mol/L)

The chemicals may be corrosive, irritating, and/or toxic. Silver nitrate stains the skin and clothing. Avoid skin and eye contact. The sodium hydroxide solution is highly corrosive and could cause blindness. If any chemical gets in your eyes, flush them with cold water for at least 15 min. Wash any spills on skin or clothing immediately with plenty of cool water. Report any spills to your teacher.

Procedure

SKILLS HANDBOOK A2.1, A6.3

Part A: Carbon Dioxide–Carbonic Acid Equilibrium

1. Put on your gloves, lab apron, and safety goggles.
2. Place 2 or 3 drops of bromothymol blue indicator in the carbon dioxide–bicarbonate equilibrium mixture.
3. Draw a sample of the carbon dioxide–bicarbonate equilibrium mixture into the syringe, then block the end with a rubber stopper.
4. Reduce the volume of the sample by slowly depressing the syringe plunger, and record your observations.

Part B: Thymol Blue Indicator

5. With the marker, label two small test tubes A and B.
6. With the 25 mL graduated cylinder, add 5 mL of distilled water to each test tube and then place them in the test-tube rack.
7. Add 1 to 3 drops of thymol blue indicator to the water in each test tube to obtain a noticeable colour.
8. Set test tube A aside as a control.
9. Add drops of hydrochloric acid to test tube B to test for any colour changes. Record your observations.
10. Add drops of 0.1 mol/L sodium hydroxide solution to test tube B to test for any colour changes. Record your observations.

Part C: Copper(II) Complexes

11. Obtain 2 mL copper(II) sulfate solution a small test tube. Place the test tube in the test-tube rack.
12. Add 3 drops of ammonia solution to establish the equilibrium mixture then continue adding more drops until a change is observed. Record your observations.
13. Add drops of hydrochloric acid to the mixture and record your observations.

Part D: Iron(III)–Thiocyanate Equilibrium

14. With the marker, label three small test tubes A, B, and C.
15. Using the 25 mL graduated cylinder, place 5 mL of the iron(III)–thiocyanate equilibrium solution in each test tube and then place the test tubes in the rack.
16. Use test tube A as a control.
17. Add drops of iron(III) nitrate solution to test tube B until a change is evident. Record your observations.
18. Add drops of 1.0 mol/L sodium hydroxide solution to test tube B until a change occurs. (Iron(III) hydroxide has a low solubility.) Record your observations.
19. Add drops of KSCN(aq) to test tube C until a change is evident. Record your observations.
20. Follow your teacher's instructions for disposal of all chemicals.

Analyze and Evaluate

(a) Answer the testable question. T/I

(b) For each of Parts A through D, identify the variables that were measured, recorded and/or manipulated. T/I

(c) Did using Le Châtelier's principle allow you to correctly predict the shift of equilibrium in Parts A through D? Explain. T/I

Apply and Extend

(d) For each of Parts A through D, use the chemical equilibrium reactions provided to explain why the changes imposed on each system produced the results you observed. T/I

Investigation 7.6.1 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

The K_{sp} of Calcium Hydroxide

Calcium hydroxide is an ionic compound that, in solid state, will dissolve slightly in liquid water. The net ionic equation for the dissolution of calcium hydroxide solid in liquid water is

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ OH^-(aq)$$

Calcium oxalate is also an ionic compound. When added to liquid water, solid sodium oxalate will dissociate according to the following net ionic equation:

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4{}^{2-}(aq)$$

Purpose

To determine the solubility product constant, K_{sp}, of solid calcium hydroxide (Part A) and solid calcium oxalate (Part B)

Equipment and Materials

SKILLS HANDBOOK A1.1, A1.2

- lab apron
- chemical safety goggles
- colourless, transparent 12 × 2 spot plate
- 24 transfer pipettes
- distilled water
- dark-coloured paper
- dropper bottles containing
  - calcium nitrate solution, $Ca(NO_3)_2(aq)$ (0.1 mol/L)
  - sodium hydroxide solution, $NaOH(aq)$ (0.1 mol/L)
  - calcium oxalate solution, $CaC_2O_4(aq)$ (0.1 mol/L)

Sodium hydroxide is an irritant. Avoid skin and eye contact. If you spill this substance on your skin, wash the affected area with plenty of cool water and inform your teacher.

Calcium oxalate is toxic if ingested. Do not eat anything in the laboratory, and wash your hands before leaving.

Procedure

SKILLS HANDBOOK A2.1, A6.3

Part A: Determine the K_{sp} of Calcium Hydroxide

1. Put on your lab apron and safety goggles.
2. Place a transparent spot plate on a dark sheet of paper. Ensure that the spot plate is new or very clean.
3. Using a clean transfer pipette, add 5 drops of distilled water to 11 consecutive wells in one row of the spot plate. Leave the first well, A1, empty. See **Figure 1** for well-labelling conventions.
4. With a clean transfer pipette, add 10 drops of calcium nitrate solution to well A1.
5. Draw the solution from A1 into an empty, clean transfer pipette and place 5 drops of the solution into A2. Return the excess solution in the pipette to well A1.

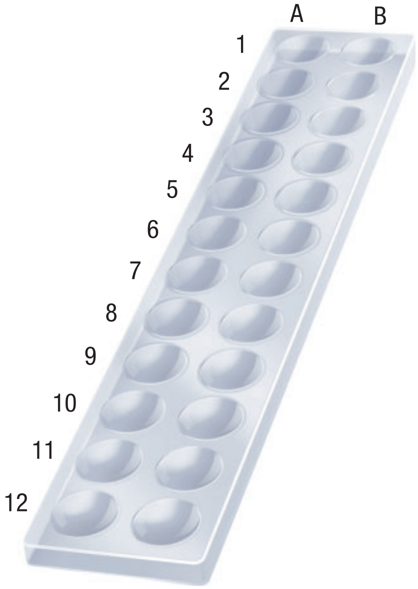


Figure 1 Well labels in a spot plate; your spot plate may have a different number of rows or columns.

6. With another clean transfer pipette, transfer 5 drops of the solution in A2 to the water in A3. Repeat this process for each of the remaining wells, using a clean transfer pipette each time. For A12, discard the 5 drops into the sink, with lots of running water.
7. With another clean transfer pipette, place 5 drops of sodium hydroxide solution to each of wells B1 to B12 on the spot plate.
8. Using a new, clean transfer pipette, transfer the entire contents of well A1 into well B1. Mix the solutions well with the tip of the pipette.
9. Repeat Step 8 for wells A2 into B2 to A12 into B12. Use a new, clean transfer pipette each time.
10. Examine all of the wells. Identify the first well in which there is no apparent precipitate.
11. Dispose of all chemical wastes as instructed by your teacher.

Part B: Determine the K_{sp} of Calcium Oxalate

12. Write a detailed procedure to determine the K_{sp} of calcium oxalate. Include safety precautions and a description of how you will record your observations (e.g., using a spreadsheet).
13. Obtain your teacher's approval, then carry out your procedure.

Observations

Part A:

(a) Prepare a 7-column, 13-row table, using the headings shown on **Table 1**.

(b) Record your observations in the second column of your table.

Part B:

(c) Prepare a 7-column, 13-row table, using the headings shown on **Table 2**.

(d) Record your observations in the second column of your table.

Analyze and Evaluate

SKILLS HANDBOOK A6.3, A6.4

Part A: Determine the K_{sp} of Calcium Hydroxide

(e) Calculate the initial $[Ca^{2+}(aq)]$ in each well of row A of the spot plate. Record the concentrations in the table you created for Part A (**Table 1**). T/I

(f) Calculate the initial $[OH^{-}(aq)]$ in each well of row B of the spot plate. Record the concentrations in the appropriate column of your table. T/I

(g) Determine the final $[Ca^{2+}(aq)]$ and $[OH^{-}(aq)]$ in wells B1 to B12, and record these values in the appropriate column of your table. T/I C A

(h) Calculate the trial ion product for the contents of each well, and record in the appropriate column of your table. Recall that the trial ion product will be the product of the final concentrations you calculated in Step (h). T/I

(i) Write the K_{sp} expression for calcium hydroxide and the calculation that determined its value in this investigation. Based on the experimental value of K_{sp}, write a statement about the solubility of calcium hydroxide. C A

(j) Identify the sources of error and uncertainty in the experimental design of Part A. T/I A

Part B: Determine the K_{sp} of Calcium Oxalate

(k) Use the table you created for Part B (**Table 2**) and answer Questions (e) through (j) based on your results for Part B of the investigation. T/I C A

(l) Evaluate the procedure you developed for Part B. Provide specific examples of how the procedure could be improved. T/I

Apply and Extend

(m) Compare your derived values for the K_{sp} of calcium hydroxide (Part A) and calcium oxalate (Part B) to the accepted values found in a reliable source such as the *CRC Handbook of Chemistry and Physics*. Calculate the percentage difference in each case and comment on the validity of your results.

Table 1 Observations and Calculations for Determining the K_{sp} of $Ca(OH)_2$

Well	Observations	Initial $[Ca^{2+}(aq)]$	Initial $[OH^{-}(aq)]$	Final $[Ca^{2+}(aq)]$	Final $[OH^{-}(aq)]$	Trial ion product
A1						
A2						
A3						
A4						

Table 2 Observations and Calculations for Determining the K_{sp} of CaC_2O_4

Well	Observations	Initial $[Ca^{2+}(aq)]$	Initial $[C_2O_4^{2-}(aq)]$	Final $[Ca^{2+}(aq)]$	Final $[C_2O_4^{2-}(aq)]$	Trial ion product
A1						
A2						
A3						

CHAPTER 7 SUMMARY

Summary Questions

1. Create a study guide based on the points listed in the margin on page 418. For each point, create three or four sub-points that provide further information, relevant examples, explanatory diagrams, or general equations.
2. Look back at the Starting Points questions on page 418. Answer these questions using what you have learned in this chapter. Compare your latest answers with those that you wrote at the beginning of the chapter. Note how your answers have changed.

Vocabulary

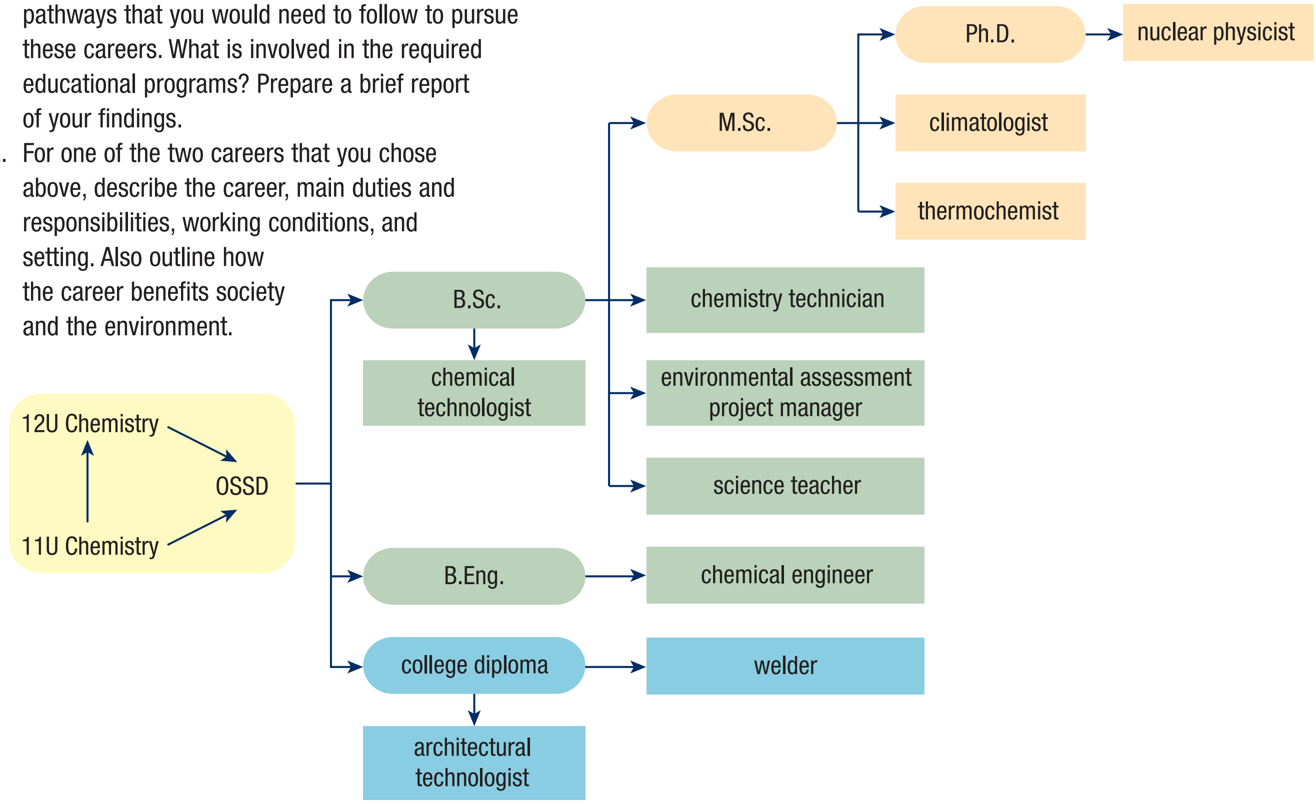
chemical equilibrium (p. 420)
dynamic equilibrium (p. 420)
equilibrium position (p. 421)
reversible reaction (p. 421)
equilibrium law (p. 429)
equilibrium constant (*K*) (p. 429)
homogeneous equilibrium (p. 433)
heterogeneous equilibrium (p. 433)
Le Châtelier's principle (p. 439)
equilibrium shift (p. 439)
ideal gas (p. 443)
partial pressure (p. 443)
reaction quotient (*Q*) (p. 449)
instantaneous concentrations (p. 450)
solubility (p. 460)
solubility equilibrium (p. 461)
solubility product constant (K_{sp}) (p. 461)
trial ion product (*Q*) (p. 466)
common ion effect (p. 469)

CAREER **PATHWAYS**

SKILLS HANDBOOK A7

Grade 12 Chemistry can lead to a wide range of careers. Some require a college diploma or a B.Sc. degree. Others require specialized or postgraduate degrees. This graphic organizer shows a few pathways to careers mentioned in this chapter.

1. Select two careers related to Chemical Equilibrium that you find interesting. Research the educational pathways that you would need to follow to pursue these careers. What is involved in the required educational programs? Prepare a brief report of your findings.
2. For one of the two careers that you chose above, describe the career, main duties and responsibilities, working conditions, and setting. Also outline how the career benefits society and the environment.



CAREER LINK

CHAPTER 7 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. Which of the following indicates that a chemical reaction system has reached equilibrium? (7.1) K/U
   (a) The temperature of the system is decreasing.
   (b) The volume of the system is changing.
   (c) The concentration of reactants is decreasing.
   (d) The concentration of products is constant.
2. Identify the example of a heterogeneous equilibrium. (7.2) K/U
   (a) $H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$
   (b) $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$
   (c) $CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$
   (d) none of the above
3. How did Fritz Haber produce ammonia gas from its elements in economically useful quantities? (7.3) K/U
   (a) He carried out the reaction at decreased pressure.
   (b) He carried out the reaction at decreased temperature.
   (c) He added a catalyst to the reaction system.
   (d) He decreased the reactant quantities.
4. For an exothermic reaction that has reached equilibrium, which conditions will result in a shift to the left? (7.4) K/U
   (a) removing products
   (b) adding reactants
   (c) adding thermal energy
   (d) removing thermal energy
5. Identify the equation that represents a chemical reaction system that will have a higher concentration of products than reactants at equilibrium. (7.5) T/I
   (a) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$
   $K = 2.19 \times 10^{-10}$ at 100 °C
   (b) $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$
   $K = 1.05 \times 10^{-1}$ at 472 °C
   (c) $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$
   $K = 51$ at 448 °C
   (d) $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$
   $K = 1 \times 10^{-30}$ at 25 °C
6. To calculate the concentrations of reactants and products of a chemical reaction system at equilibrium, which of the following values is/are needed? (7.5) K/U
   (a) initial concentrations of reactants and products
   (b) rate of change of reactant and product concentrations
   (c) reaction temperature
   (d) all of the above
7. Consider the dissolution of solid sodium chloride, NaCl(s), in water to form aqueous ions of sodium, $Na^+(aq)$, and chloride, $Cl^-(aq)$. The equation that represents this chemical reaction system is
   $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
   Which of the following are included in the equation for the solubility product constant, K_{sp}? (7.6) K/U
   (a) $[Na^+(aq)]$ and $[Cl^-(aq)]$ only
   (b) $[Na^+(aq)]$, $[Cl^-(aq)]$, and $[NaCl(s)]$
   (c) $[NaCl(s)]$ only
   (d) $[Na^+(aq)]$ and $[NaCl(s)]$ only
8. Which of the following compounds is most soluble in water? Assume that all K_{sp} values are for identical conditions. (7.6) K/U
   (a) zinc hydroxide, $K_{sp} = 7.7 \times 10^{-17}$
   (b) calcium phosphate, $K_{sp} = 2.2 \times 10^{-33}$
   (c) magnesium fluoride, $K_{sp} = 7.4 \times 10^{-11}$
   (d) lithium carbonate, $K_{sp} = 8.2 \times 10^{-4}$

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

9. In a dynamic equilibrium the concentrations of reactants and products are always changing. (7.1) K/U
10. If the equilibrium constant, K, is equal to 1, the position of equilibrium favours products much more than reactants. (7.2) K/U
11. Haber's addition of iron(III) oxide as a catalyst to the process of creating ammonia affected the ratio of product to reactant. (7.3) K/U
12. According to Le Châtelier's principle, a chemical system at equilibrium adjusts so as to counteract any disturbance. (7.4) K/U
13. An exothermic reaction that is at equilibrium will shift to the left when products are removed. (7.4) K/U
14. The magnitude of the equilibrium constant, K, provides information about the extent of a reaction because it indicates whether reactants or products are favoured. (7.5) K/U
15. The solubility product constant, K_{sp}, is a constant for a given substance under all conditions. (7.6) K/U
16. If the trial ion product, Q, is less than the solubility product constant, K_{sp}, a substance will precipitate from solution. (7.6) K/U

Go to Nelson Science for an online self-quiz.

WEB LINK

CHAPTER 7 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Which of the following is present in a chemical reaction system that has reached equilibrium? (7.1) K/U
   (a) equal concentrations of reactants and products
   (b) constant concentrations of reactants and products
   (c) no conversion among reactants and products
   (d) all of the above
2. Which of the following is an example of a homogeneous equilibrium? (7.2) K/U
   (a) $C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$
   (b) $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$
   (c) $Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4\,CO(g)$
   (d) all of the above
3. Which of the following occurs if a product is added to a chemical reaction system at equilibrium? (7.4) K/U
   (a) The equilibrium shifts left, toward reactants.
   (b) The equilibrium shifts right, toward products.
   (c) The equilibrium shifts both left and right equally.
   (d) The equilibrium undergoes no change.
4. Which of the following would not affect the position of equilibrium of the chemical reaction system represented by the following chemical equation? (7.4) K/U
   $SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$
   (a) removing $Cl_2(g)$
   (b) increasing the volume of the reaction vessel
   (c) adding a catalyst
   (d) reducing the temperature
5. When is a chemical reaction system at equilibrium? (7.5) K/U
   (a) when $Q > K$
   (b) when $Q < K$
   (c) when $Q = K$
   (d) when $Q = \frac{1}{K}$
6. Which concentrations are used to calculate the value of the reaction quotient, Q, of a chemical reaction system? (7.5) K/U
   (a) equilibrium concentrations of reactants and products
   (b) concentrations of reactants and products at a particular instant in time
   (c) initial concentrations of reactants and equilibrium concentrations of products
   (d) equilibrium concentrations of reactants and initial concentrations of products
7. Consider the chemical reaction system represented by the following balanced chemical equation:
   $MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,F^-(aq)$
   Identify the correct expression for the solubility product constant, K_{sp}, for this chemical reaction system. (7.6) K/U
   (a) $K_{sp} = [Mg^{2+}(aq)]^2[F^-(aq)]$
   (b) $K_{sp} = [Mg^{2+}(aq)][F^-(aq)]$
   (c) $K_{sp} = [Mg^{2+}(aq)][F^-(aq)]^2$
   (d) $K_{sp} = [Mg^{2+}(aq)]^2[F^-(aq)]^2$

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

8. A chemical reaction system is at equilibrium when the rate at which products form is equal to the rate at which reactants form. (7.1) K/U
9. A reversible chemical reaction produces a different set of equilibrium concentrations of reactants and products in the forward direction than in the reverse direction. (7.1) K/U
10. The equilibrium constant for any chemical reaction system does not vary with temperature. (7.2) K/U
11. When writing the equilibrium expression for the following chemical reaction system, liquid methanol, $CH_3OH(l)$, is not included:
    $2\,H_2(g) + CO(g) \rightleftharpoons CH_3OH(l)$ (7.2) K/U
12. Fritz Haber was able to increase the rate of synthesis of ammonia gas, $NH_3(g)$, from gaseous hydrogen, $H_2(g)$, and nitrogen, $N_2(g)$, by adjusting the pressure and temperature of the reaction. (7.3) K/U
13. If an exothermic chemical reaction is allowed to reach equilibrium at one temperature and then the temperature is lowered, the equilibrium will shift in the direction of the products. (7.4) K/U
14. If the reaction quotient, Q, is equal to the equilibrium constant, K, the system is at equilibrium. (7.5) K/U
15. If the reaction quotient, Q, is less than the equilibrium constant, K, the system will shift toward reactants to achieve equilibrium. (7.5) K/U
16. At 25 °C, a substance with a solubility product constant, K_{sp}, of 2.9×10^{-3} is more soluble than a substance with a solubility product constant of 7.2×10^{-5}. (7.6) K/U

Match each term on the left with the most appropriate description on the right.

17. (a) equilibrium constant
    (b) equilibrium shift
    (c) equilibrium position
    (d) reaction quotient

    (i) determined by initial concentrations of reactants and products
    (ii) determined by relative amounts of reactants and products
    (iii) determined by equilibrium concentrations of reactants and products
    (iv) determined by the addition or removal of a reactant or product

    (7.1, 7.2, 7.4, 7.5) K/U

Understanding

Write a short answer to each question.

18. **Figure 1** shows the reaction progress of two different chemical reactions. Describe the equilibrium position of each system in terms of whether reactants or products are favoured. (7.1) T/I

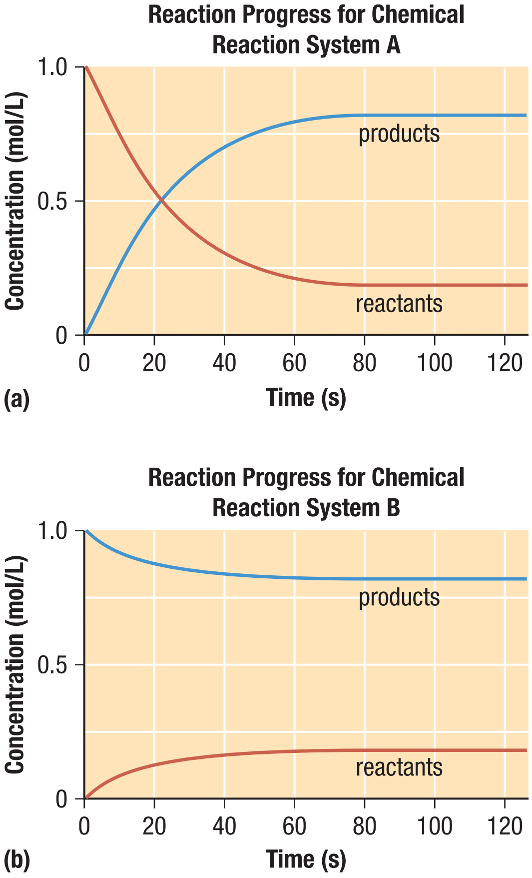


Figure 1

19. Explain what is meant by the equilibrium position of a chemical reaction. (7.1) K/U

20. Suppose that 3.00 mol of nitric oxide gas, NO(g), is introduced into a 1.00 L evacuated flask. When the system comes to equilibrium, 1.00 mol of dinitrogen monoxide gas, $N_2O(g)$, has formed.

    $2\,N_2O(g) + O_2(g) \rightleftharpoons 4\,NO(g)$

    Use an ICE table to determine the equilibrium concentrations of each substance. (7.1) T/I C

21. A chemist places 2.00 mol of diatomic bromine gas, $Br_2(g)$, in a 2.00 L reaction flask and allows the gas to decompose to monatomic bromine gas, Br(g):

    $Br_2(g) \rightleftharpoons 2\,Br(g)$

    At equilibrium, 0.064 mol of monatomic bromine gas is present in the flask. Calculate the equilibrium concentration of diatomic bromine gas. (7.1) T/I

22. Explain the difference between a homogeneous equilibrium and a heterogeneous equilibrium. (7.2) K/U

23. Write the equilibrium law equation for the chemical reaction systems represented by the following balanced chemical equations:
    (a) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$
    (b) $3\,Fe(s) + 4\,H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\,H_2(g)$
    (c) $NH_4NO_2(s) \rightleftharpoons N_2(g) + 2\,H_2O(g)$
    (d) $2\,NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)$ (7.2) K/U

24. Write a balanced chemical equation that describes the chemical reaction system represented by each of the following equilibrium expressions: (7.2) K/U

    (a) $K = \dfrac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$

    (b) $K = \dfrac{[NO(g)]^2[Br_2(g)]}{[NOBr(g)]^2}$

    (c) $K = \dfrac{[H_2O(g)][CH_4(g)]}{[CO(g)][H_2(g)]^3}$

    (d) $K = \dfrac{[CH_4(g)][H_2S(g)]^2}{[CS_2(g)][H_2(g)]^4}$

25. The chemical reaction system represented by the equation below is at equilibrium with the concentrations shown.

    $Cl_2(g) + CO(g) \rightleftharpoons COCl_2(g)$

    Equilibrium concentrations:

    $[CO] = 1.11 \times 10^{-1}$ mol/L;
    $[Cl_2] = 1.03 \times 10^{-1}$ mol/L;
    $[COCl_2] = 1.17 \times 10^{-1}$ mol/L

    Determine the value of the equilibrium constant, *K*. (7.2) T/I

26. For the chemical reaction system represented by the equation below, $K = 3.72 \times 10^{-2}$:

$2\ ClF_3(g) \rightleftharpoons Cl_2(g) + 3\ F_2(g)$

At equilibrium, the concentration of chlorine gas, $Cl_2(g)$, is 1.62×10^{-1} mol/L and of fluorine gas, $F_2(g)$, is 1.85×10^{-1} mol/L. Calculate the equilibrium concentration of chlorine trifluoride gas, $ClF_3(g)$. (7.2) T/I

27. Consider the chemical reaction system represented by the following equation:

$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$

In an investigation, the initial concentrations were $[SO_2(g)] = 0.40$ mol/L; $[O_2(g)] = 1.6$ mol/L; and $[SO_3(g)] = 29.7$ mol/L. The equilibrium concentration of $[SO_2(g)]$ was 1.2 mol/L. Determine the value of the equilibrium constant, K, for this chemical reaction system. (7.2) T/I

28. The chemical reaction system represented by the following equation has an equilibrium constant, K, equal to 1.24×10^{-1}:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Concentrations at equilibrium are observed to be $[PCl_5(g)] = 4.06 \times 10^{-1}$ mol/L and $[PCl_3(g)] = 1.17 \times 10^{-1}$ mol/L. What is the equilibrium concentration of chlorine gas, $Cl_2(g)$? (7.2) T/I A

29. In a closed vessel, elemental phosphorus, P(s), combines with elemental chlorine, $Cl_2(g)$, to form phosphorus trichloride gas, $PCl_3(g)$:

$2\ P(s) + 3\ Cl_2(g) \rightleftharpoons 2\ PCl_3(g)$

If the equilibrium constant is equal to 2.74×10^{-2} and the concentration of phosphorus trichloride gas at equilibrium is 1.09×10^{-1} mol/L, what is the equilibrium concentration of chlorine? (7.2) T/I

30. Consider the chemical reaction system represented by the equation below:

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g);\quad K = 626$ at 200 °C

If the equilibrium concentrations of gaseous hydrogen, $H_2(g)$, and ammonia, $NH_3(g)$, are 0.50 mol/L and 0.46 mol/L respectively, calculate the equilibrium concentration of nitrogen gas, $N_2(g)$. (7.2) T/I

31. Gaseous hydrogen, $H_2(g)$, and iodine, $I_2(g)$, combine in a reversible reaction to form hydrogen iodide gas, HI(g). The forward reaction is exothermic. (7.4) K/U T/I
    (a) Write a balanced chemical equation for this chemical reaction system.
    (b) If more iodine gas is added after the reaction reaches equilibrium, predict whether the reaction will shift to the right or the left. Explain.
    (c) If thermal energy is added after the reaction reaches equilibrium, is the reaction likely to shift to the left or the right? Explain.

32. In a closed container, the chemical reaction system represented by the following equation progresses to equilibrium:

$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

The volume of the container is decreased. Predict the direction in which the equilibrium will shift and explain why. (7.4) K/U T/I

33. Sulfur dioxide gas, $SO_2(g)$, and oxygen gas, $O_2(g)$, combine in a reversible reaction to form sulfur trioxide gas, $SO_3(g)$. If more sulfur trioxide gas is added after the reaction reaches equilibrium, predict whether the equilibrium will shift and, if so, in which direction. Give reasons for your prediction. (7.4) K/U T/I

34. **Figure 2** shows the changes in concentrations of three substances, X, Y, and Z, as they take part in a chemical reaction that reaches equilibrium. All three substances are gases. (7.4) T/I C

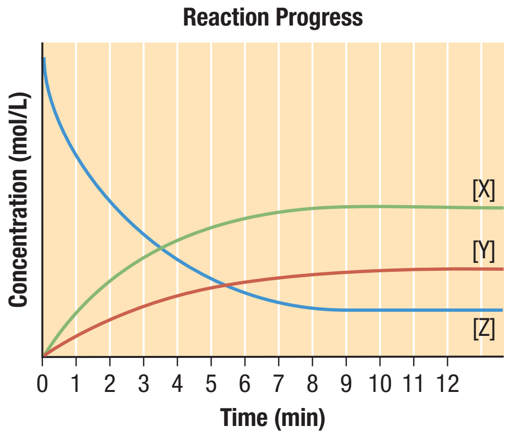


Figure 2

    (a) Write an equation to describe the equilibrium.
    (b) Predict how the graph will change if more of compound Z is added at 10 min. Give reasons for your prediction.

35. Why are catalysts added to some industrial processes that involve an equilibrium? (7.4) K/U

36. Suppose that the chemical reaction system represented by the equation below is at equilibrium. How will the addition of argon, Ar(g), affect the chemical reaction system? (7.4) K/U T/I

$2\ H_2S(g) \rightleftharpoons 2\ H_2(g) + S_2(g)$

37. The following are the values of the equilibrium constant, K, for four different chemical reaction systems. For each of the chemical reaction systems, describe the equilibrium position of the given temperature as mostly products, mostly reactants, or equal concentrations of reactants and products. (7.5) K/U
    (a) $K = 10^{-12}$ at 25 °C
    (b) $K = 10^{3}$ at -109 °C
    (c) $K = 10^{21}$ at -5 °C
    (d) $K = 10^{-1}$ at 554 °C

38. Explain the difference between the reaction quotient, Q, and the equilibrium constant, K. (7.5) K/U T/I

39. The chemical reaction system that can be used to produce the biofuel methanol, $CH_3OH(g)$, is represented by the following equation:

$$2\ H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

$$K = 10.5 \text{ at } 500\ K$$

When the concentrations of hydrogen, $H_2(g)$; carbon monoxide, $CO(g)$; and methanol are 0.25 mol/L, 0.25 mol/L, and 0.040 mol/L, respectively, is the system at equilibrium? If not, predict the direction in which the equilibrium will shift and explain why. (7.5) T/I

40. A chemist is investigating the chemical reaction system by which nitric oxide, $NO(g)$, is converted to nitrogen, $N_2(g)$, and oxygen, $O_2(g)$:

$$2\ NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

Initially she places 1.6 mol nitric oxide, 1.6 mol nitrogen, and 0.60 mol oxygen in a 1.00 L vessel. At equilibrium, she finds that the concentration of nitric oxide is 1.4 mol/L. Calculate the equilibrium constant, K, for this chemical reaction system. (7.5) T/I

41. A team of researchers is investigating the effect of temperature on the reversible reaction in which carbon monoxide gas, $CO(g)$, and water vapour, $H_2O(g)$, are converted to hydrogen gas, $H_2(g)$, and carbon dioxide gas, $CO_2(g)$. In one trial, the initial concentrations of reactants and products they place in a sealed vessel are carbon monoxide gas, 0.80 mol/L; water vapour, 2.40 mol/L; carbon dioxide, 0.62 mol/L; and hydrogen, 0.50 mol/L. The temperature in the vessel is maintained at 1000 °C and the reaction is allowed to come to equilibrium. They determine that the equilibrium concentration of carbon dioxide gas is 0.92 mol/L. Find the value of the equilibrium constant, K, for this chemical reaction system. (7.5) T/I

42. Initially, 1.00 mol each of gaseous carbon dioxide, $CO_2(g)$, and hydrogen, $H_2(g)$, is injected into a 10.0 L reaction chamber at 986 °C. What is the predicted concentration of each entity at equilibrium? The balanced equation for the chemical reaction system is

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

$K = 1.60$ at 986 °C (7.5) T/I

43. At the beginning of an investigation, 0.50 mol of iodine gas, $I_2(g)$, and 0.50 mol of chlorine gas, $Cl_2(g)$, are placed into a 2.00 L reaction vessel at 25 °C. Find the concentrations of all entities at equilibrium for the chemical reaction system given by the following balanced equation:

$$I_2(g) + Cl_2(g) \rightleftharpoons 2\ ICl(g)$$

$K = 81.9$ at 25 °C (7.5) T/I

44. The equilibrium constant, K, is 4.20×10^{-6} at a temperature of 1100 K for the chemical reaction system represented by the following equation:

$$2\ H_2S(g) \rightleftharpoons 2\ H_2(g) + S_2(g)$$

What is the predicted equilibrium concentration of $S_2(g)$ if an initial quantity of 0.200 mol of $H_2S(g)$ is added to a sealed 1.00 L vessel at 1100 K? (7.5) T/I

45. Hydrogen chloride gas, $HCl(g)$, decomposes into its elements according to the balanced equation

$$2\ HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

The equilibrium constant, K, is 3.2×10^{-34} at 25 °C. Calculate the equilibrium concentrations of all entities if 2.00 mol hydrogen chloride gas is initially placed in a closed 1.00 L vessel. (7.5) T/I

46. Solid zinc hydroxide, $Zn(OH)_2(s)$, dissolves in water to form zinc ions, $Zn^{2+}(aq)$, and hydroxide ions, $OH^-(aq)$:

$$Zn(OH)_2(aq) \rightleftharpoons Zn^{2+}(aq) + 2\ OH^-(aq)$$

(a) Write the expression for the solubility product constant, K_{sp}, of zinc hydroxide.

(b) If the value of the solubility product constant, K_{sp}, for zinc hydroxide is 7.7×10^{-17} at 25 °C, calculate the molar solubility of zinc hydroxide at 25 °C. (7.6) T/I

47. A student mixes two solutions: 10.0 mL of 0.0040 mol/L lead(II) nitrate, $Pb(NO_3)_2(aq)$, and 15.0 mL of 0.25 mol/L potassium chloride, $KCl(aq)$. If the solubility product constant, K_{sp}, for lead(II) chloride, $PbCl_2$, is 1.2×10^{-5} at 25 °C, will a precipitate form when these two solutions are mixed? Why? (7.6) T/I

Analysis and Application

48. Use the concept of dynamic equilibrium to explain why a bottle of pop stays carbonated longer if the bottle cap is replaced after opening (**Figure 3**). (7.1) T/I

Figure 3

49. A student mixes two solutions in a dish and notices that bubbles are produced and a colour change occurs. After a few minutes, the bubbles stop and the colour has reached a constant shade. The student concludes that the reaction has reached equilibrium. Do you agree? Explain your reasoning. (7.1) T/I

50. Fluoride toothpastes have been developed to reduce the incidence of dental cavities. These toothpastes supply fluoride ions, F^-, which replace hydroxide ions, OH^-, in solid hydroxyapatite, $Ca_5(PO_4)_3(OH)(s)$, in teeth. The resulting compound is fluorapatite, $Ca_5(PO_4)_3F(s)$. Given this information, do you think the equilibrium constant for the dissolution of fluorapatite is higher or lower than that of hydroxyapatite? Explain your reasoning. (7.2) T/I A

51. A chemist places 1 mol each of nitrogen, $N_2(g)$, and hydrogen, $H_2(g)$, in a sealed vessel. The reactants undergo a reversible reaction:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Determine the amount of ammonia, $NH_3(g)$, that would form if x mol of hydrogen, $H_2(g)$, is consumed in the reaction. (7.2) T/I

52. An investigator gathers the data in **Table 1** by carrying out the reaction represented by the following equation:

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

Table 1 Observed Equilibrium Concentrations

Trial	$[PCl_5(g)]$	$[PCl_3(g)]$	$[Cl_2(g)]$
1	0.023	0.23	0.55
2	0.010	0.15	0.37
3	0.085	0.99	0.47
4	1.00	3.66	1.5

(a) Show that the data in Table 1 are consistent with the equilibrium law.

(b) What is the equilibrium constant for this reaction? (7.2) T/I A

53. The Haber synthesis of ammonia, $NH_3(g)$, is represented by the equation below:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g);\ \Delta H = -92\text{ kJ}$$

Le Châtelier's principle predicts that the equilibrium concentration of ammonia, $NH_3(g)$, will be greater at high pressure and low temperature. In industrial production of ammonia, this reaction is typically carried out at 500 °C and 200 atm. Under these conditions, the equilibrium chemical reaction system proceeds to about 15 % completion. Using collision theory, explain why lower temperatures are not used. (7.3, 7.4) T/I

54. In a chemical manufacturing process that involves a system at equilibrium, the reactants are continually added and the products are continually removed to maximize yield. Explain why both steps are necessary, using Le Châtelier's principle. (7.4) T/I A

55. Myoglobin is a protein present in muscle that binds oxygen more tightly than hemoglobin. It functions to store oxygen within muscle to ensure that a sufficient oxygen reserve is readily available. Relate your understanding of the magnitude of the equilibrium constant, K, to the differences in function of hemoglobin (as a transporter of oxygen from lungs) and myoglobin (as an oxygen storage reservoir). Why is the equilibrium constant for hemoglobin binding to oxygen lower than the equilibrium constant for myoglobin binding to oxygen? (7.4) T/I A

56. The reaction between sulfur dioxide, $SO_2(g)$, and oxygen, $O_2(g)$, to form sulfur trioxide, $SO_3(g)$, is reversible. The following equation represents this chemical reaction system:

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \quad \Delta H = -196\text{ kJ}$$

This chemical reaction system is used during the industrial production of sulfuric acid. The reaction is carried out at a temperature of 450 °C and a pressure of 2 atm, and in the presence of a catalyst. A chemical engineer suggests that money might be saved by eliminating the catalyst and raising the temperature of the reaction. Is the engineer's suggestion valid? Explain your reasoning. (7.4) T/I A

57. Some equilibria are described as being "weak" because very little product is present in these systems at equilibrium. Predict the magnitude of the values of the equilibrium constant, K, for these chemical reaction systems. (7.5) T/I

58. Water hardness is caused by the presence of Ca^{2+} and Mg^{2+} ions. One way of removing these ions is to add sodium carbonate, $Na_2CO_3(s)$, which causes precipitation of calcium carbonate, $CaCO_3(s)$, and magnesium carbonate, $MgCO_3(s)$. A 5.0 L volume of water has a Ca^{2+} concentration of 0.0040 mol/L. What is the maximum mass of sodium carbonate that can be added to this volume without causing any precipitate to form? The K_{sp} for $CaCO_3(s)$ is 4.8×10^{-9} at 25 °C. (7.6) A

59. Name two examples of compounds that, when added to a solution containing barium sulfate, $BaSO_4(aq)$, will decrease the solubility of barium sulfate. Explain your answer. (7.6) T/I A

60. The temperature of groundwater that circulates through rock near volcanoes may be increased by thermal energy released from the hot rock beneath the volcano. This heated water can flow through rock below the ground and, in the process, dissolve some of the minerals in the rock. When the water rises to the surface and cools, the minerals precipitate out to form deposits around many hot springs (**Figure 4**). Use your understanding of solubility to explain these observations. (7.6) T/I A

Figure 4 The precipitation of minerals gives many hot springs beautiful colours.

Evaluation

61. During a class presentation, a student states that unsaturated solutions are in dynamic equilibrium, but saturated solutions are not. Do you agree or disagree with the student's statement? Make a diagram to support your answer. (7.1, 7.2, 7.6) T/I C
62. Many, but not all, industrial chemical processes involve catalysts. Do you think that chemical engineers should focus on identifying catalysts for all industrial processes? Defend your answer. (7.3) T/I
63. While searching the Internet for information on chemical reactions, you find a website that includes the following statement: "There are many ways to shift a chemical equilibrium toward the products of a reaction. Increasing temperature and decreasing pressure are two examples of changes that will cause equilibrium to shift toward the products." Do you think the person who wrote this website has a complete understanding of chemical equilibria? Defend your answer. (7.4, 7.5, 7.6) T/I

Reflect on Your Learning

64. Which concepts in this chapter did you find most interesting? Why? A
65. Describe three ways the information in this chapter can help you understand things you observe in your everyday life. Do you think that your understanding of chemical equilibrium will change any of your behaviours? If so, which ones? A
66. Identify two concepts from this chapter that you had a hard time understanding. How can you improve your understanding of these concepts? A

Research

WEB LINK

67. Create a poster describing why ammonia is important in maintaining the global food supply. C A
68. As a scuba diver descends, the surrounding water pressure increases. This forces more nitrogen, $N_2(g)$, in the compressed air the diver is breathing to dissolve in the diver's bloodstream:

    $N_2(g) \rightleftharpoons N_2(aq)$

    "The bends," or decompression sickness, can occur if the diver ascends to the surface too quickly. Nitrogen narcosis is another condition that results from the increased solubility of nitrogen in the blood at high pressures. Research the causes, symptoms, and methods used to combat the bends and nitrogen narcosis in divers. Write a short report summarizing your findings. C A
69. Research the equilibrium process involved in stalactite and stalagmite formation in limestone caves. Write a balanced chemical equation to describe what happens during the formation of these structures. Explain how Le Châtelier's principle is involved. C A
70. Research the use of cobalt chloride as an indicator for humidity. Explain the chemical reaction that underlies this process. What property of the system is used to indicate the level of humidity? If possible, find an example of a product that illustrates this application. Present your findings in a short written or oral report. C A
71. According to his Nobel lecture, Fritz Haber wanted to find an economical process for fixing nitrogen to make fertilizer. Compare the amount of ammonia being used today for fertilizer to the other uses of ammonia. What are the five chief uses of ammonia other than fertilizer? A C

CHAPTER 8

Acid–Base Equilibrium

KEY CONCEPTS

After completing this chapter you will be able to

- explain how acids, bases, and buffers affect, and are used in, our daily lives
- use the concept of equilibrium to compare strong and weak acids and bases
- explain equilibrium expressions, such as K_w, K_a, and K_b
- use key terms to communicate ideas, procedures, and results related to acid–base equilibrium and systems
- solve equilibrium problems involving K_a, K_b, pH, and pOH
- predict whether a specific salt solution will be acidic, basic, or neutral
- analyze acid–base titration data and determine pH at the equivalence point
- describe a buffer solution

How Do Acids and Bases Affect Industrial Processes, Living Organisms, and the Environment?

Acids and bases are common substances with important biological, social, economic, and environmental implications. Acids and bases are found in many foods, beverages, industrial chemicals, and pharmaceuticals. For example, fruits, pop, salads, battery fluid, and Aspirin are common acidic substances. Dishwashing soap, household ammonia, milk of magnesia, and morphine are common bases.

Acids and bases play important roles in the functioning of living organisms. For example, hydrochloric acid—produced by cells lining your stomach—helps digest food. Bases released into your large intestine help complete the digestion process.

In the natural environment, many plants and animals use acidic or basic substances to defend themselves. For example, some ants spray methanoic acid (formic acid) at predators or prey to disable them. The plant *Atropa belladonna* (also called belladonna or deadly nightshade) produces a number of toxic bases that cause delirium and hallucinations. Belladonna is also the source of a base called atropine, which is used as a drug in the treatment of various nervous system disorders.

Acid precipitation, produced by the combustion of fossil fuels, has led to the acidification of lakes and terrestrial ecosystems. You may have heard of the damage caused to the environment around Sudbury, Ontario, as a result of acid emissions from metal smelters nearby. Bases, such as calcium hydroxide, were used to counteract the destructive effects of acid precipitation on lakes and ponds. This treatment has contributed to the recovery of the Sudbury area's ecology.

Aqueous solutions of acids and bases are dynamic equilibria that obey the equilibrium law and adjust in accordance with Le Châtelier's principle.

STARTING **POINTS**

Answer the following questions using your current knowledge. You will have a chance to revisit these questions later, applying concepts and skills from the chapter.

1. Explain why the pH of pure distilled water (at SATP) is equal to 7.
2. Solutions of hydrochloric acid, HCl(aq), and hydrofluoric acid, HF(aq), of the same concentration are not equally acidic. Which of the two solutions has a lower pH? Why?
3. When equal amounts of hydrochloric acid, HCl(aq), and sodium hydroxide, NaOH(aq), are combined, the resulting solution is neutral (pH = 7). When equal amounts of ethanoic acid, $HC_2H_3O_2$(aq), and sodium hydroxide, NaOH(s), are mixed, the resulting solution is basic (pH > 7). When equal amounts of hydrochloric acid, HCl(aq), and baking soda, $NaHCO_3$(s), are mixed, the resulting solution is acidic (pH < 7). Try to account for these observations.

Mini **Investigation**

Disappearing and Reappearing Ink

Skills: Performing, Observing, Analyzing

SKILLS HANDBOOK A1

In this investigation, you will make your own disappearing ink using an acid–base indicator called phenolphthalein. You will test the ink on pieces of white cotton fabric and white paper.

Equipment and Materials: chemical safety goggles; lab apron; 100 mL graduated cylinder; 150 mL beaker; medicine dropper; cotton balls or small paintbrush; dropper bottle containing 1 % phenolphthalein solution (in ethanol); swatch of white cotton fabric; white paper; 10 mL ammonia solution, $NH_3(aq)$ (0.1 mol/L); 10 mL sodium hydroxide solution, NaOH(aq) (0.1 mol/L)

Sodium hydroxide is corrosive. Avoid skin or eye contact. Should sodium hydroxide come in contact with your skin or eyes, wash the affected area for 15 min with cool water and inform your teacher.

Phenolphthalein solution is flammable. Keep it away from open flames.

1. Put on your chemical safety goggles and lab apron.
2. Measure 60 mL of water in a graduated cylinder, then transfer the water into a 150 mL beaker.
3. Add 2–3 drops of 1 % phenolphthalein solution to the water in the beaker and stir.
4. Measure 30 mL of sodium hydroxide solution. Add this to the mixture in the beaker, and stir.
5. Place a few drops of the solution from Step 4 on the swatch of white fabric to create a visible spot. Observe for a few minutes. Record your observations.
6. Dampen a cotton ball with ammonia solution and brush it over the spot created in Step 5. Observe.
7. Place a drop of the solution from Step 4 on the white paper and observe for a few minutes. Record your observations.
8. Dispose of any remaining solution and clean your work area as directed by your teacher.

A. Summarize your observations of the “ink” spots. K/U

B. Why does the ink disappear in Step 5? K/U

C. Why did the ink reappear when mixed with ammonia solution in Step 6? K/U

D. Suggest reasons for your observations in Step 7. K/U

8.1 The Nature of Acids and Bases

People first recognized acids as a class of substances that taste sour. Vinegar tastes sour because it is a dilute solution of acetic acid. The sour taste of lemons is caused by citric acid. Bases, sometimes called alkalis, are characterized by their bitter taste and slippery feel. Commercial preparations for unclogging drains are highly basic. Scientists have studied acids and bases for over 200 years and have developed several theories that help explain what acids and bases are and why they behave the way they do. We will examine two acid–base theories: the Arrhenius theory and the Brønsted–Lowry theory.

The Arrhenius Theory of Acids and Bases

The first person to recognize the essential nature of acids and bases was the Swedish chemist Svante Arrhenius (1859–1927) (**Figure 1**). Arrhenius performed experiments and explained his observations by suggesting that acids produce hydrogen ions, $H^+(aq)$, in aqueous solution. A hydrogen ion is a hydrogen atom without an electron. In essence, a hydrogen ion is a proton. Arrhenius also proposed that bases produce hydroxide ions, $OH^-(aq)$, when they dissolve. This explanation is known as the **Arrhenius theory** of acids and bases.

Figure 1 In 1903, Svante Arrhenius won a Nobel Prize in Chemistry for his proposal that ionic substances split into charged ions when they dissolve in water.

Arrhenius theory a theory stating that, in an aqueous solution, an acid is a substance that produces hydrogen ions and a base is a substance that produces hydroxide ions

According to the Arrhenius theory, hydrogen chloride, $HCl(g)$, is an acid because when it dissolves in water it produces hydrogen ions, $H^+(aq)$, and chloride ions, $Cl^-(aq)$. The dissolved hydrogen ions give the solution its acidic properties (for example, its sour taste).

$$\mathrm{HCl(g)} \xrightarrow{\text{water}} \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)}$$

According to the Arrhenius theory, sodium hydroxide, $NaOH(s)$, is a base because when it dissolves in water it dissociates into sodium ions, $Na^+(aq)$, and hydroxide ions, $OH^-(aq)$. The hydroxide ions give the solution its basic (alkaline) properties (for example, its bitter taste and slippery feel).

$$\mathrm{NaOH(s)} \xrightarrow{\text{water}} \mathrm{Na^+(aq)} + \mathrm{OH^-(aq)}$$

The Arrhenius theory was a major step forward in explaining acid–base chemistry. However, this theory is limited because it allows for only one kind of base—compounds containing the hydroxide ion—and it assumes that all acid–base reactions occur in aqueous solutions. Like all theories, Arrhenius's proposal was tentative and subject to change as further investigations produced other evidence. Indeed, later studies showed that basic solutions can also be formed by compounds, such as ammonia, $NH_3(aq)$, that do not contain the hydroxide ion. Chemists continued searching for a theory that explained this observation.

The Brønsted–Lowry Theory of Acids and Bases

Brønsted–Lowry theory a theory stating that an acid is a hydrogen ion (proton) donor and a base is a hydrogen ion (proton) acceptor

A more general explanation of acids and bases was suggested by the Danish chemist Johannes Brønsted (1879–1947) and the English chemist Thomas Lowry (1874–1936) (**Figure 2**). In the **Brønsted–Lowry theory**,

An acid is a hydrogen ion donor.
A base is a hydrogen ion acceptor.

This theory applies to all of the Arrhenius acids and bases, plus some others that are not categorized as acids and bases under the Arrhenius definition.

The Brønsted–Lowry Theory and Acidic Solutions

Hydrofluoric acid, $HF(aq)$, is typically produced by dissolving gaseous hydrogen fluoride, $HF(g)$, in water. The Arrhenius theory predicts that hydrogen ions and fluoride ions will be produced. Experimental evidence suggests, however, that the hydrogen ion is not stable on its own. Rather, the hydrogen ion appears to react with a water molecule. When hydrogen fluoride dissolves in water, therefore, each hydrogen fluoride molecule reacts with a water molecule to form a **hydronium ion**, $H_3O^+(aq)$, and a fluoride ion, $F^-(aq)$ (**Figure 3**). The oxygen atom of the water molecule pulls a hydrogen ion away from the hydrogen fluoride molecule, leaving behind a fluoride ion. Thus, in this reaction, hydrogen fluoride is an acid according to the Brønsted–Lowry theory because it "donates" the proton that bonds with the water molecule to form the hydronium ion. Water is a Brønsted–Lowry base because it "accepts" a proton from the hydrogen fluoride molecule. The water molecule acts as a Brønsted–Lowry base in this reaction because its oxygen atom has lone electron pairs. One of these electron pairs forms a coordinate covalent bond with the "donated" hydrogen ion, forming a hydronium ion.

hydronium ion a water molecule that has accepted a hydrogen ion, H_3O^+

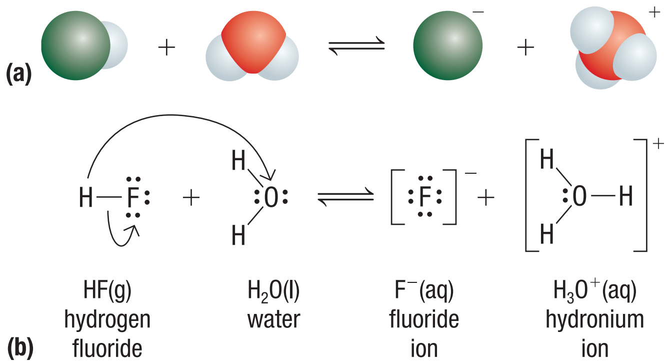


Figure 3 The Brønsted–Lowry theory explaining the reaction of hydrogen fluoride with water can be illustrated as (a) a space-fill representation or (b) Lewis structures.

As Figure 3 illustrates, the reaction of hydrogen fluoride and water is reversible and results in a dynamic equilibrium in an aqueous solution. The dissolved hydronium ions are responsible for the solution's acidic properties.

In general, Brønsted–Lowry bases contain at least one atom with one or more lone electron pairs (most often, O, N, or P).

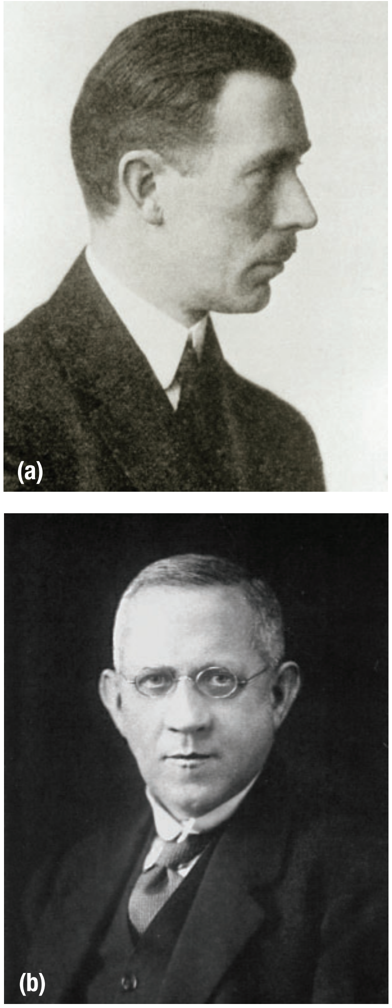


Figure 2 (a) J. Brønsted (1879–1947) and (b) T. Lowry (1874–1936) proposed new acid–base theories centred on hydrogen ion transfer.

The Brønsted–Lowry Theory and Basic Solutions

When gaseous ammonia, $NH_3(g)$, dissolves in water, ammonia molecules react with water molecules, producing a dynamic equilibrium. In this reaction, a water molecule donates a hydrogen ion to the ammonia molecule, forming an ammonium ion, $NH_4^+(aq)$, and a hydroxide ion, $OH^-(aq)$ (**Figure 4**). Thus, the water molecule acts as an acid (a proton donor) and the ammonia acts as a base (a proton acceptor) according to the Brønsted–Lowry theory. The hydroxide ions are responsible for the solution's basic properties.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

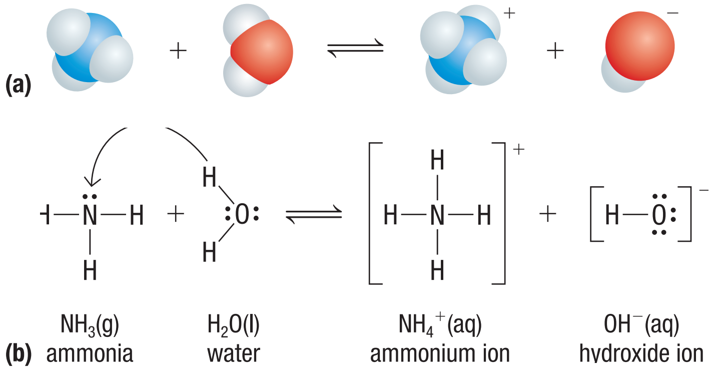


Figure 4 The Brønsted–Lowry theory explaining the reaction of ammonia with water can be illustrated as (a) a space-fill representation or (b) Lewis structures.

Conjugate Acid–Base Pairs

Since acid–base reactions are reversible, a hydrogen ion (proton) transfer may occur in the forward reaction and also in the reverse reaction. Thus, there is a Brønsted–Lowry acid (hydrogen ion donor) and a Brønsted–Lowry base (hydrogen ion acceptor) on each side of the reaction equation. Imagine the equilibrium reaction of a hypothetical acid, HA(aq), with water to form an acidic solution (**Figure 5(a)**). This reaction system is represented by the equation

$$\mathrm{HA(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{A^-(aq)} + \mathrm{H_3O^+(aq)}$$

In the forward reaction, the acid molecule donates a hydrogen ion to a water molecule, which acts as a base. This results in the formation of an anion, A^-(aq), and a hydronium ion, H_3O^+(aq). In the reverse reaction, the hydronium ion transfers a hydrogen ion to the A^-(aq) ion. Now the hydronium ion acts as an acid (called a "conjugate acid") and the A^-(aq) ion acts as a base (called a "conjugate base"). In general, a **conjugate acid** is an acid formed when a base accepts a hydrogen ion from an acid. A **conjugate base** is a base formed when an acid loses a hydrogen ion to a base.

conjugate acid the substance that forms when a base, according to the Brønsted–Lowry theory, accepts a hydrogen ion (proton)

conjugate base the substance that forms when an acid loses a hydrogen ion (proton)

Similarly, imagine the equilibrium reaction of a hypothetical base, B(aq), with water to form a basic solution (**Figure 5(b)**).

$$\mathrm{B(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{HB^+(aq)} + \mathrm{OH^-(aq)}$$

In the forward reaction, the base molecule takes a hydrogen ion from a water molecule, which acts as an acid. This results in the formation of a cation, HB^+(aq) (the conjugate acid), and a hydroxide ion, OH^-(aq) (the conjugate base).

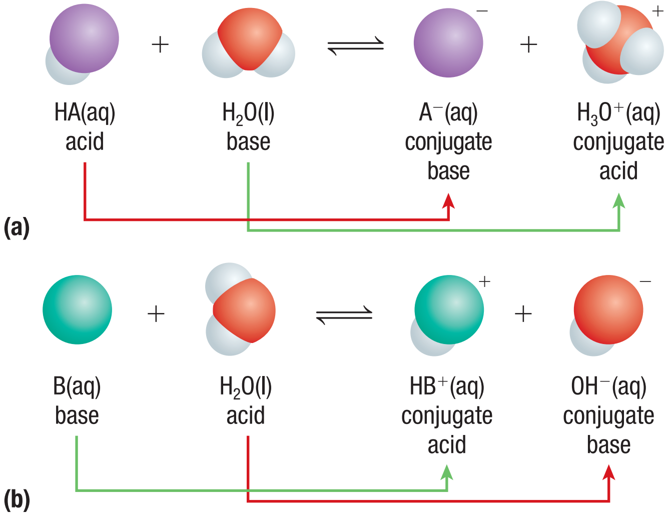


Figure 5 Note the conjugate acid–base pairs in the equations representing the reactions between (a) a hypothetical acid, HA(aq), and water and (b) a hypothetical base, B(aq), and water.

conjugate acid–base pair two substances related to each other by the donating and accepting of a single hydrogen ion

For any acid–base reaction, there will always be one **conjugate acid–base pair** made up of an acid and its conjugate base and another conjugate acid–base pair made up of a base and its conjugate acid. Within each pair, the formulas differ only by a hydrogen ion.

The Brønsted–Lowry Theory and Non-aqueous Reactions

The Arrhenius theory assumes that acid–base reactions occur in aqueous solutions. The Brønsted–Lowry theory is not limited to aqueous solutions because it can be extended to reactions in other states. For example, consider the reaction between gaseous hydrogen chloride and gaseous ammonia:

$$\mathrm{HCl(g)} + \mathrm{NH_3(g)} \rightleftharpoons \mathrm{NH_4Cl(s)}$$

In this reaction, the hydrogen chloride molecule donates a hydrogen ion to the ammonia molecule (**Figure 6**). An ammonium ion and a chloride ion are produced.

These ions form ammonium chloride crystals (**Figure 7**). According to the Arrhenius concept this is not considered an acid–base reaction because neither hydrogen ions nor hydroxide ions are produced. However, according to the Brønsted–Lowry theory it *is* an acid–base reaction: hydrogen chloride is an acid, ammonia is a base, NH_4^+ is a conjugate acid, and Cl^- is a conjugate base.

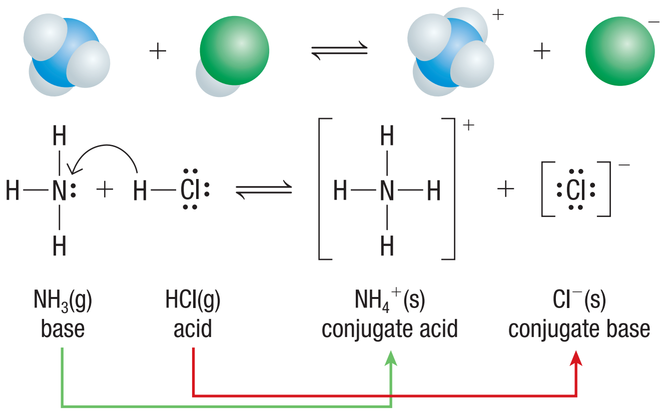


Figure 6 Ammonia reacts with hydrochloric acid to form ammonium ions and chloride ions.

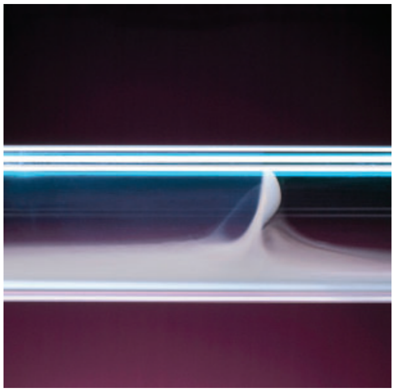


Figure 7 When gaseous hydrogen chloride and ammonia meet in a tube, a white disc of ammonium chloride crystals, $NH_4Cl(s)$, forms.

Amphiprotic (Amphoteric) Substances

Note that a substance can be classified as an acid or base, according to the Brønsted–Lowry theory, only for a specific reaction. A substance may act as an acid in one reaction and a base in another reaction. For example, in the reaction of hydrogen fluoride with water (Figure 3), water acts as a base, but in the reaction of ammonia with water (Figure 4), water acts as an acid. A substance that may act as a Brønsted–Lowry acid in some reactions and as a Brønsted–Lowry base in others is called **amphiprotic** (or **amphoteric**). Both water and the hydrogen carbonate ion, $HCO_3^-(aq)$, are amphiprotic:

amphiprotic (amphoteric) able to donate or accept a hydrogen ion (proton) and thus act as both a Brønsted–Lowry acid and a Brønsted–Lowry base

$$\underset{\text{base}}{HCO_3^-(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_2CO_3(aq)} + \underset{\text{conjugate base}}{OH^-(aq)}$$

$$\underset{\text{acid}}{HCO_3^-(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate base}}{CO_3^{2-}(aq)} + \underset{\text{conjugate acid}}{H_3O^+(aq)}$$

Tutorial 1 Acid–Base Pairs and Amphiprotic Entities

In this tutorial, you will identify conjugate acid–base pairs and amphiprotic entities in acid–base reactions.

Sample Problem 1: Identifying Conjugate Acid–Base Pairs

Use the Brønsted–Lowry theory to identify the acid, the base, the conjugate acid, and the conjugate base in the reaction represented by the following equation:

$$HC_2H_3O_2(aq) + H_2O(l) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

Solution

Remember that, according to the Brønsted–Lowry theory, an acid donates hydrogen ions and a base accepts them. $HC_2H_3O_2(aq)$ donates a hydrogen ion. Therefore, $HC_2H_3O_2(aq)$ is the acid in this reaction. Its conjugate base is $C_2H_3O_2^-(aq)$. $H_2O(l)$ accepts the hydrogen ion, so $H_2O(l)$ is the base in this reaction. Its conjugate acid is $H_3O^+(aq)$.

$$\underset{\text{acid}}{HC_2H_3O_2(aq)} + \underset{\text{base}}{H_2O(l)} \rightarrow \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{C_2H_3O_2^-(aq)}$$

Sample Problem 2: Explaining Amphiprotic Entities

Explain why the hydrogen carbonate ion, $HCO_3^-(aq)$, is amphiprotic, but the fluoride ion, $F^-(aq)$, is not.

Solution

The hydrogen carbonate ion, $HCO_3^-(aq)$, may gain a proton, $H^+(aq)$, to become carbonic acid, $H_2CO_3(aq)$. Alternatively, the hydrogen carbonate ion may lose a proton to become the carbonate ion, $CO_3^{2-}(aq)$. The fluoride ion, $F^-(aq)$, may accept a proton to become a hydrofluoric acid, HF(aq). However, the fluoride ion, $F^-(aq)$, cannot lose a proton since it does not have a proton to lose.

Practice

1. Identify the acid, the base, the conjugate acid, and the conjugate base in the equilibrium reactions represented by the following equations: K/U
   - (a) $HCHO_2(aq) + H_2O(l) \rightleftharpoons CHO_2^-(aq) + H_3O^+(aq)$
   - (b) $C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_2(aq) + H_3O^+(aq)$
   - (c) $H_2CO_3(aq) + OH^-(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l)$
   - (d) $HSO_4^-(aq) + HPO_4^{2-}(aq) \rightleftharpoons H_2PO_4^-(aq) + SO_4^{2-}(aq)$
   - (e) $HSO_4^-(aq) + HCl(aq) \rightleftharpoons Cl^-(aq) + H_2SO_4(aq)$
2. Explain why the hydrogen sulfate ion, $HSO_4^-(aq)$, is amphiprotic. K/U

LEARNING **TIP**

Standard Conditions

Unless stated otherwise, conditions in problems in this chapter are SATP: 25 °C and 100 kPa.

The Acid Ionization Constant, K_a

The reaction of a weak acid, HA, with water forms a dynamic equilibrium involving H_3O^+ and a conjugate base, A^-:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq).$$

We may write an equilibrium law equation for this reaction. The equilibrium constant, K_a, is called the **acid ionization constant**. K_a is used for reactions in which an acid, HA(aq), reacts with water to form a conjugate base, $A^-(aq)$.

acid ionization constant (K_a) the equilibrium constant for the ionization of an acid; also called the acid dissociation constant

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[H_2O(l)][HA(aq)]}$$

We can simplify this equation in two ways:

First, we know that water plays an important role in causing the acid to ionize. As you read earlier, hydrogen ions, $H^+(aq)$, do not exist as individual ions in aqueous solution; rather, every hydrogen ion is bound to a water molecule as a hydronium ion, $H_3O^+(aq)$. However, for convenience, we can write the reaction equation as though the acid, HA(aq), simply separates into $H^+(aq)$ and $A^-(aq)$ ions:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

Second, in Chapter 7 you learned that if the concentration of a chemical substance remains constant during a reaction, that substance is omitted from the equilibrium law equation. In a dilute solution, we can assume that the concentration of liquid water remains essentially constant when an acid is dissolved. Thus, $H_2O(l)$ is omitted from the equilibrium law equation.

The equilibrium law equation, with these modifications included, is called the acid ionization constant equation and is written as follows:

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]} \text{ where } [H^+(aq)] \text{ is equivalent to } [H_3O^+(aq)]$$

Table 1 shows acid ionization constants (K_a values) for several acids.

Table 1 Some Acid Ionization Constants

Acid	Acid ionization constant, K_a
hydrocyanic, HCN(aq)	6.2×10^{-10}
benzoic, $HC_6H_5CO_2(aq)$	6.3×10^{-5}
propanoic, $HC_3H_5O_2(aq)$	1.3×10^{-5}
ethanoic (acetic), $HC_2H_3O_2(aq)$	1.8×10^{-5}
hydrofluoric, HF(aq)	6.6×10^{-4}
nitrous, $HNO_2(aq)$	4.6×10^{-4}
methanoic (formic), $HCHO_2(aq)$	1.8×10^{-4}

Tutorial 2 Writing Acid Ionization Constant Equations

In this tutorial, you will write acid ionization constant equations for different reactions.

Sample Problem 1: Writing K_a Equations

(a) Write the acid ionization constant equation for the equilibrium reaction of nitrous acid, $HNO_2(aq)$, with water.

(b) Write the acid ionization constant equation for the equilibrium reaction of ethanoic acid and water:

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

Solution

(a) First write the equilibrium reaction equation for the ionization of nitrous acid in water. You may write the equation with H1(aq) or H3O1(aq). Both reaction equations with their corresponding ionization constant equations are shown below. Both are correct. Remember not to include the concentration of H2O(l) in acid ionization constant equations.

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

$$K_a = \frac{[H_3O^+(aq)][NO_2^-(aq)]}{[HNO_2(aq)]}$$

or

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$$

$$K_a = \frac{[H^+(aq)][NO_2^-(aq)]}{[HNO_2(aq)]}$$

(b) $$K_a = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

Practice

1. Write acid ionization constant equations for the following acids at equilibrium: K/U
   (a) hydrocyanic acid, HCN(aq)
   (b) nitrous acid, $HNO_2(aq)$
   (c) $HSO_4^-(aq)$

A Competition for Protons

Recall that, in the general equation for the reaction of an acid with water, there are always two bases:

$$\underset{\text{acid}}{HA(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{conjugate}\\\text{base}}}{A^-(aq)}$$

It is important to note that these two bases, $H_2O(l)$ and $A^-(aq)$, compete for the hydrogen ion. If H_2O has a much greater affinity for H^+ than does A^- (if it is a stronger base), the equilibrium position will be far to the right. Most of the dissolved acid will be in the ionized form, $A^-(aq)$. Conversely, if A^- is a much stronger base than H_2O, then the equilibrium position will lie far to the left. As a result, most of the dissolved acid will be present at equilibrium as HA(aq) molecules.

Note that, since these equations represent equilibrium reaction systems, calling the entities on the left of the arrow "acid" and "base" and the entities on the right "conjugate acid" and "conjugate base" is arbitrary. It is equally correct to call the entities on the right of the arrow "base" and "acid" and the entities on the left "conjugate base" and "conjugate acid."

8.1 Review

Summary

- According to the Arrhenius theory, in aqueous solution an acid produces hydrogen ions, H^+, and a base produces hydroxide ions, OH^-.
- According to the Brønsted–Lowry theory, an acid is a hydrogen ion (proton) donor and a base is a hydrogen ion acceptor.
- When an acid, HA, reacts with water, the water acts as a base and forms a conjugate acid, H_3O^+. The acid forms a conjugate base, A^-, according to the equation

$$\mathrm{HA(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{A^-(aq)}$$

- The acid equilibrium constant, K_a, is represented by

$$K_a = \frac{[\mathrm{H_3O^+(aq)}][\mathrm{A^-(aq)}]}{[\mathrm{HA(aq)}]}, \text{ which may be simplified as } K_a = \frac{[\mathrm{H^+(aq)}][\mathrm{A^-(aq)}]}{[\mathrm{HA(aq)}]}$$

UNIT TASK BOOKMARK

In the Unit Task outlined on page 582 you will investigate a consumer product that is acidic or basic. You may use the information on the nature of acids and bases in this section as you work on the Unit Task.

Questions

1. Define or illustrate the meaning of the following terms: K/U
   (a) K_a
   (b) amphiprotic
   (c) hydronium ion
   (d) hydroxide ion
   (e) conjugate acid
   (f) conjugate base
2. How does the hydrogen ion concentration compare with the hydroxide ion concentration if a solution is
   (a) neutral?
   (b) acidic?
   (c) basic? K/U
3. Differentiate between the following: K/U
   (a) an Arrhenius acid and an Arrhenius base
   (b) a Brønsted–Lowry acid and a Brønsted–Lowry base
4. Write the equilibrium equation for the reaction of each of the following substances in water. Include hydronium ions in your equations. K/U
   (a) HF
   (b) HNO_2
   (c) HCO_3^-
   (d) HCN
5. Create a table with the following column headings: Substance, Arrhenius theory, and Brønsted–Lowry theory. Complete the table with each of the substances listed, stating whether each is an acid, a base, or both under the two acid–base theories. Explain your answers. K/U C
   (a) $NH_4^+(aq)$
   (b) $NH_3(aq)$
   (c) $H_2O(l)$
   (d) $C_2H_3O_2^-(aq)$
   (e) $H_3PO_4(aq)$
   (f) $Ca(OH)_2(aq)$
   (g) $HCl(aq)$
   (h) $H_3O^+(aq)$
   (i) $HC_2H_3O_2(aq)$
   (j) $H_2PO_4^-(aq)$
6. Identify the acid, its conjugate base, the base, and its conjugate acid in the equilibrium reaction systems represented by the following equations: K/U
   (a) $\mathrm{HNO_2(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{NO_2^-(aq)} + \mathrm{H_3O^+(aq)}$
   (b) $\mathrm{NH_3(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{NH_4^+(aq)} + \mathrm{OH^-(aq)}$
7. Complete each equilibrium equation and then identify the acid, base, conjugate acid, conjugate base, and all amphiprotic entities. K/U C
   (a) $\mathrm{H_3PO_4(aq)} + \mathrm{NH_3(aq)} \rightleftharpoons$
   (b) $\mathrm{HCO_2H(aq)} + \mathrm{CN^-(aq)} \rightleftharpoons$
8. Write acid equilibrium constant equations for each of the following acids: K/U
   (a) HF(aq)
   (b) $HCO_3^-(aq)$
   (c) $HC_4H_7O_2(aq)$
9. For each of the following naturally occurring acids and bases, write the Brønsted–Lowry equation for the reaction with water and identify the acids and bases: K/U A
   (a) methanoic acid (formic acid), $HCHO_2(l)$, produced by ants
   (b) atropine, $C_{17}H_{23}NO_3(aq)$, produced by the belladonna plant
   (c) sodium hydrogen carbonate, $NaHCO_3(s)$, a mineral found in some types of rock
10. A student in your class made the following statement: "All substances that are acids based on the Arrhenius theory are also acidic using the Brønsted–Lowry theory." Do you agree or disagree with this statement? Explain. K/U

Strong and Weak Acids and Bases

8.2

Many medicines are acids or bases. Tylenol (acetaminophen) and Aspirin (acetylsalicylic acid, or ASA) are two common painkillers that are acids. The pH of a 0.25 mol/L solution of acetaminophen is 5.3 while the pH of an equally concentrated solution of ASA is 2.0. Why the difference? Since the K_a of acetaminophen is 1.2×10^{-10} while the K_a of ASA is 3.27×10^{-4}, acetaminophen is much less likely than ASA to ionize to form $H^+(aq)$ ions in aqueous solution. This makes a difference to patients who need relief from pain but cannot tolerate additional acidity in their stomachs.

In earlier Chemistry courses you probably learned a little about strong and weak acids. You may also be aware that there are strong and weak bases. What decides the strength of an acid or a base? This property depends on the equilibrium position of the compound's ionization reaction. Stronger acids and bases have ionization equilibrium positions farther to the right. Weaker acids and bases have equilibrium positions farther to the left. Thus, in water, strong acids or bases will ionize more than weak acids or bases. ASA is a stronger acid than is acetaminophen.

Strong Acids and Weak Acids

When acids dissolve and ionize in water, they form a dynamic equilibrium between reactants and products. A **strong acid** is an acid for which the equilibrium position in an aqueous solution lies far to the right. This means that, at equilibrium, almost all the HA molecules have broken apart to produce ions (**Figure 1(a)**). **Table 1** summarizes some different ways of defining a strong acid. A **weak acid** is one for which the equilibrium position is far to the left. Most of the acid originally placed in the solution is HA molecules at equilibrium. That is, a weak acid ionizes only to a very small extent in aqueous solution, and so exists primarily as non-ionized molecules (**Figure 1(b)**).

strong acid an acid that ionizes almost 100 % in water, producing hydrogen ions

weak acid an acid that only partly ionizes in water, producing hydrogen ions

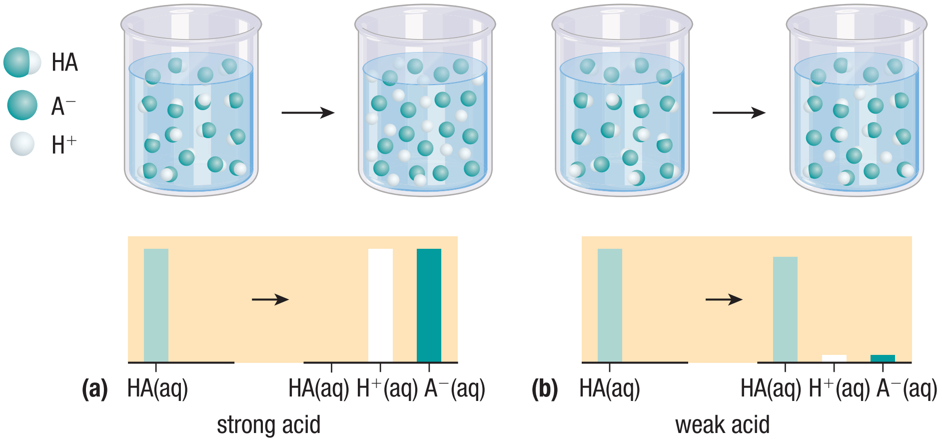


Figure 1 (a) A strong acid is almost completely ionized in water, resulting in relatively high concentrations of $H^+(aq)$ and $A^-(aq)$ ions and a much lower concentration of HA(aq) molecules. (b) A weak acid consists of a relatively high concentration of non-ionized HA(aq) molecules and much lower concentrations of $H^+(aq)$ and $A^-(aq)$ ions.

Table 1 Various Ways to Describe Acid Strength

Property	Strong acid	Weak acid
Value of acid ionization constant, K_a	K_a is large	K_a is small
Position of the ionization equilibrium	far to the right	far to the left
Equilibrium concentration of $H^+(aq)$ compared with original concentration of HA	$[H^+(aq)]_{equilibrium} \approx [HA(aq)]_{initial}$	$[H^+(aq)]_{equilibrium} << [HA(aq)]_{initial}$

As previously discussed, the acid ionization constant, K_a, is the equilibrium constant for the ionization of an acid. The general equation is

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

where K_a always refers to the reaction of an acid, HA(aq), with water to form the conjugate base, A^-(aq), and the hydrogen ion, H^+(aq) (representing the hydronium ion, H_3O^+(aq)). Note that, since the concentration (density) of water is a constant, it is incorporated into the value of K_a. **Table 2** shows some values of K_a.

Table 2 Values of K_a for Some Common Acids

Acid formula	Name	Value of K_a
$HClO_4$(aq)	perchloric acid	very large
HNO_3(aq)	nitric acid	very large
HCl(aq)	hydrochloric acid	very large
HSO_4^-(aq)	hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$(aq)	chlorous acid	1.2×10^{-2}
HF(aq)	hydrofluoric acid	6.6×10^{-4}
HNO_2(aq)	nitrous acid	4.6×10^{-4}
$HC_2H_3O_2$(aq)	ethanoic acid	1.8×10^{-5}
HClO(aq)	hypochlorous acid	3.5×10^{-8}
HCN(aq)	hydrocyanic acid	6.2×10^{-10}
NH_4^+(aq)	ammonium ion	5.8×10^{-10}
HCO_3^-(aq)	hydrogen carbonate ion	4.7×10^{-11}

increasing acid strength

There is an important connection between the strength of an acid and the strength of its conjugate base. The stronger an acid, the weaker its conjugate base, and conversely, the weaker an acid, the stronger its conjugate base (**Figure 2**).

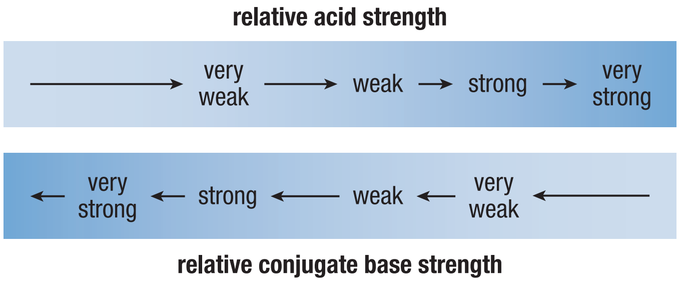


Figure 2 The relationship of acid strength and conjugate base strength for the reaction $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

Oxyacids and Organic Acids

Most familiar acids are **oxyacids**, which have the acidic hydrogen (ionizable hydrogen) atom attached to an oxygen atom. Sulfuric acid is a typical example of a strong oxyacid. Many common weak acids, such as phosphoric acid, H_3PO_4(aq); nitrous acid, HNO_2(aq); and hypochlorous acid, HClO(aq), are also oxyacids.

oxyacid an acid in which the acidic hydrogen atom is attached to an oxygen atom

You learned about organic acids—also called carboxylic acids—in Unit 1. An **organic acid** has a carbon backbone and a carboxyl group (**Figure 3**). Most organic acids are weak acids. Examples are ethanoic acid, $HC_2H_3O_2(aq)$, and benzoic acid, $HC_7H_5O_2(aq)$. Note that the acidic hydrogen atom is written at the beginning of the chemical formula. The remaining hydrogen atoms are not acidic—they do not form $H^+(aq)$ in water. This varies from how you wrote formulas for organic acids in Unit 1.

organic acid an acid (except carbonic acid, $H_2CO_3(aq)$) containing carbon, oxygen, and hydrogen atoms; also called carboxylic acid

There are some important acids in which the acidic hydrogen atom is attached to an atom other than oxygen. The most significant of these are the acids of the halogens (specifically, HF(aq), HCl(aq), HBr(aq), and HI(aq)).

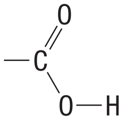


Figure 3 Organic acids (carboxylic acids) contain the carboxyl group. The hydrogen atom attached to oxygen is the ionizable hydrogen.

Strong Bases and Weak Bases

Like acids, bases may be either strong or weak, depending on the position of their equilibrium in solution. A strong base forms an equilibrium that lies farther to the right (toward products) when it reacts with water. A weak base forms an equilibrium that lies farther to the left (toward reactants) when it reacts with water.

Strong Bases

The bases sodium hydroxide, NaOH, and potassium hydroxide, KOH, dissociate completely in aqueous solution to form cations and hydroxide ions, leaving virtually no undissociated base entities in the solution.

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$
$$KOH(s) \rightarrow K^+(aq) + OH^-(aq)$$

Thus, a 1.0 mol/L sodium hydroxide solution really contains 1.0 mol/L $Na^+(aq)$ and 1.0 mol/L $OH^-(aq)$. Since it dissociates completely, sodium hydroxide is called a **strong base**: a base that dissociates completely in aqueous solution.

strong base a base that dissociates completely in water, producing hydroxide ions

All the hydroxides of the Group 1 elements—LiOH, NaOH, KOH, RbOH, and CsOH—are strong bases. The Group 2 (alkaline earth) hydroxides—$Ca(OH)_2$, $Ba(OH)_2$, and $Sr(OH)_2$—are also strong bases. For the Group 2 bases, 2 mol of hydroxide ions are produced for every 1 mol of metal hydroxide dissolved:

$$\underset{\text{1 mol}}{Ca(OH)_2(aq)} \rightarrow \underset{\text{1 mol}}{Ca^{2+}(aq)} + \underset{\text{2 mol}}{2\,OH^-(aq)}$$

Although the alkaline earth hydroxides are strong bases, they are only slightly soluble. The low solubility of these bases can sometimes be an advantage. For example, many antacid medicines are suspensions of metal hydroxides, such as aluminum hydroxide, $Al(OH)_3(s)$, and magnesium hydroxide, $Mg(OH)_2(s)$. The low solubility of these compounds prevents a quick dissociation, which would release a high concentration of hydroxide ions that could harm the tissues lining the mouth, esophagus, and stomach. Although the hydroxide compounds in the antacid do not dissolve well in saliva, they readily dissolve in the highly acidic solution of the stomach. This is because, as dissolved $OH^-(aq)$ ions react with $H^+(aq)$ ions in stomach acid, the dissociation equilibrium position shifts to the right and more base dissociates.

Calcium hydroxide, $Ca(OH)_2$, often called slaked lime, is used in "scrubbers" to remove sulfur dioxide from the exhaust of power plants and refineries. Sulfur dioxide, if released into the air, may react with atmospheric moisture. This reaction produces sulfurous acid, leading to acid precipitation. In the scrubbing process, a suspension of slaked lime is sprayed into the stack gases to react with sulfur dioxide gas according to the following reaction steps:

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$
$$Ca(OH)_2(aq) + H_2SO_3(aq) \rightleftharpoons CaSO_3(s) + 2\,H_2O(l)$$

The final products of these reactions—calcium sulfite and water—are less harmful to the environment than is sulfur dioxide.

Weak Bases

Many compounds are bases even though they do not contain the hydroxide ion. These compounds increase the concentration of hydroxide ions in aqueous solution because of their reaction with water. In other words, these bases are Brønsted–Lowry bases. For example, according to the Brønsted–Lowry theory, ammonia, $NH_3(aq)$, is a base because it reacts with water to form aqueous hydroxide ions:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

In this reaction, water is a Brønsted–Lowry acid and ammonia is a Brønsted–Lowry base. Note that even though ammonia contains no hydroxide ions, it still increases the concentration of hydroxide ions in solution because of its reaction with water. Since the equilibrium position of this reaction is far to the left, ammonia is considered to be a **weak base**. Compounds that react with water as ammonia does are generally weak bases.

weak base a base that only partially reacts with water to produce hydroxide ions

Bases such as ammonia have at least one unshared pair of electrons that is capable of forming a coordinate covalent bond with a hydrogen ion. **Figure 4** shows the reaction of an ammonia molecule with a water molecule.

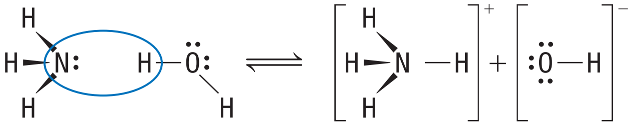
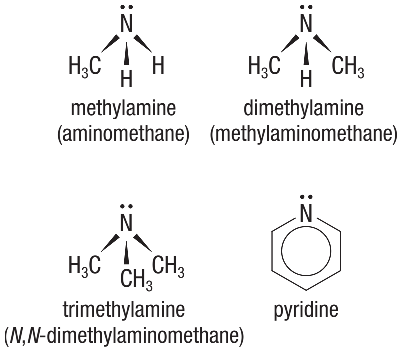


Figure 4 Ammonia and water react to form ammonium ions and hydroxide ions.

There are many bases that, like ammonia, produce hydroxide ions by reacting with water (**Figure 5**). In most of these bases, the lone pair of electrons is located on a nitrogen atom.

Recall the general equation for the reaction of a base, B, with water:

$$\underset{\text{base}}{B(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{BH^+(aq)} + \underset{\substack{\text{conjugate}\\\text{base}}}{OH^-(aq)}$$



methylamine (aminomethane)
dimethylamine (methylaminomethane)
trimethylamine (*N*,*N*-dimethylaminomethane)
pyridine

Figure 5 Some examples of bases that do not contain hydroxide ions in their structures but produce hydroxide ions in aqueous solution by reaction with water

Brønsted-Lowry bases react with water to produce $OH^-(aq)$ ions and a conjugate acid, which together determine the acid–base properties of the aqueous solution. Weak bases, like weak acids, form dynamic equilibria in aqueous solutions. We can write an equilibrium constant for the ionization of a base.

For the reaction of a generic base with water, the equilibrium law equation, K, is written as follows:

$$K = \frac{[OH^-(aq)][BH^+(aq)]}{[B(aq)][H_2O(l)]}$$

However, since the concentration (density) of water is a constant, it can be incorporated into the value of K (just as it was in the equilibrium law equation for K_a). This yields a new constant, K_b, called the **base ionization constant**:

base ionization constant (K_b) the equilibrium constant for the ionization of a base; also called the base dissociation constant

$$K_b = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)]}$$

For example, consider the ionization of ammonia in water. When ammonia reacts with water the equilibrium equation is as follows:

$$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$

The K_b equation for this reaction is

$$K_b = \frac{[OH^-(aq)][NH_4^+(aq)]}{[NH_3(aq)]}$$

The equilibrium position of the reaction between ammonia and water lies far to the left, as is the case with all weak bases. Thus, the K_b values of ammonia and other weak bases tend to be small (for example, for ammonia, $K_b = 1.8 \times 10^{-5}$). **Table 3** lists some common bases and their K_b values. Weak bases are the conjugate bases of weak acids. For example, the ethanoate ion, $C_2H_3O_2^-(aq)$, is the conjugate base of ethanoic acid, $HC_2H_3O_2(aq)$. Similarly, the hypochlorite ion, $ClO^-(aq)$, is the conjugate base for hypochlorous acid, $HClO(aq)$.

UNIT TASK **BOOKMARK**

What is the K_a or K_b value of the consumer product that you have chosen for the Unit Task, outlined on page 582?

Table 3 K_b Values of Selected Weak Bases at 25 °C

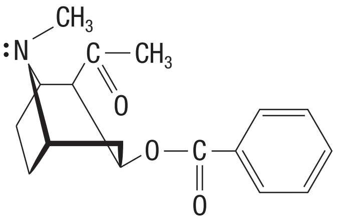
Name of base	Formula	K_b
dimethylamine	$(CH_3)_2NH(aq)$	9.6×10^{-4}
butylamine	$C_4H_9NH_2(aq)$	5.9×10^{-4}
methylamine	$CH_3NH_2(aq)$	4.4×10^{-4}
aniline	$C_6H_5NH_2(aq)$	4.1×10^{-10}
ammonia	$NH_3(aq)$	1.8×10^{-5}
hydrazine	$N_2H_4(aq)$	1.7×10^{-6}
morphine	$C_{17}H_{19}NO_3(aq)$	7.5×10^{-7}
hypochlorite ion	$ClO^-(aq)$	3.45×10^{-7}
pyridine	$C_5H_5N(aq)$	1.7×10^{-9}
ethanoate ion	$C_2H_3O_2^-(aq)$	5.6×10^{-10}
urea	$NH_2CONH_2(aq)$	1.5×10^{-14}

ORGANIC BASES

An organic compound that increases the concentration of hydroxide ions in aqueous solution is called an **organic base**. All organic bases contain carbon atoms and many also contain nitrogen atoms. One group of organic bases is called the alkaloids. Most alkaloids are derived from plants, fungi, and bacteria. Many drugs are based on alkaloids. These drugs include powerful painkillers such as codeine and morphine, and illicit drugs such as cocaine. Caffeine and nicotine are also alkaloids.

All of these compounds are weak organic bases because they contain at least one nitrogen atom with an unbonded pair of electrons that can accept a hydrogen ion, $H^+(aq)$, from water, leaving behind a hydroxide ion that makes the solution more basic. The diagram of cocaine in **Figure 6** shows the pair of electrons on the nitrogen atom.

organic base an organic compound that increases the concentration of hydroxide ions in aqueous solution



cocaine

Figure 6 Cocaine is an addictive alkaloid.

Water as an Acid and a Base

Recall from Section 8.1 that water is the most common amphiprotic substance: it can behave as either an acid or a base. Strangely, water can behave as both an acid and a base in the same reaction. This reaction is called the **autoionization of water** and involves the transfer of a hydrogen ion from one water molecule to another water molecule. The products are a hydroxide ion and a hydronium ion (**Figure 7**).

autoionization of water the transfer of a hydrogen ion from one water molecule to another

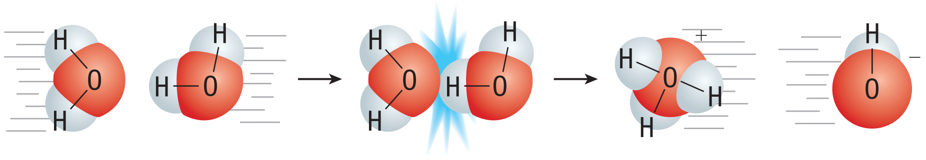


Figure 7 Two water molecules must collide in exactly the right orientation to form a hydronium ion and a hydroxide ion.

In this reaction, one water molecule acts as a Brønsted–Lowry acid by releasing a hydrogen ion, and the other acts as a Brønsted–Lowry base by accepting the hydrogen ion. We can write a chemical equation for the autoionization of water:

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Since this is an equilibrium reaction, we can write an equilibrium law equation:

$$K = \frac{[H_3O^+(aq)][OH^-(aq)]}{[H_2O(l)]^2}$$

As always, we omit $[H_2O(l)]$, leaving the following simplified equation:

$$K = [H_3O^+(aq)][OH^-(aq)]$$

ion-product constant for water (K_w) the equilibrium constant for the autoionization of water

This constant is called the **ion-product constant for water, K_w**. We can also write K_w in an even simpler way if we use H^+ instead of H_3O^+:

$$\boxed{K_w = [H^+(aq)][OH^-(aq)]}$$

Experiments show that, at 25 °C in pure water,

$$[H^+(aq)] = 1.0 \times 10^{-7}\text{mol/L} \quad \text{and} \quad [OH^-(aq)] = 1.0 \times 10^{-7}\text{mol/L}$$

Therefore, we can calculate the value of K_w at 25 °C as follows:

$$\begin{aligned} K_w &= [H^+(aq)][OH^-(aq)] \\ &= (1.0 \times 10^{-7})(1.0 \times 10^{-7}) \\ K_w &= 1.0 \times 10^{-14} \end{aligned}$$

It is important to recognize the meaning of K_w. In any aqueous solution at 25 °C, no matter what the solution contains, the product of $[H^+(aq)]$ and $[OH^-(aq)]$ must always equal 1.0×10^{-14}. There are three possible situations:

- A neutral solution, where $[H^+(aq)] = [OH^-(aq)]$
- An acidic solution, where $[H^+(aq)] > [OH^-(aq)]$
- A basic solution, where $[OH^-(aq)] > [H^+(aq)]$

In each case, however, at 25 °C, $[H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$.

The Relationship between K_w, K_a, and K_b

The ionization reaction of a weak acid, HA(aq), is represented as

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

The acid ionization constant equation is

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

We know that A^-, the conjugate base of HA, is itself a base. As we did for other weak bases, we can write an ionization equation for the reaction of A^- with water:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

And we can write the corresponding base ionization constant equation:

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

If we add together the ionization reactions for HA(aq) and $A^-(aq)$, as we did in Chapter 5 when solving Hess's law problems, we can obtain an overall equation:

$$\begin{array}{l} \cancel{HA(aq)} + H_2O(l) \rightleftharpoons \cancel{A^-(aq)} + H_3O^+(aq) \\ \underline{\cancel{A^-(aq)} + H_2O(l) \rightleftharpoons \cancel{HA(aq)} + OH^-(aq)} \\ \qquad 2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \end{array}$$

Note that this overall reaction is exactly the same as the equation for the autoionization of water. Each of these equations represents an equilibrium with an associated equilibrium constant. For the ionization of the acid, HA(aq):

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

For the ionization of the conjugate base, A^-(aq):

$$K_b = \frac{[HA(aq)][OH^-(aq)]}{[A^-(aq)]}$$

For the overall equation (autoionization of water):

$$K_w = [H_3O^+(aq)][OH^-(aq)]$$

Since there is a mathematical relationship between these three equations, there is also a mathematical relationship between their corresponding equilibrium constants, K_a, K_b, and K_w. If we multiply the K_a for the acid, HA(aq), by the K_b for its conjugate base, A^-(aq), the product is K_w:

$$\begin{aligned} K_aK_b &= \frac{[H_3O^+(aq)]\cancel{[A^-(aq)]}}{\cancel{[HA(aq)]}} \times \frac{\cancel{[HA(aq)]}[OH^-(aq)]}{\cancel{[A^-(aq)]}} \\ &= [H_3O^+(aq)][OH^-(aq)] \\ K_aK_b &= K_w \end{aligned}$$

This relationship holds for all weak acids and bases: for a weak acid HA(aq) and its conjugate base A^-(aq), or for a weak base B(aq) and its conjugate acid BH(aq),

$$K_aK_b = K_w$$

This relationship explains the trend we observed earlier: as the strength of the acid increases, the strength of its conjugate base decreases, and vice versa (**Figure 8**).

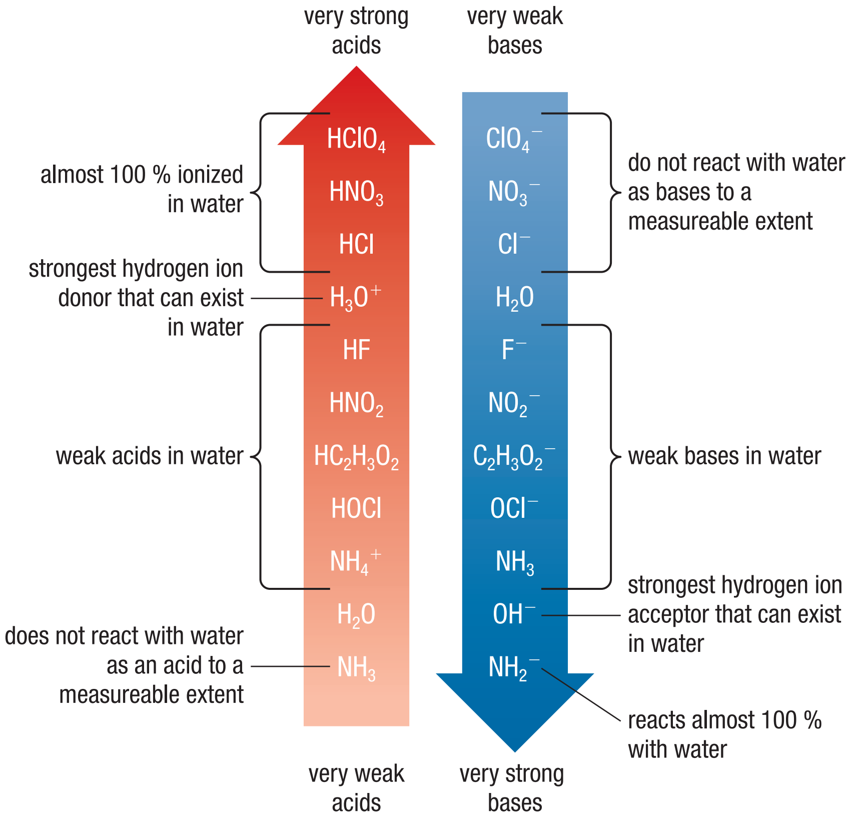


Figure 8 The relative strengths of acids and bases and their respective conjugate bases and conjugate acids. This illustrates which substances are likely to react with water.

Although a strong acid always has a very weak conjugate base, do not conclude that a weak acid has a strong conjugate base. For example, ethanoic acid is a weak acid ($K_a = 1.8 \times 10^{-5}$), but its conjugate base (ethanoate ion, $C_2H_3O_2^-(aq)$) is also a weak base ($K_b = 5.6 \times 10^{-10}$). In general, you can make the following assumptions:

- A strong acid or base has a very weak conjugate.
- A weak acid or base has a weak conjugate.
- A very weak acid or base has a strong conjugate.

Tutorial 1 Calculating K_b or K_a

You can use the equation $K_aK_b = K_w$ to calculate the value of K_a or K_b when given one or the other. For this reason, most tables of ionization constants list only K_a values for weak acids; the K_b values for their corresponding conjugate bases can be calculated.

Sample Problem 1: Calculating K_b from K_a

The hydrogen phosphate ion, $HPO_4^{2-}(aq)$, has a K_a of 1.3×10^{-13} at SATP. What is the base ionization constant, K_b, for the phosphate ion, $PO_4^{3-}(aq)$?

Given: K_a for $HPO_4^{2-}(aq) = 1.3 \times 10^{-13}$; $K_w = 1.0 \times 10^{-14}$

Required: K_b for $PO_4^{3-}(aq)$

Analysis: Use the equation $K_aK_b = K_w$ to solve for K_b, knowing that $K_w = 1.0 \times 10^{-14}$.

Solution:

$$\begin{aligned} K_aK_b &= K_w \\ K_b &= \frac{K_w}{K_a} \\ &= \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-13}} \\ K_b &= 2.4 \times 10^{-2} \end{aligned}$$

Statement: The base ionization constant, K_b, for the phosphate ion is 2.4×10^{-2}.

Practice

1. The value of K_a for the ammonium ion, NH_4^+, is 5.8×10^{-10}. What is the value of the base ionization constant, K_b, for ammonia, NH_3, at SATP? K/U [ans: 1.7×10^{-5}]
2. K_b for the fluoride ion, F^-, is 1.5×10^{-11}. What is the value of K_a for HF at SATP? K/U [ans: 6.7×10^{-4}]

pH and pOH

Recall that, in pure water at 25 °C, the autoionization of water produces a hydrogen ion concentration of 1.0×10^{-7} mol/L and a hydroxide ion concentration of 1.0×10^{-7} mol/L. We may convert these very small concentration values into more convenient positive integer values by using logarithms. The negative logarithm of the hydrogen ion concentration is called **pH**. The negative logarithm of the hydroxide ion concentration is called **pOH**. Thus,

pH the negative logarithm of the concentration of hydrogen ions in an aqueous solution

pOH the negative logarithm of the concentration of hydroxide ions in an aqueous solution

$$pH = -\log[H^+(aq)] \quad \text{and} \quad pOH = -\log[OH^-(aq)]$$

Since pH is a logarithmic value based on 10, the pH changes by 1 for every 10-fold change in $[H^+(aq)]$. For example, a solution of pH 3 has a $H^+(aq)$ ion concentration 10 times greater than a solution of pH 4 and 100 times greater than a solution of pH 5. Also, note that since pH is defined as $-\log[H^+(aq)]$, pH decreases as $[H^+(aq)]$ increases and vice versa. The pH of common aqueous solutions at 25 °C ranges from 0 to 14. This range of pH values is called the pH scale and is shown in **Figure 9**.

We may use the pH equations to calculate the pH of pure water as follows:

$$\begin{aligned} [H^+(aq)] &= 1.0 \times 10^{-7}\ \text{mol/L} \\ pH &= -\log(1.0 \times 10^{-7}) \\ &= -(-7.00) \\ pH &= 7.00 \end{aligned}$$

We may use the pOH equation to calculate the pOH of pure water as follows:

$$[\mathrm{OH^-(aq)}] = 1.0 \times 10^{-7}\ \mathrm{mol/L}$$
$$\mathrm{pOH} = -\log(1.0 \times 10^{-7})$$
$$= -(-7.00)$$
$$\mathrm{pOH} = 7.00$$

In pure water, therefore, pH = 7 and pOH = 7.

This result does not only apply to pure (neutral) water, but to all neutral aqueous solutions. In all neutral aqueous solutions, both pH and pOH are equal to 7. Earlier you learned that, in pure water and all aqueous solutions, the product of $[\mathrm{H^+(aq)}]$ and $[\mathrm{OH^-(aq)}]$ always equals 1.0×10^{-14}, the value of K_w. For a solution to be neutral, the concentration of hydrogen ions must equal the concentration of hydroxide ions. These conditions can only be met if the concentration of hydrogen ions and hydroxide ions are both 1.0×10^{-7} mol/L. Thus, in pure water and all neutral aqueous solutions,

$$[\mathrm{H^+(aq)}] = 1.0 \times 10^{-7}\ \mathrm{mol/L\ and\ pH} = 7$$
$$[\mathrm{OH^-(aq)}] = 1.0 \times 10^{-7}\ \mathrm{mol/L\ and\ pOH} = 7$$

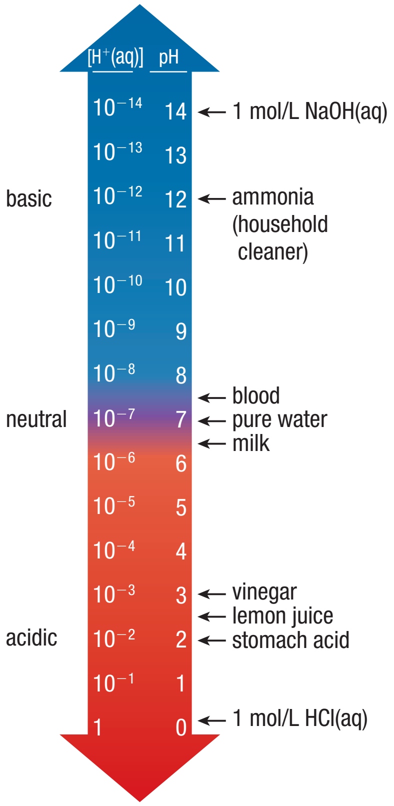


Figure 9 The pH scale showing hydrogen ion concentrations and the pH values of some common substances

pH and pOH of Acidic and Basic Solutions

Acidic and basic solutions are formed when acids and bases are dissolved in water. Recall that acids increase the concentration of $\mathrm{H^+(aq)}$ ions in solution and bases increase the concentration of $\mathrm{OH^-(aq)}$ ions in solution. If we add an acid to pure water, the $[\mathrm{H^+(aq)}]$ will increase to a value higher than 10^{-7} mol/L, and the pH will be lower than 7. For example, in a 0.010 mol/L HCl(aq) solution,

$$[\mathrm{H^+(aq)}] = 1.0 \times 10^{-2}\ \mathrm{mol/L}$$
$$\mathrm{pH} = -\log(1.0 \times 10^{-2})$$
$$\mathrm{pH} = 2$$

Thus, when we dissolve an acid in water, there is an increase in $[\mathrm{H^+(aq)}]$ and a decrease in pH. However, while there is an increase in $[\mathrm{H^+(aq)}]$, there is also a proportional decrease in the concentration of hydroxide ions because, as mentioned earlier, in all aqueous solutions at 25 °C, $[\mathrm{H^+(aq)}][\mathrm{OH^-(aq)}] = 1.0 \times 10^{-14}$. Thus, since $[\mathrm{H^+(aq)}] = 1.0 \times 10^{-2}$ mol/L

and $[\mathrm{H^+(aq)}][\mathrm{OH^-(aq)}] = 1.0 \times 10^{-14}$

then, $(1.0 \times 10^{-2})[\mathrm{OH^-(aq)}] = 1.0 \times 10^{-14}$

$$[\mathrm{OH^-(aq)}] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}}$$
$$[\mathrm{OH^-(aq)}] = 1.0 \times 10^{-12}\ \mathrm{mol/L}$$

We may now calculate the pOH of this solution:

$$\mathrm{pOH} = -\log(1.0 \times 10^{-12})$$
$$\mathrm{pOH} = 12$$

Thus, for a 0.010 mol/L HCl(aq) solution,

$$[\mathrm{H^+(aq)}] = 1.0 \times 10^{-2}\ \mathrm{mol/L\ and\ pH} = 2$$
$$[\mathrm{OH^-(aq)}] = 1.0 \times 10^{-12}\ \mathrm{mol/L\ and\ pOH} = 12$$

As you can see in the example above, we may use the equation

$$[\mathrm{H^+(aq)}][\mathrm{OH^-(aq)}] = 1.0 \times 10^{-14}$$

to determine $[\mathrm{H^+(aq)}]$ or $[\mathrm{OH^-(aq)}]$ (and then pH and pOH) of any aqueous solution at 25 °C when the concentration of one ion or the other is known.

A useful equation in acid–base chemistry may be developed by using the negative logarithm of each component of the K_w equation, as follows:

$$[H^+(aq)][OH^-(aq)] = K_w$$

$$-\log([H^+(aq)][OH^-(aq)]) = -\log K_w$$

Since, mathematically, the logarithm of the product of two values is equal to the sum of the logarithms of the individual values, then

$$(-\log[H^+(aq)]) + (-\log[OH(aq)]) = -\log K_w$$
$$pH + pOH = -\log K_w$$

Since $K_w = 1.0 \times 10^{-14}$ and $-\log(1.0 \times 10^{-14}) = 14$ for all aqueous solutions at 25 °C, then pH + pOH = 14 for all aqueous solutions at 25 °C. This equation is useful because it allows us to calculate the pH or pOH of an aqueous solution at 25 °C if one or the other value is already known.

If, instead of adding an acid to pure water, we add a base, $[OH^-(aq)]$ will temporarily increase. As most of the hydroxide ions react with hydrogen ions, $[H^+(aq)]$ will decrease to a value below 1.0×10^{-7} mol/L and the pH will be greater than 7. At the same time, $[OH^-(aq)]$ will be higher than 1.0×10^{-7} mol/L and the pOH will be lower than 7. Using these relationships, we may state the following quantitative characteristics of solutions:

In neutral solutions,

- $[H^+(aq)] = 1.0 \times 10^{-7}$ mol/L and pH = 7
- $[OH^-(aq)] = 1.0 \times 10^{-7}$ mol/L and pOH = 7

In acidic solutions,

- $[H^+(aq)] > 1.0 \times 10^{-7}$ mol/L and pH < 7
- $[OH^-(aq)] < 1.0 \times 10^{-7}$ mol/L and pOH > 7

In basic solutions,

- $[H^+(aq)] < 1.0 \times 10^{-7}$ mol/L and pH > 7
- $[OH^-(aq)] > 1.0 \times 10^{-7}$ mol/L and pOH < 7

Tutorial 2 Calculating pH from pOH or pOH from pH

In this tutorial, you will learn to calculate pH or pOH when given the other value.

Sample Problem 1: Calculating pOH from pH

A sample of tap water has a measured pH value of 6.8 at 25 °C. What is its pOH?

Given: pH = 6.8

Required: pOH

Analysis: pH + pOH = 14.00

Solution:

$$\begin{aligned} pH + pOH &= 14.00 \\ pOH &= 14.00 - pH \\ &= 14.00 - 6.8 \\ pOH &= 7.2 \end{aligned}$$

Statement: The pOH of the solution is 7.2.

Sample Problem 2: Calculating pH from pOH

The pOH of a sample of human blood is 6.59 at 25 °C. What is its pH value?

Given: pOH = 6.59

Required: pH

Analysis: pH + pOH = 14.00

Solution:

$$\begin{aligned} \text{pH} + \text{pOH} &= 14.00 \\ \text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 6.59 \\ \text{pOH} &= 7.41 \end{aligned}$$

Statement: The pH of the blood sample is 7.41.

For guidance on using the correct number of significant digits in pH calculations, see Appendix A6.3.

Practice

1. Calculate the pOH of a solution that has a pH of 4. K/U [ans: 10]
2. Calculate the pH of a solution that has a pOH of 8.47. K/U [ans: 5.53]
3. Calculate the pH of a solution with a pOH of 2.41. Is this solution acidic, basic, or neutral? K/U [ans: 11.59; basic]

Measuring pH

Scientists in many different disciplines use pH meters to measure the pH of solutions. A **pH meter** is an electronic device with a probe that can be inserted into a solution of unknown pH. The probe contains an acidic aqueous solution enclosed by a special glass membrane that allows $H^+(aq)$ ions to pass through. If the unknown solution has a different pH than the solution in the probe, the meter registers the resulting electric potential and displays the data as a pH reading (**Figure 10**). WEB LINK

pH meter a device that measures the acidity or alkalinity of a solution electronically and displays the result as a pH value

Figure 10 A pH meter shows the pH of a solution.

UNIT TASK **BOOKMARK**

Is the consumer product that you have chosen for the Unit Task (page 582) a strong or weak acid or base? What is its pH? What impact does this have on its effectiveness?

acid–base indicator a substance that changes colour within a specific pH range

Figure 11 These beakers contain solutions with pH values ranging from 1 on the far left to 13 on the far right, along with a little boiled red cabbage and its juice.

Although a pH meter gives a very accurate measurement of a solution's pH, pH meters are not always available or practical. Another common way to determine the pH of a solution is to use an acid–base indicator. An **acid–base indicator** is a substance that has different colours in solutions with different pH values. Since the colour of an acid–base indicator varies with the pH of the solution, you can use an indicator to determine the approximate pH of a solution. For example, juice from red cabbage can range in colour from red to brown, depending on the pH of the solution with which it is mixed (**Figure 11**). Many plants produce naturally coloured substances that are acid–base indicators. For example, tea, red grape juice, and blueberries all change colour with pH. CAREER LINK

Litmus paper is another widely used acid–base indicator. It is a common indicator because it is readily available, inexpensive, and stores well. The dye used in litmus paper comes from lichen. After the water-soluble dye compound is extracted from the lichen, absorbent paper is soaked in the solution. When the paper dries, the litmus indicator is bonded to the paper. There are two types of litmus paper: blue and red. Acidic solutions turn blue litmus red; basic solutions turn red litmus blue. A neutral solution leaves red litmus red and blue litmus blue.

Relating pH or pOH, and Ion Concentration

You may use acid–base indicators or a pH meter to determine the pH of a solution in an investigation. However, at times, you may need to determine the hydrogen or hydroxide ion concentration of a solution from the pH or pOH. Conversely, you may sometimes know the hydrogen ion or hydroxide ion concentration of a solution and need to determine the pH or pOH values.

The following equations allow you to calculate pH from $[H^+(aq)]$ and $[H^+(aq)]$ from pH:

$$\text{pH} = -\log[H^+(aq)]$$
$$10^{-\text{pH}} = [H^+(aq)]$$

Similarly, the following equations allow you to calculate pOH from $[OH^-(aq)]$ and $[OH^-(aq)]$ from pOH:

$$\text{pOH} = -\log[OH^-(aq)]$$
$$10^{-\text{pOH}} = [OH^-(aq)]$$

In the following tutorial, you will practice converting between pH and $[H^+(aq)]$ and between pOH and $[OH^-(aq)]$.

Tutorial 3 Calculating pH, pOH, $[H^+(aq)]$, or $[OH^-(aq)]$

You will often be given the concentration of an acid or base in solution and need to determine the pH of the solution from the concentration of hydrogen ions. You may also need to calculate pOH if you know the concentration of hydroxide ions. In this tutorial, you will convert between these different values.

Sample Problem 1: Calculating pH from $[H^+(aq)]$

A solution of NaOH has a $[H^+(aq)]$ of 5.2×10^{-11} mol/L. What is the pH of the solution?

Given: $[H^+(aq)] = 5.2 \times 10^{-11}$ mol/L

Required: pH

Analysis: $\text{pH} = -\log[H^+(aq)]$

Solution:

SKILLS HANDBOOK **A6.2, A6.3**

$\mathrm{pH} = -\log[\mathrm{H}^+(aq)]$
$\quad = -\log(5.2 \times 10^{-11})$
$\mathrm{pH} = 10.284$

At this point you need to consider significant figures for logarithms. The number of decimal places in the log value must equal the number of significant figures in the original value.

Since there are 2 significant figures in the value of $[\mathrm{H}^+(aq)]$,

$$\begin{aligned} &\qquad\downarrow \\ [\mathrm{H}^+(aq)] &= 5.2 \times 10^{-11} \\ \mathrm{pH} &= 10.28 \\ &\qquad\uparrow \end{aligned}$$

the pH value should be rounded to 2 digits after the decimal.

$\mathrm{pH} = 10.28$

Statement: The solution has a pH of 10.28.

Sample Problem 2: Calculating $[\mathrm{H}^+(aq)]$ from pH

A solution of ethanoic acid has a pH of 5.30. What is the concentration of hydrogen ions in the solution in mol/L?

Given: $\mathrm{pH} = 5.30$

Required: $[\mathrm{H}^+(aq)]$

Analysis: $[\mathrm{H}^+(aq)] = 10^{-\mathrm{pH}}$

Solution:

$[\mathrm{H}^+(aq)] = 10^{-\mathrm{pH}}$
$\quad = 10^{-(5.30)}$ (2 digits following the decimal point)
$[\mathrm{H}^+(aq)] = 5.0 \times 10^{-6}$ (2 significant digits)

Statement: The solution has a hydrogen ion concentration of 5.0×10^{-6} mol/L.

Sample Problem 3: Calculating pOH from $[\mathrm{OH}^-(aq)]$

A solution of ammonia has an $[\mathrm{OH}^-(aq)]$ of 8.2×10^{-12} mol/L. What is the pOH of the solution?

Given: $[\mathrm{OH}^-(aq)] = 8.2 \times 10^{-12}$ mol/L

Required: pOH

Analysis: $\mathrm{pOH} = -\log[\mathrm{OH}^-(aq)]$

Solution:

$\mathrm{pOH} = -\log[\mathrm{OH}^-(aq)]$
$\quad = -\log(8.2 \times 10^{-12})$ (2 significant digits)

$\mathrm{pOH} = 11.09$ (2 digits following the decimal point)

Statement: The solution has a pH of 11.09.

Sample Problem 4: Calculating pH and pOH from $[\mathrm{H}^+(aq)]$

A solution of sulfuric acid has a hydrogen ion concentration of 1.0×10^{-3} mol/L at 25 °C. Calculate the pH and pOH of this solution.

Given: $[\mathrm{H}^+(aq)] = 1.0 \times 10^{-3}$ mol/L

Required: pH, pOH

Analysis: $\mathrm{pH} = -\log[\mathrm{H}^+(aq)]$; $K_w = [\mathrm{H}^+(aq)][\mathrm{OH}^-(aq)]$; $\mathrm{pOH} = -\log[\mathrm{OH}^-(aq)]$

Solution: First, calculate the pH of the solution:

$$\begin{aligned} \text{pH} &= -\log[\text{H}^+(\text{aq})] \\ &= -\log(1.0 \times 10^{-3}) \text{ (2 significant digits)} \end{aligned}$$

$$\text{pH} = 3.00 \text{ (2 digits following the decimal point)}$$

Next, use the equation for K_w to calculate the concentration of hydroxide ions:

$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$$

$$[\text{OH}^-(\text{aq})] = \frac{K_w}{[\text{H}^+(\text{aq})]}$$

$$= \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}}$$

$$[\text{OH}^-(\text{aq})] = 1.0 \times 10^{-11} \text{ mol/L}$$

Finally, calculate the pOH of the solution:

$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-(\text{aq})] \\ &= -\log(1.0 \times 10^{-11}) \text{ (2 significant digits)} \end{aligned}$$

$$\text{pOH} = 11.00 \text{ (2 digits following the decimal point)}$$

Statement: The solution has a pH of 3.00 and a pOH of 11.00.

There is an alternative method of solving Sample Problem 4. Once you know the pH of the solution, you can use the equation pH + pOH = 14 to find pOH.

Practice

1. Calculate the pH of a solution with a $[\text{H}^+(\text{aq})]$ of 1.8×10^{-9} mol/L. K/U [ans: 8.74]
2. Calculate the $[\text{H}^+(\text{aq})]$ in a solution that has a pH of 2.5. K/U [ans: 3.2×10^{-3} mol/L]
3. Calculate the pOH of a solution with an $[\text{OH}^-(\text{aq})]$ of 3.2×10^{-4} mol/L. K/U [ans: 3.49]
4. Calculate the pH and pOH of a solution in which $[\text{OH}^-(\text{aq})] = 1.0$ mol/L. K/U [ans: pOH = 0.00; pH = 14.00]

Research This

Hazardous to Your Teeth

Skills: Researching, Analyzing, Evaluating, Communicating

SKILLS HANDBOOK A5

You should eat and drink a variety of foods and beverages to get all the nutrients you need in your diet. Unfortunately, some common foods and beverages may have adverse health effects on your teeth because something in those foods promotes the erosion of tooth enamel.

1. Conduct research and identify a food or beverage item that is associated with the erosion of tooth enamel.
2. Research the chemical process of tooth erosion.
3. Research how tooth erosion can be prevented.

A. What food or beverage item did you identify and what is its typical pH? K/U

B. Explain the chemical process of tooth erosion and what can be done to prevent it. T/I

C. Weigh the costs and benefits to overall health if a person were to stop consuming the food or beverage you identified. Would you recommend any change regarding consuming this food or beverage? A

D. Create a brief report to educate others about your findings and recommendation. Your report could be in any appropriate format of your choice. C A

WEB LINK

8.2 Review

Summary

- A strong acid or base completely ionizes in water. Its K_a or K_b value is very large.
- A weak acid or base ionizes only slightly in water. Its K_a or K_b value is relatively small.
- Water undergoes autoionization. The ion-product constant for the autoionization of water, K_w, is related to the concentration of hydrogen and hydroxide ions by the equation $K_w = [H^+(aq)][OH^-(aq)]$.
- K_w, K_a, and K_b are related by the equation $K_w = K_aK_b$.
- pH can be determined from the hydrogen ion concentration of a solution using the equation $\text{pH} = -\log[H^+(aq)]$. Similarly, $\text{pOH} = -\log[OH^-(aq)]$.
- pH and pOH are related by the equation $\text{pH} + \text{pOH} = 14$.
- The pH scale is used to describe the acidity or alkalinity of a solution.
- pH meters and acid–base indicators can be used to measure the pH of a solution.

Questions

1. Arrange the following sets of entities according to increasing strength as acids: H_2O, H_3O^+, HCl, $HC_2H_3O_2$, H_2S K/U
2. Arrange the following entities according to increasing strength as bases: F^-, Cl^-, NO_2^-, and CN^-. (Refer to Table 2 on page 496.) K/U
3. Calculate the K_b for the conjugate base of each of the following acids at SATP: K/U
   (a) methanoic acid, $HCHO_2(aq)$, $K_a = 1.8 \times 10^{-4}$
   (b) carbonic acid, $H_2CO_3(aq)$, $K_a = 4.4 \times 10^{-7}$
   (c) hypochlorous acid, $HClO(aq)$, $K_a = 3.5 \times 10^{-8}$
   (d) boric acid, $H_3BO_3(aq)$, $K_a = 5.8 \times 10^{-10}$
4. Calculate the K_a for the conjugate acid of the following bases at SATP: K/U
   (a) pyridine, $C_5H_5N(aq)$, $K_b = 1.7 \times 10^{-9}$
   (b) hydrazine, $N_2H_4(aq)$, $K_b = 1.7 \times 10^{-6}$
   (c) morphine, $C_{17}H_{19}NO_3(aq)$, $K_b = 7.5 \times 10^{-7}$
   (d) dimethylamine, $(CH_3)_2NH(aq)$, $K_b = 9.6 \times 10^{-4}$
5. Use the information given to state whether each solution is acidic or basic and to calculate its unknown $OH^-(aq)$ or $H^+(aq)$ concentration. K/U
   (a) 1.0×10^{-5} mol/L $OH^-(aq)$
   (b) 10.0 mol/L $H^+(aq)$
   (c) 5.0×10^{-7} mol/L $H^+(aq)$
   (d) 7.5×10^{-11} mol/L $OH^-(aq)$
   (e) 7.1×10^{-14} mol/L $H^+(aq)$
   (f) 1.2×10^{-6} mol/L $OH^-(aq)$
6. Determine the hydrogen and hydroxide ion concentrations in the following products: K/U
   (a) vinegar with a pH of 3.23
   (b) oven cleaner with a pH of 13.42
   (c) toilet bowl cleaner with a pH of 2.22
   (d) baking soda with a pH of 8.95
7. Calculate the pH of each of the following solutions at SATP: K/U
   (a) $[H^+(aq)] = 6.2 \times 10^{-11}$ mol/L
   (b) $[OH^-(aq)] = 7.1 \times 10^{-14}$ mol/L
   (c) $\text{pOH} = 4.98$
8. Calculate the pOH of each of the following solutions at SATP: K/U
   (a) $[OH^-(aq)] = 3.1 \times 10^{-4}$ mol/L
   (b) $[H^+(aq)] = 1.0 \times 10^{-7}$ mol/L
   (c) $\text{pH} = 3.84$
9. Calculate $[H^+(aq)]$ and $[OH^-(aq)]$ for each of the following solutions: K/U
   (a) $\text{pH} = 12.00$
   (b) $\text{pH} = 1.54$
   (c) $\text{pOH} = 11.00$
   (d) $\text{pOH} = 4.69$
10. Comment on this statement: "A strong acid is more dangerous than a weak acid." C A
11. While looking up acids on the Internet, a student came across the term "superacid." Research superacids. Write a short report outlining their production, uses, and hazards. C A

WEB LINK

8.3 Explore Applications of Acids

SKILLS MENU

- Researching
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating
- Identifying Alternatives

Equilibrium in an Industrial Process

Scientists have been making and using sulfuric acid, $H_2SO_4(aq)$, for about 400 years. Sulfuric acid is used to make fibres, dyes, explosives, fertilizers, and car batteries. It is also used in the manufacture of some pharmaceutical drugs and other chemical products.

Sulfuric acid must be handled carefully, however. It can be a very dangerous acid, reacting violently with water to release a lot of thermal energy. This indicates that the reaction is exothermic. Spills of sulfuric acid on land can cause significant local environmental damage. Spills into waterways could be even more serious, contaminating aquatic ecosystems and possibly threatening drinking water supplies for people in the area.

Sulfuric acid is produced through a method called the "contact process." The first step in the contact process includes forming sulfur dioxide, $SO_2(g)$. The sulfur dioxide is then converted into sulfur trioxide, $SO_3(g)$.

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) + \text{energy}$$

The sulfur trioxide gas is in turn converted to oleum, $H_2S_2O_7(g)$, which reacts with water to produce concentrated sulfuric acid.

The contact process relies on the concepts of equilibrium and kinetics. Industrial chemists use Le Châtelier's principle to predict how changing the conditions in the system will affect the equilibrium. Changes to the system can include adjusting the temperature, volume, pressure, and concentrations of reactants and products. The chemists' aim is to maximize yield, and reduce waste and energy use. CAREER LINK

According to Le Châtelier's principle, the production of sulfur trioxide is predicted to increase when the pressure is high, there is excess reactant, or the temperature is low. But, as a general rule, the reaction rate increases when the pressure and temperature are both high. This causes a problem, since a high temperature will reduce yield. The solution to this problem is the use of a catalyst. The catalyst allows the reaction to proceed quickly at low temperatures, and thus increases yield. The catalyst used in the reaction from SO_2 to SO_3 is vanadium(V) oxide, $V_2O_5(s)$ (**Figure 1**).

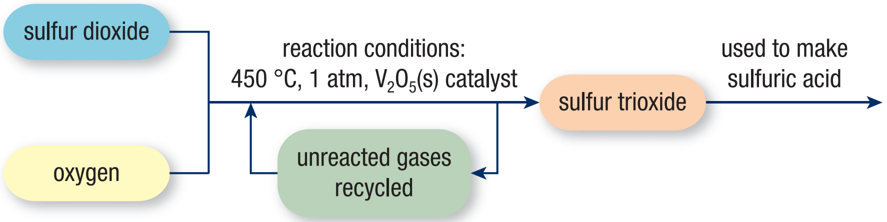


Figure 1 The conditions necessary for the industrial production of sulfur trioxide

During the contact process, equal volumes of sulfur dioxide and oxygen are pumped into the reaction chamber. This means that oxygen is in excess for the reaction. The excess oxygen pushes the reaction (and equilibrium) to the right. This is an inexpensive way to increase the yield of sulfur trioxide.

The Application

A chemical company wants to build a sulfuric acid production plant in your community. The chosen site is near a river that is the municipal water source. The company promises many new jobs that will boost the local economy. Some members of the community are delighted at the prospect of additional jobs. Others have concerns about the safety and environmental implications of the plant.

The company has been given approval to proceed with construction and operation on the condition that they follow strict rules regarding the safe transportation of raw materials and products, the disposal of wastes, and the health and safety of workers within the plant.

Your Goal

SKILLS HANDBOOK A5

To make recommendations to ensure that the plant runs safely, efficiently, and with minimum environmental risk.

Research

Your research should focus on plant design, rules, and procedures to manage risk.

As you compile your recommendations, consider the following questions:

- What are the raw materials for manufacturing sulfuric acid? Where do they come from? What hazards are associated with them? How are they transported? How can these hazards be minimized?
- Chemical accidents are rare, but they do occur. In 2007 there was a sulfuric acid spill into a river near North Bay, Ontario. How could the same thing be prevented from happening again? What should be done in the event of an accident or spill?
- Consider the conditions necessary for the contact process. What specific hazards are associated with these conditions? What could be done to make the plant as safe as possible?
- Are there any waste disposal issues associated with the contact process? If so, how should they be addressed? WEB LINK

Summarize

As you refine your recommendations, be sure that you have considered potential hazards associated with transportation, plant operation, worker safety, disposal, accident prevention, and spill cleanup.

Communicate

- Compile your recommendations into a well-organized summary in the format of your choice, such as a short speech, a written report, or an electronic audiovisual presentation.
- Present your recommendations to your classmates. Review your classmates' recommendations. Make note of any points that you have not considered.
- Discuss your conclusions with a classmate.

Plan for **Action**

Write a letter to a chemical industry journal describing your recommendations for any companies considering setting up a sulfuric acid plant in Canada. Your letter should make it clear that you understand the chemistry behind the process, and that you want any plant to operate as safely as possible.

8.4 Calculations Involving Acidic Solutions

In Section 8.2, we considered fundamental definitions relevant to acid–base solutions. Now we can describe the equilibria in these systems in a more quantitative way.

When we deal with acid–base equilibria, we must focus on the solution components and their chemistry. For example, what entities are present in a 1.0 mol/L solution of HCl(aq)? Since hydrochloric acid is a strong acid, we assume that it is completely ionized. Thus, although the label on the bottle says 1.0 mol/L HCl(aq), the solution contains virtually no HCl(aq) molecules. Typically, container labels indicate the substance(s) used to make the solution but do not necessarily describe the solution components after ionization. Thus a 1.0 mol/L HCl(aq) solution contains mostly water, a significant amount of H^+(aq) ions and Cl^-(aq) ions, and only a very tiny amount of dissolved HCl(aq) molecules. This solution also contains OH^-(aq) ions, but in a highly acidic solution, OH^-(aq) ions are present only in very tiny concentrations and are considered to be minor entities. In solving acid–base problems, the importance of writing the major entities in the solution as the first step is often the key to solving these problems successfully.

LEARNING **TIP**

Problem-Solving Strategy for Acid–Base Problems

Think chemistry. Focus on the solution components and their reactions. It will almost always be possible to choose one reaction that is the most important.

Be systematic. Acid–base problems require a step-by-step approach.

Be flexible. Although all acid–base problems are similar in many ways, important differences do occur. Treat each problem as a unique challenge. Do not try to force a given problem into matching any you have solved before. Look for both the similarities and the differences.

Be patient. The complete solution to a complicated problem cannot be seen immediately in all its detail. Pick the problem apart into its workable steps.

Be confident. Look within the problem for the solution, and let the problem guide you. Assume that you can think it out. Do not rely on memorizing solutions to problems. In fact, memorizing solutions is usually detrimental because you tend to try to force a new problem to be the same as one you have seen before. Understand and think; don't just memorize.

To illustrate the main ideas involved, let us calculate the pH of 1.0 mol/L HCl(aq). We first list the major entities: H^+ (aq), Cl^-(aq), and H_2O(l). When analyzing the acid–base characteristics of aqueous solutions, we consider the contributions of H^+(aq) and OH^-(aq) ions from the autoionization of water and external sources (dissolved acids and bases) separately. Since we want to calculate the pH, we will focus on those major entities that can produce H^+(aq) ions. Obviously, we must consider H^+(aq) from the ionization of HCl(aq). We know that HCl(aq) makes a significant contribution of H^+(aq) ions since it is a strong acid and therefore ionizes completely. However, we must also determine whether the autoionization of water is a significant source of H^+(aq) ions as well.

In pure water at 25 °C, $[H^+(aq)]$ is 1.0×10^{-7} mol/L. According to Le Châtelier's principle, in the acidic solution the H^+(aq) ions from the ionized HCl(aq) will drive the autoionization of water equilibrium to the left. Thus, the concentration of H^+(aq) produced by the autoionization of water will be even less than 1.0×10^{-7} mol/L. This is a negligible quantity compared with the 1.0 mol/L H^+(aq) contributed by the ionization of HCl(aq). Therefore, for this solution, we do not include the H^+(aq) ions produced by the autoionization of water in the calculation of pH; we only use the $[H^+(aq)]$ produced by the ionization of HCl(aq). Since HCl(aq) is a strong acid,

$$[H^+(aq)] = 1.0 \text{ mol/L}$$

$$\begin{aligned} \text{pH} &= -\log[H^+] \\ &= -\log(1.0) \\ \text{pH} &= 0 \end{aligned}$$

Remember that, when analyzing equilibrium problems for solutions of acids and bases, all ions must be accounted for—hydrogen ions, hydroxide ions, conjugate bases, and conjugate acids—because these entities may all have an effect on the acid–base characteristics of the solution.

Calculations Involving Solutions of Strong Acids

Recall that a strong acid ionizes almost completely in water. Therefore, when solving problems involving strong acids, we can assume that the concentration of hydrogen ions in the solution is equal to the given concentration of the acid in the solution.

Tutorial 1 Determining $[H^+(aq)]$, $[OH^-(aq)]$, pH, and pOH

In this tutorial, you will learn how to calculate the $[H^+(aq)]$, $[OH^-(aq)]$, pH, and pOH of a solution of a strong acid, given the concentration of the acidic solution.

Sample Problem 1: Calculating $[H^+(aq)]$, $[OH^-(aq)]$, pH, and pOH from Solution Concentration

A scientist dilutes a commercial solution of nitric acid, $HNO_3(aq)$, by adding water. The final solution has 0.25 mol $HNO_3(l)$ in a total volume of 1.00 L. Determine the concentration of hydrogen ions and hydroxide ions, and the pH and pOH of the final solution at SATP.

Given: 0.25 mol HNO_3 (aq) in 1.00 L solution

Required: $[H^+(aq)]$ and $[OH^-(aq)]$

Solution:

Step 1. Calculate the amount concentration of the solution.

Since the solution that the scientist prepared has 0.25 mol nitric acid in a total volume of 1.00 L, the amount concentration is 0.25 mol/L $HNO_3(aq)$, or

$$[HNO_3(aq)] = 0.25 \text{ mol/L}$$

Step 2. Determine the concentration of hydrogen ions in solution.

Nitric acid is a strong acid that ionizes 100 % in water, according to the equation

$$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$$

Therefore, every molecule of HNO_3 produces 1 hydrogen ion. You can therefore write

$$[H^+(aq)] = [HNO_3(aq)]$$

Step 3. Identify the major entities in solution.

The main entities in solution are $H^+(aq)$, $NO_3^-(aq)$, and $H_2O(l)$.

Step 4. Identify the major source(s) of hydrogen ions.

Since $HNO_3(aq)$ is a strong acid, you may ignore the $H^+(aq)$ ions contributed by the autoionization of water. Therefore, the only significant source of $H^+(aq)$ in solution is the ionization of $HNO_3(aq)$.

Step 5. Determine $[H^+(aq)]$.

Since HNO_3 ionizes completely, then

$$[H^+(aq)] = 0.25 \text{ mol/L}$$

Step 6. Calculate the pH of the solution from $[H^+(aq)]$.

$$\begin{aligned} pH &= -\log[H^+(aq)] \\ &= -\log(0.25 \text{ mol/L}) \\ pH &= 0.60 \end{aligned}$$

Step 7. Use the K_w equation to calculate $[OH^-(aq)]$. Rearrange the equation so that the term you need is on the left side, then substitute in the known values.

$$\begin{aligned} K_w &= [H^+(aq)][OH^-(aq)] \\ [OH^-(aq)] &= \frac{K_w}{[H^+(aq)]} \\ &= \frac{1.0 \times 10^{-14}}{0.25} \text{ mol/L} \\ [OH^-(aq)] &= 4.0 \times 10^{-14} \text{ mol/L} \end{aligned}$$

Step 8. Use $[OH^-(aq)]$ to calculate the pOH of the solution.

$$\begin{aligned} pOH &= -\log [OH^-(aq)] \\ &= -\log (4.0 \times 10^{-14}) \\ pOH &= 13.40 \end{aligned}$$

Statement: For a 0.25 mol/L solution of $HNO_3(aq)$, the concentration of hydrogen ions is 0.25 mol/L, the concentration of hydroxide ions is 4.0×10^{-14} mol/L, pH is 0.60, and pOH is 13.40.

Practice

1. A hydrochloric acid solution has a concentration of 0.0700 mol/L. Calculate $[OH^-(aq)]$. K/U [ans: 1.43×10^{-13} mol/L].
2. A 2.00 L hydrobromic acid solution, HBr(aq), contains 0.070 mol of acid. Calculate the pH and pOH of the solution. K/U [ans: pH = 1.46; pOH = 12.54]

Calculations Involving Solutions of Weak Acids

When strong acids dissolve in water, virtually all of the acid molecules ionize into anions and hydrogen ions. However, weak acids do not completely ionize in water. Therefore, in a solution of a weak acid, there is a relatively large concentration of non-ionized acid molecules and much smaller concentrations of anions and hydrogen ions. Nevertheless, you may calculate the pH of a weak acid solution if you know the K_a value of the weak acid.

Percentage Ionization of Weak Acids

Before we calculate the pH of a weak acid solution, we will calculate the percentage ionization of a weak acid when it is dissolved in water. Consider the ionization of the generic weak acid, HA, in water. Since HA is a weak acid, only a small fraction of the molecules will ionize to form dissolved hydrogen ions and $A^-(aq)$ ions. If 0.10 mol of HA is added to 1.00 L of water, most of the HA molecules will remain non-ionized. Scientists commonly refer to the **percentage ionization** of weak acids, which is defined as follows:

percentage ionization the percentage of a solute that ionizes when it dissolves in a solvent

$$\text{percentage ionization} = \frac{\text{concentration of ionized acid}}{\text{initial concentration of acid}} \times 100\ \%$$

WEB LINK

For the general weak acid ionization reaction

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

we may write the following equation:

$$\text{percentage ionization} = \frac{[H^+(aq)]}{[HA(aq)]} \times 100\ \%$$

and therefore

$$[H^+(aq)] = \frac{\text{percentage ionization}}{100\ \%} \times [HA(aq)]$$

where [HA(aq)] is the initial concentration of the acid.

Chemical analysis indicates that most weak acids ionize much less than 50 %. One common weak acid, ethanoic acid, $HC_2H_3O_2(aq)$, has a percentage ionization of about 1.3 % in aqueous solution at SATP. CAREER LINK

$$HC_2H_3O_2(aq) \xrightleftharpoons{1.3\ \%} H^+(aq) + C_2H_3O_2^-(aq)$$

In other words, in a 0.10 mol/L solution of ethanoic acid, only 1.3 % of the $HC_2H_3O_2(aq)$ molecules ionize to form hydrogen ions and ethanoate ions.

$$[H^+(aq)] = \frac{1.3}{100} \times 0.10\ \text{mol/L}$$

$$[H^+(aq)] = 1.3 \times 10^{-3}\ \text{mol/L}$$

Figure 1 Methanoic acid, also called formic acid, is one of the substances produced by ants that make their bite so painful.

Tutorial 2 Percentage Ionization and K_a of a Weak Acid

If you know the pH of a weak acid solution, you can calculate the percentage ionization of the acid. In this tutorial, you will calculate first the percentage ionization of a weak acid in solution, and then the K_a value of an acid.

Sample Problem 1: Calculating Percentage Ionization from pH

A chemist prepares a 0.10 mol/L solution of methanoic acid, $HCHO_2(aq)$, an acid produced by some ant species to protect themselves (**Figure 1**). The pH of the solution is 2.38. Determine the percentage ionization of the acid in the solution.

Given: pH = 2.38

Required: percentage ionization of methanoic acid

Solution:

Step 1. Calculate the $H^+(aq)$ concentration from the pH.

$$[H^+(aq)] = 10^{-pH}$$
$$= 10^{-2.38}$$
$$[H^+(aq)] = 4.169 \times 10^{-3}\ \text{mol/L}$$

Step 2. Calculate the percentage ionization of the acid in solution.

$$\frac{\text{percentage ionization}}{100} = \frac{[\mathrm{H^+(aq)}]}{[\mathrm{HA(aq)}]}$$

$$\text{percentage ionization} = \frac{[\mathrm{H^+(aq)}]}{[\mathrm{HA(aq)}]} \times 100\ \%$$

$$= \frac{4.169 \times 10^{-3}}{0.10} \times 100\%$$

$$\text{percentage ionization} = 4.2\ \%$$

Statement: Methanoic acid ionizes 4.2 %.

Sample Problem 2: Calculating K_a from Percentage Ionization

A chemistry student prepares a solution of ethanoic acid, $HC_2H_3O_2(aq)$, with a concentration of 0.1000 mol/L. If the percentage ionization of ethanoic acid is 1.3 %, what is the acid ionization constant, K_a, for ethanoic acid?

Given: concentration of solution, $c_{HC_2H_3O_2}$ = 0.1000 mol/L; percentage ionization = 1.3 %

Required: K_a for ethanoic acid

Solution:

Step 1. Write the ionization equation for ethanoic acid. Use that to write the equation for K_a.

$$\mathrm{HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)}$$

$$K_a = \frac{[\mathrm{H^+(aq)}][\mathrm{C_2H_3O_2^-(aq)}]}{[\mathrm{HC_2H_3O_2(aq)}]}$$

Step 2. Use the percentage ionization equation to determine how much of the acid ionizes.

You are told that the percentage ionization of ethanoic acid in solution is 1.3 % and the concentration of the initial solution is 0.1000 mol/L. Therefore, the decrease in concentration of ethanoic acid molecules at equilibrium will be

$$(0.1000\ \text{mol/L})\left(\frac{1.3}{100}\right) = 0.0013\ \text{mol/L}$$

According to the balanced ionization equation, the mole ratio is 1:1:1. Therefore, you know that the concentrations of $H^+(aq)$ and $C_2H_3O_2^-(aq)$ each increase by 0.0013 mol/L.

Step 3. Organize the information above in an ICE table (**Table 1**) in which x represents the change in $[HC_2H_3O_2(aq)]$ that occurs as the reaction reaches equilibrium.

Table 1 ICE Table for the Ionization of Ethanoic Acid

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_2H_3O_2^-(aq)$
I	0.1000		0		0
C	–0.0013		+0.0013		+0.0013
E	0.0987		0.0013		0.0013

Step 4. Substitute the equilibrium concentrations into the K_a equation and solve for K_a.

$$K_a = \frac{[\mathrm{H^+(aq)}][\mathrm{C_2H_3O_2^-(aq)}]}{[\mathrm{HC_2H_3O_2(aq)}]}$$

$$= \frac{(0.0013)(0.0013)}{(0.0987)}$$

$$K_a = 1.7 \times 10^{-5}$$

Statement: The acid ionization constant, K_a, for ethanoic acid is 1.7×10^{-5}.

Practice

1. Calculate the percentage ionization of a 0.050 mol/L solution of propanoic acid, $HC_3H_5O_2(aq)$, with a pH of 2.78. K/U [ans: 3.3 %]
2. A 0.100 mol/L solution of hydrofluoric acid, HF(aq), has a percentage ionization of 7.8 %. Calculate the K_a for hydrofluoric acid. K/U [ans: 6.6×10^{-4}]

Calculating the pH of Weak Acid Solutions

A weak acid ionizing in water behaves much like any equilibrium reaction system. Remembering this, we will proceed carefully and systematically to calculate the pH of a weak acid solution. Although some of the procedures we develop here may seem unnecessary, they will be helpful as the problems become more complicated.

Figure 2 Hydrofluoric acid used to be widely used for etching glass. However, because of the health risks posed by its corrosiveness, it is being replaced by other, safer compounds.

Tutorial 3 Calculating the pH of a Weak Acid Solution

This tutorial shows two different methods for calculating the pH of a weak acid solution, given the value of the acid ionization constant.

Sample Problem 1: Calculating the pH of a Weak Acid Solution from K_a

The standard value for the K_a of hydrofluoric acid, HF(aq), is 6.6×10^{-4}. Calculate the pH of a 1.00 mol/L solution of hydrofluoric acid (**Figure 2**).

Given: $K_a = 6.6 \times 10^{-4}$; concentration, [HF(aq)] = 1.00 mol/L

Required: pH

Solution:

Step 1. Identify the major entities in the solution.

From its small K_a value, you know that hydrofluoric acid is a weak acid and will ionize only slightly. Thus, the major entities in solution are HF(aq) and $H_2O(aq)$.

Step 2. Decide which of the major entities produces $H^+(aq)$ ions.

Both HF(aq) and $H_2O(aq)$ can do so:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Step 3. Identify the major source(s) of $H^+(aq)$ ions.

By comparing the K_a for HF(aq) with the K_w for $H_2O(l)$, you can see that hydrofluoric acid is a much stronger acid than water. Thus you may ignore the insignificant contribution of $H^+(aq)$ made by the autoionization of water. Therefore, it is the ionization of HF(aq) that will determine the equilibrium concentration of $H^+(aq)$ and hence the pH.

Step 4. Write the equilibrium constant equation for the reaction that is the primary source of $H^+(aq)$ ions.

$$K_a = \frac{[H^+(aq)][F^-(aq)]}{[HF(aq)]}$$
$$6.6 \times 10^{-4} = \frac{[H^+(aq)][F^-(aq)]}{[HF(aq)]}$$

Step 5. Determine the changes in concentration that occur as the reaction reaches equilibrium, using an ICE table.

Before any HF(aq) molecules ionize, the concentration of HF(aq) is 1.00 mol/L, and the concentrations of $H^+(aq)$ and $F^-(aq)$ are both 0 mol/L. Ignore $H^+(aq)$ ions produced by the autoionization of water. As the reaction progresses toward equilibrium, HF(aq) molecules will ionize to produce $H^+(aq)$ and $F^-(aq)$ ions in a 1:1 molar ratio. Thus, at equilibrium, $[H^+(aq)] = [F^-(aq)]$.

Let x represent the change in [HF(aq)] that occurs as the reaction reaches equilibrium. Your ICE table should be similar to **Table 2**.

Table 2 ICE Table for the Ionization of Hydrofluoric Acid

	$HF(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$F^-(aq)$
I	1.00		0		0
C	$-x$		$+x$		$+x$
E	$1.00 - x$		x		x

Step 6. Substitute the equilibrium concentrations from the ICE table into the equilibrium constant equation:

$$K_a = \frac{[H^+(aq)][F^-(aq)]}{[HF(aq)]}$$

$$6.6 \times 10^{-4} = \frac{[H^+(aq)][F^-(aq)]}{[HF(aq)]}$$

$$= \frac{(x)(x)}{1.00 - x}$$

$$6.6 \times 10^{-4} = \frac{x^2}{1.00 - x}$$

Step 7. Solve the equilibrium constant equation.

First, determine if a simplifying assumption may be made to solve this equation. The hundred rule states that, if the concentration to which x is added or subtracted is at least 100 times the value of the equilibrium constant, the simplifying assumption will give an error of less than 5 %. In general, a difference of less than 5 % justifies the simplifying assumption. In this case, apply the hundred rule to determine whether x is small enough for us to assume that $1.00 - x \approx 1.00$, just as you did in similar equilibrium problems in Chapter 7:

$$\frac{[HF(aq)_{\text{initial}}]}{K_a} = \frac{1.00}{6.6 \times 10^{-4}}$$

$$\frac{[HF(aq)_{\text{initial}}]}{K_a} = 1515.2$$

Since the $\frac{[HF(aq)_{\text{initial}}]}{K_a}$ ratio is much greater than 100, you may assume that

$1.00 - x \approx 1.00$

Thus, the equilibrium equation we will use is

$$6.6 \times 10^{-4} \approx \frac{x^2}{1.00}$$

Step 8. Solve for *x*.

$$6.6 \times 10^{-4} \approx \frac{x^2}{1.00}$$

$$x^2 \approx (6.6 \times 10^{-4})(1.00)$$

$$x^2 \approx 6.6 \times 10^{-4}$$

$$x \approx \sqrt{6.6 \times 10^{-4}}$$

$$x \approx 2.6 \times 10^{-2}$$

Step 9. Use the 5 % rule to check your result.

This assumption was used in the denominator of the equilibrium equation used in Step 7. The procedure for doing this is the same as the procedure used in similar equilibrium problems in Chapter 7. To test the assumption, compare the calculated value of *x* to the initial concentration of the acid, [HF(aq)]. If *x* is less than or equal to 5 % of the initial concentration, you may be confident that the simplifying assumption made in Step 7 is valid.

$$\frac{x}{[\mathrm{HF(aq)}]} \times 100\ \% = \frac{2.6 \times 10^{-2}}{1.00} \times 100\ \%$$

$$\frac{x}{[\mathrm{HF(aq)}]} \times 100 = 2.6\ \%$$

Since 2.6 % < 5 %, the error in this result is acceptable.

Step 10. Use the ICE table and the value of *x* to determine the hydrogen ion concentration at equilibrium and then calculate pH.

Since $[\mathrm{H^+(aq)}] = x$ (from the ICE table)

and $x \approx 2.6 \times 10^{-2}$

$[\mathrm{H^+(aq)}] \approx 2.6 \times 10^{-2}$ mol/L

$$\mathrm{pH} = -\log[\mathrm{H^+(aq)}]$$

$$\mathrm{pH} \approx -\log(2.6 \times 10^{-2})$$

$$\mathrm{pH} \approx 1.59$$

Statement: The pH of the solution is 1.59.

Sample Problem 2: Calculating pH from K_a

The hypochlorite ion, $\mathrm{ClO^-(aq)}$, is a strong bleaching agent often found in household bleaches and disinfectants. It is also the active ingredient that forms when swimming pool water is treated with chlorine (**Figure 3**). In addition to its bleaching abilities, the hypochlorite ion has a relatively high affinity for hydrogen ions and forms weakly acidic hypochlorous acid, HClO(aq). Calculate the pH of a 0.100 mol/L solution of hypochlorous acid. (You will have to look up the value of K_a in Table 1, Appendix B5.)

Given: concentration, $c_{\mathrm{HClO}} = 0.100$ mol/L

Required: pH

Solution:

Step 1. Identify the major entities in solution at equilibrium.

Major entities are HClO(aq) and H_2O(aq).

Step 2. Look up the value of K_a.

$K_a = 3.5 \times 10^{-8}$

Step 3. Identify the primary source of hydrogen ions.

Although HClO(aq) and H_2O(l) can both produce $\mathrm{H^+(aq)}$, the K_a of hypochlorous acid (3.5×10^{-8}) is many orders of magnitude larger than K_w (1.0×10^{-14}). Therefore, assume that all of the $\mathrm{H^+(aq)}$ comes from hypochlorous acid.

Figure 3 This chlorine dispenser floats in a swimming pool and slowly releases chlorine. When the chlorine reacts with water it produces hypochlorous acid, HClO(aq). This weak acid kills bacteria and other micro-organisms.

Step 4. Write the equilibrium constant equation for the reaction that is the primary source of $H^+(aq)$ ions.

$$K_a = \frac{[H^+(aq)][ClO^-(aq)]}{[HClO(aq)]}$$

$$3.5 \times 10^{-8} = \frac{[H^+(aq)][ClO^-(aq)]}{[HClO(aq)]}$$

Step 5. Determine initial and equilibrium concentrations.

Set up an ICE table for the ionization of HClO(aq), letting x represent the change in [HClO(aq)] (**Table 3**).

Table 3 ICE Table for the Ionization of Hypochlorous Acid

	HClO(aq)	$\rightleftharpoons$	**H^+(aq)**	+	**ClO^-(aq)**
I	0.100		0		0
C	$-x$		$+x$		$+x$
E	$0.100 - x$		x		x

Step 6. Substitute values from the ICE table into the equilibrium constant equation.

$$3.5 \times 10^{-8} = \frac{[H^+(aq)][ClO^-(aq)]}{[HClO(aq)]}$$

$$= \frac{(x)(x)}{0.100 - x}$$

$$3.5 \times 10^{-8} = \frac{x^2}{0.100 - x}$$

Step 7. Use the hundred rule to determine whether any simplifying assumptions may be made.

$$\frac{[HClO(aq)_{\text{initial}}]}{K_a} = \frac{0.100}{3.5 \times 10^{-8}}$$

$$\frac{[HClO(aq)_{\text{initial}}]}{K_a} = 2.9 \times 10^6$$

Since the $\frac{[HClO(aq)_{\text{initial}}]}{K_a}$ ratio is much greater than 100, assume that

$0.100 - x \approx 0.100$

Thus, the equilibrium equation you will use is

$$3.5 \times 10^{-8} \approx \frac{x^2}{0.100}$$

Step 8. Solve for x.

$$3.5 \times 10^{-8} \approx \frac{x^2}{0.100}$$

$$x^2 \approx (3.5 \times 10^{-8})(0.100)$$

$$x^2 \approx 3.5 \times 10^{-9}$$

$$x \approx \sqrt{3.5 \times 10^{-9}}$$

$$x \approx 5.9 \times 10^{-5}$$

Step 9. Use the 5 % rule to check your results.

$$\frac{x}{[HClO(aq)]} \times 100\ \% = \frac{5.9 \times 10^{-5}}{0.100} \times 100\ \%$$

$$\frac{x}{[HClO(aq)]} \times 100\ \% = 0.059\ \%$$

Since 0.059 % < 5 %, the error in this result is acceptable.

Step 10. Determine $[H^+(aq)]$ at equilibrium and calculate pH.

Since $[H^+(aq)] = x$ (from the ICE table)

and $x \approx 5.9 \times 10^{-5}$

$[H^+(aq)] \approx 5.9 \times 10^{-5}$

$$\begin{aligned} pH &= -\log[H^+(aq)] \\ &\approx -\log(5.9 \times 10^{-5}) \\ pH &\approx 4.23 \end{aligned}$$

Statement: The pH of a 0.100 mol/L hypochlorous acid solution, $HClO(aq)$, is 4.23.

Practice

1. What is the pH of a 6.18×10^{-3} mol/L solution of hydrocyanic acid, $HCN(aq)$? (Look up the value of K_a for $HCN(aq)$ in Table 1, Appendix B5.) K/U [ans: 5.7]
2. What is the pH of a 0.10 mol/L solution of nitrous acid, $HNO_2(aq)$? (Look up the value of K_a for $HNO_2(aq)$ in Table 1, Appendix B5.) K/U [ans: 2.2]

You have now seen how to use the K_a values for weak acids to determine the pH of a solution. We can also reverse the calculations to determine K_a from pH.

Tutorial 4 Calculating the K_a of a Weak Acid Solution

In this tutorial, you will learn a problem-solving strategy to help you determine the acid ionization constant for a weak acid given the pH of the equilibrium solution.

Sample Problem 1: Calculating K_a from pH

A solution of hypochlorous acid, $HClO(aq)$, has a concentration of 0.100 mol/L. If the pH of the solution is 4.23, calculate the K_a of hypochlorous acid.

Given: pH = 4.23; $[HClO(aq)] = 0.100$ mol/L

Required: K_a

Solution:

Step 1. Identify the source(s) of hydrogen ions. Assume that, while $HClO(aq)$ is a weak acid, it is a much stronger acid than water and so all of the $H^+(aq)$ in solution comes from the ionization of hypochlorous acid molecules, not water molecules. You will validate this assumption after calculating K_a.

Step 2. Write the ionization reaction equation and the equilibrium constant equation.

$$HClO(aq) \rightleftharpoons H^+(aq) + ClO^-(aq)$$

$$K_a = \frac{[H^+(aq)][ClO^-(aq)]}{[HClO(aq)]}$$

The reaction equation shows that for each mole of $H^+(aq)$ produced, 1 mol of $ClO^-(aq)$ is produced. Therefore, at equilibrium, $[H^+(aq)] = [ClO^-(aq)]$.

Step 3. Determine the concentration of the initial acid at equilibrium.

Since $HClO(aq)$ is a weak acid, assume that only a small fraction of $HClO(aq)$ molecules ionize. Therefore, assume that, at equilibrium,

$[HClO(aq)] = 0.100$ mol/L

Step 4. Determine the $[H^+(aq)]$ at equilibrium using the known pH of the solution.

$$\begin{aligned} pH &= 4.23 \\ [H^+(aq)] &= 10^{-pH} \\ &= 10^{-4.23} \\ [H^+(aq)] &= 5.9 \times 10^{-5}\ \text{mol/L} \end{aligned}$$

Step 5. Substitute the equilibrium concentrations into the acid ionization equation and solve for K_a.

$$\begin{aligned} K_a &= \frac{[H^+(aq)][ClO^-(aq)]}{[HClO(aq)]} \\ &= \frac{(5.9 \times 10^{-5})(5.9 \times 10^{-5})}{0.100} \\ K_a &= 3.5 \times 10^{-8} \end{aligned}$$

Step 6. Validate the assumption made in Step 1.

Since the calculated value of K_a (3.5×10^{-8}) is much larger than K_w (1.0×10^{-14}), our assumption that $HClO(aq)$ is the main source of $H^+(aq)$ is valid.

Step 7. Validate the assumption made in Step 3.

You assumed that at equilibrium,

$[HClO(aq)] = 0.100$ mol/L

$$\frac{[HClO(aq)_{initial}]}{K_a} = \frac{0.100}{3.5 \times 10^{-8}}$$

$$\frac{[HClO(aq)_{initial}]}{K_a} = 2857143$$

Since the $\frac{[HClO(aq)_{initial}]}{K_a}$ ratio is much greater than 100, our assumption is valid.

Statement: The value of the acid ionization constant, K_a, of hypochlorous acid is 3.5×10^{-8}.

Practice

1. A 0.050 mol/L solution of nicotinic acid, $HC_2H_6NO_2(aq)$, has a pH of 3.08. Calculate K_a for nicotinic acid. K/U [ans: 1.4×10^{-5}]
2. The pH of a 0.25 mol/L solution of benzoic acid, $HC_7H_5O_2(aq)$, is 2.40. Determine K_a for benzoic acid. K/U [ans: 6.3×10^{-5}]

Polyprotic Acids

The common strong acids are hydrochloric acid, $HCl(aq)$, nitric acid, $HNO_3(aq)$, and perchloric acid, $HClO_4(aq)$. An acid of this type is called a **monoprotic acid** because it has only one ionizable hydrogen atom. Hydrogen atoms that may ionize to form $H_3O^+(aq)$ ions are sometimes called "acidic hydrogens."

An acid that has more than one ionizable hydrogen atom is called a **polyprotic acid**. Sulfuric acid, $H_2SO_4(aq)$, and phosphoric acid, $H_3PO_4(aq)$, are examples of acids that are polyprotic. Sulfuric acid has 2 hydrogen atoms that may ionize to form $H_3O^+(aq)$ ions in water (**Figure 4**). Phosphoric acid has 3 such hydrogen atoms. We can describe these acids even more precisely using the terms "diprotic" (able to produce 2 hydronium ions) and "triprotic" (able to produce 3 hydronium ions). In the case of sulfuric acid, the first ionization reaction is strong. The single arrow in the following equation indicates that virtually every $H_2SO_4(aq)$ molecule ionizes into $H^+(aq)$ and $HSO_4^-(aq)$ and the reverse reaction is insignificant:

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$

The second ionization—that of the $HSO_4^-(aq)$ ion—is weak, however. This results in a much higher concentration of $HSO_4^-(aq)$ ions than $SO_4^{2-}(aq)$ ions in solution:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

Note that both strong and weak acids may be polyprotic.

monoprotic acid an acid that possesses only one ionizable (acidic) hydrogen atom

polyprotic acid an acid that possesses more than one ionizable (acidic) hydrogen atom

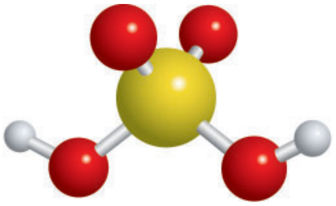


Figure 4 Sulfuric acid has 2 hydrogen atoms (represented as white spheres) that may be removed, one at a time, when the acid ionizes.

Ionization of Polyprotic Acids

Polyprotic acids do not ionize completely in one step. Ionizations occur in two or more steps and release only one hydrogen ion at a time. Each step in the ionization of a polyprotic acid has its own acid ionization constant. The K_a values for a polyprotic acid are numbered according to the reaction step they represent. K_{a1} is for the first ionization reaction step, K_{a2} is for the second ionization, and so on. The steps involved in the ionization of oxalic acid, $H_2C_2O_4(aq)$, a weak diprotic acid, are as follows:

- First ionization reaction

$$H_2C_2O_4(aq) \rightleftharpoons H^+(aq) + HC_2O_4^-(aq) \quad (K_{a1} = 5.4 \times 10^{-2})$$

$$K_{a1} = \frac{[H^+(aq)][HC_2O_4^-(aq)]}{[H_2C_2O_4(aq)]}$$

UNIT TASK **BOOKMARK**

Does your chosen consumer product include a polyprotic acid? If so, does this compound affect how the product reacts? The Unit Task is outlined on page 582.

- Second ionization reaction

$$HC_2O_4^-(aq) \rightleftharpoons H^+(aq) + C_2O_4^{2-}(aq) \quad (K_{a2} = 5.4 \times 10^{-5})$$

$$K_{a2} = \frac{[H^+(aq)][C_2O_4^{2-}(aq)]}{[HC_2O_4^-(aq)]}$$

Note that K_{a1} is significantly greater than K_{a2}. For most polyprotic acids the initial acid is the strongest and each subsequent acid gets weaker (**Table 4**).

Table 4 Acid Ionization Constants for Polyprotic Acids at SATP

Acid	Formula	K_{a1}	K_{a2}	K_{a3}
oxalic acid	$H_2C_2O_4(aq)$	5.4×10^{-2}	5.4×10^{-5}	–
ascorbic acid	$H_2C_6H_6O_6(aq)$	7.9×10^{-5}	1.6×10^{-12}	–
sulfuric acid	$H_2SO_4(aq)$	very large	1.0×10^{-2}	–
hydrosulfuric acid	$H_2S(aq)$	1.1×10^{-7}	1.3×10^{-13}	–
phosphoric acid	$H_3PO_4(aq)$	7.1×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
arsenic acid	$H_3AsO_4(aq)$	5×10^{-3}	8×10^{-8}	4.0×10^{-12}
carbonic acid	$H_2CO_3(aq)$	4.4×10^{-7}	4.7×10^{-11}	–

Having multiple ionizations and different K_a values may make these problems appear to be more difficult to solve. If you break them down one step at a time, however, you will find that calculating the pH of a polyprotic acid is not much more challenging than calculating the pH of any other acid. When calculating the pH for a typical polyprotic acid, you usually only use the first reaction in the ionization sequence. This is because the percentage ionization of the second hydrogen ion is so small that its effect on the hydrogen ion concentration is insignificant.

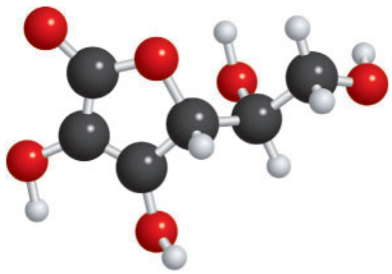


Figure 5 Ascorbic acid (vitamin C) helps maintain the elasticity of skin and promotes wound healing.

Tutorial 5 Calculating the pH of a Polyprotic Acid Solution

In this tutorial, you will learn how to calculate the pH of a polyprotic acid. Notice that only the first ionization reaction is a significant contributor to $[H^+(aq)]$.

Sample Problem 1: Calculating the pH of a Polyprotic Acid

Ascorbic acid (vitamin C) is essential in our diet (**Figure 5**). Calculate the pH of a 0.10 mol/L solution of ascorbic acid (vitamin C), $H_2C_6H_6O_6(aq)$. The K_a values for ascorbic acid are given in Table 4.

Given: $[H_2C_6H_6O_6(aq)] = 0.10$ mol/L; $K_{a1} = 7.9 \times 10^{-5}$; $K_{a2} = 1.6 \times 10^{-12}$

Required: pH of final solution; equilibrium concentrations of $H_2C_6H_6O_6(aq)$, $HC_6H_6O_6^-(aq)$, and $C_6H_6O_6^{2-}(aq)$

Solution:

Step 1. Identify the major entities in solution at equilibrium.

The major entities in solution are $H_2C_6H_6O_6(aq)$ and $H_2O(l)$.

Step 2. Identify the primary source of hydrogen ions.

Since K_{a2} is much smaller than K_{a1} and K_W, the first ionization reaction has the greatest effect on the pH of the solution.

$$H_2C_6H_6O_6(aq) \rightleftharpoons H^+(aq) + HC_6H_6O_6^-(aq) \quad K_{a1} = 7.9 \times 10^{-5}$$

Step 3. Write the equilibrium constant equation for the reaction that is the primary source of $H^+(aq)$ ions.

$$K_a = \frac{[H^+(aq)][HC_6H_6O_6^-(aq)]}{[H_2C_6H_6O_6(aq)]}$$

$$7.9 \times 10^{-5} = \frac{[H^+(aq)][HC_6H_6O_6^-(aq)]}{[H_2C_6H_6O_6(aq)]}$$

Step 4. Determine initial and equilibrium concentrations.

Set up an ICE table for the first ionization of $H_2C_6H_6O_6(aq)$, letting x represent the change in $[H_2C_6H_6O_6(aq)]$ (**Table 5**).

Table 5 ICE Table for the First Ionization of Ascorbic Acid

	$H_2C_6H_6O_6(aq)$ $\rightleftharpoons$	$HC_6H_6O_6^-(aq)$ +	$H^+(aq)$
I	0.10	0	0
C	$-x$	$+x$	$+x$
E	$0.10 - x$	x	x

Step 5. Substitute values from the ICE table into the equilibrium constant equation.

$$7.9 \times 10^{-5} = \frac{[H^+(aq)][HC_6H_6O_6^-(aq)]}{[H_2C_6H_6O_6(aq)]}$$

$$= \frac{(x)(x)}{0.10 - x}$$

$$7.9 \times 10^{-5} = \frac{x^2}{0.10 - x}$$

Step 6. Use the hundred rule to determine if any simplifying assumptions may be made.

$$\frac{[H_2C_6H_6O_6(aq)_{\text{initial}}]}{K_a} = \frac{0.10}{7.9 \times 10^{-5}}$$

$$\frac{[H_2C_6H_6O_6(aq)_{\text{initial}}]}{K_a} = 1.3 \times 10^3$$

Since the $\frac{[H_2C_6H_6O_6(aq)_{\text{initial}}]}{K_a}$ ratio is much greater than 100, assume that

$0.10 - x \approx 0.10$

Thus, the equilibrium equation that you will use is

$$7.9 \times 10^{-5} \approx \frac{x^2}{0.10}$$

Step 7. Solve for x.

$$7.9 \times 10^{-5} \approx \frac{x^2}{0.10}$$

$$x^2 \approx (7.9 \times 10^{-5})(0.10)$$

$$x^2 \approx 7.9 \times 10^{-6}$$

$$x \approx \sqrt{7.9 \times 10^{-6}}$$

$$x \approx 2.8 \times 10^{-3}$$

Step 8. Use the 5 % rule to check your results.

$$\frac{x}{[H_2C_6H_6O_6(aq)]} \times 100\ \% = \frac{2.8 \times 10^{-3}}{0.1} \times 100\ \%$$

$$\frac{x}{[H_2C_6H_6O_6(aq)]} \times 100\ \% = 2.8\ \%$$

Since 2.8 % < 5 %, the error in this result is acceptable.

Step 9. Determine $[H^+(aq)]$ at equilibrium and calculate pH.

Since $[H^+(aq)] = x$ (from the ICE table)

$$\begin{aligned} \text{and } x &\approx 2.8 \times 10^{-3}, \\ [H^+(aq)] &\approx 2.8 \times 10^{-3}\ \text{mol/L} \\ \text{pH} &= -\log[H^+(aq)] \\ &\approx -\log(2.8 \times 10^{-3}) \\ \text{pH} &\approx 2.55 \end{aligned}$$

Use the K_a values of ascorbic acid (from Table 4) to determine the equilibrium concentrations of $H_2C_6H_6O_6(aq)$, $HC_6H_6O_6^-(aq)$, and $C_6H_6O_6^{2-}(aq)$ in the equilibrium solution as follows:

First calculate the concentrations of $H_2C_6H_6O_6(aq)$ and $HC_6H_6O_6^-(aq)$ by substituting the value of x into the equilibrium concentration formulas for these entities in the ICE table.

$$\begin{aligned} [H_2C_6H_6O_6(aq)] &\approx 0.10\ \text{mol/L} - x \\ &\approx 0.10\ \text{mol/L} - 2.8 \times 10^{-3}\text{mol/L} \\ [H_2C_6H_6O_6(aq)] &\approx 0.097\ \text{mol/L} \\ [HC_6H_6O_6^-(aq)] &= x \\ [HC_6H_6O_6^-(aq)] &\approx 2.8 \times 10^{-3}\ \text{mol/L} \end{aligned}$$

The concentration of $C_6H_6O_6^{2-}(aq)$ cannot be calculated using expressions derived from the first ionization reaction because $C_6H_6O_6^{2-}(aq)$ is not produced by this ionization reaction; it is produced in the second ionization reaction. You must use the second ionization constant equation and the value of K_{a2} to calculate this value. Thus,

$$K_{a2} = \frac{[H^+(aq)][C_6H_6O_6^{2-}(aq)]}{[HC_6H_6O_6^-(aq)]}$$

$$[C_6H_6O_6^{2-}(aq)] = \frac{[HC_6H_6O_6^-(aq)]K_{a2}}{[H^+(aq)]}$$

The value of K_{a2} may be found in Table 4: $K_{a2} = 1.6 \times 10^{-12}$

Substitute the values of $[H^+(aq)]$ and $[HC_6H_6O_6^-(aq)]$, calculated earlier, into this equation. Remember your assumption that the second ionization reaction is insignificant and so does not change these concentration values appreciably. Thus,

$$[C_6H_6O_6^{2-}(aq)] = \frac{(2.8 \times 10^{-3})(1.6 \times 10^{-12})}{2.8 \times 10^{-3}}$$

$$[C_6H_6O_6^{2-}(aq)] = 1.6 \times 10^{-12}\ \text{mol/L}$$

Notice that $[C_6H_6O_6^{2-}(aq)] = K_{a2}$.

Statement: The equilibrium concentrations of $H_2C_6H_6O_6(aq)$, $HC_6H_6O_6^-(aq)$, and $C_6H_6O_6^{2-}(aq)$ are, respectively, 0.097 mol/L, 2.8×10^{-3} mol/L, and 1.6×10^{-12} mol/L. Notice that the concentrations of the anions are very low, compared to the initial acid concentration.

Practice

1. Calculate the pH of 1.00 mol/L phosphoric acid, $H_3PO_4(aq)$. K/U [ans: 1.1]
2. Calculate the pH of 0.100 mol/L sodium bisulfate, $NaHSO_4(aq)$ K/U [ans: 1.50]

8.4 Review

Summary

- Percentage ionization is one way to describe the degree of ionization of a weak acid. The higher the percentage ionization, the stronger the acid.
- Polyprotic acids ionize one hydrogen ion at a time. Each step has a characteristic K_a value. Typically, for a polyprotic acid, $K_{a1} > K_{a2} > K_{a3}$

Questions

1. A lab technician prepares the following solutions. Calculate the $[H^+(aq)]$ and pH of each of the following solutions at SATP: K/U
   (a) a 0.0100 mol/L solution of hydrocyanic acid, $HCN(aq)$; $K_a = 6.2 \times 10^{-10}$
   (b) a 0.25 mol/L solution of hydrofluoric acid, $HF(aq)$; $K_a = 6.6 \times 10^{-4}$
   (c) a 0.0010 mol/L solution of lactic acid, $HC_3H_5O_3(aq)$; $K_a = 1.4 \times 10^{-4}$
   (d) a 0.150 mol/L solution of methanoic acid, $HCO_2H(aq)$, $K_a = 1.8 \times 10^{-4}$
2. The following solutions are required for an industrial process. Predict the percentage ionization of each acid. K/U
   (a) a 0.50 mol/L solution of propionic acid with a pH of 2.6
   (b) a 0.15 mol/L solution of peracetic acid with a pH of 4.5
   (c) a 0.01 mol/L solution of sorbic acid with a pH of 3.4
3. Determine the acid ionization constant, K_a, for each of the following weak acids: K/U
   (a) a 0.20 mol/L solution of ascorbic acid, $HC_6H_7O_6(aq)$, with a pH of 2.40
   (b) a 0.100 mol/L solution of nitrous acid, $HNO_2(aq)$, with a pH of 2.10
4. Calculate the percentage ionization of ethanoic acid, $HC_2H_3O_2(aq)$, in a 1.00 mol/L solution. $K_a = 1.8 \times 10^{-5}$ K/U
5. A textile artist plans to dye a skein of yarn. The dye recipe specifies adding 5 mL of 1.0 mol/L hydrochloric acid to 5 L of water, prior to adding the dye, some pickling salt, and the yarn. The artist does not have hydrochloric acid, but finds a bottle of vinegar. What volume of vinegar should she use to make her dye bath? (Assume that vinegar is 0.8 mol/L ethanoic acid, $HC_2H_3O_2(aq)$, and that this acid ionizes about 1.3 %.) T/I A
6. In a study of the effect of lactic acid on muscles, a biologist prepares a 0.100 mol/L solution of lactic acid, $HC_3H_5O_3(aq)$. The acid is 3.7 % ionized. What is the K_a for lactic acid? K/U A
7. Ascorbic acid, $H_2C_6H_6O_6(s)$, is an organic diprotic acid that is better known as vitamin C. A solution contains 0.091 mol of ascorbic acid in 1 L of solution. Determine the pH of this solution, given the following values: $K_1 = 6.7 \times 10^{-5}$; $K_2 = 2.5 \times 10^{-12}$ K/U
8. When a strong acid such as hydrochloric acid is spilled in the lab it must be neutralized before it is cleaned up. Would it be better to use sodium bicarbonate or sodium hydroxide to neutralize the spill? Explain your reasoning. C A
9. Benzoic acid is a commonly used food preservative. It inhibits the growth of many moulds and bacteria. K/U A
   (a) A solution of benzoic acid with a concentration of 8.3×10^{-3} mol/L has a pH of 3.14. Calculate the K_a value for benzoic acid.
   (b) Predict whether the pH of a non-carbonated fruit drink, containing benzoic acid at a concentration of 8.3×10^{-3} mol/L, would be greater or less than 3.14. Explain your reasoning.
10. Chloroacetic acid, $HC_2H_2O_2Cl(aq)$, is a weak acid commonly used in industry to synthesize the hormone epinephrine. It has a K_a of 1.36×10^{-3}. K/U C A
    (a) Determine the percent ionization of a 0.50 mol/L solution.
    (b) Research some of the medical uses of epinephrine, and the risks and benefits of its use. Present your findings in a format of your choice.

WEB LINK

8.5 Calculations Involving Basic Solutions

In Section 8.4 we explored a series of calculations for strong and weak acids. These calculations have parallels for strong and weak bases. In general, the calculations are done in exactly the same way, but with the relevant base-related values (K_b, $[OH^-(aq)]$, pOH) substituted for the acid-related values (K_a, $[H^+(aq)]$, pH).

Calculations Involving Solutions of Strong Bases

The pOH of strong bases depends entirely on the $[OH^-(aq)]$ contributed by the ionization of the base solute in water. We may ignore the small contribution made by the autoionization of water. Also, we may assume that the metal cation produced by the ionization of a strong base has no effect on the pH of the solution.

As we have already seen, we may calculate the pOH of a basic solution from the solution's pH by applying the equation

$$\text{pH} + \text{pOH} = 14$$

We may also determine solution characteristics for strong bases from the solution concentration, as we did for acids. Tutorial 1 provides examples.

Tutorial 1 Determining $[H^+(aq)]$, $[OH^-(aq)]$, and pH

In this tutorial, you will calculate the $[H^+(aq)]$ and $[OH^-(aq)]$ in a solution of a strong base, given the concentration of the base.

Sample Problem 1: Calculating $[H^+(aq)]$ and $[OH^-(aq)]$ from Solution Concentration

A chemist mixes a 0.025 mol/L solution of barium hydroxide, $Ba(OH)_2(aq)$, a strong base. Calculate $[H^+(aq)]$ and $[OH^-(aq)]$ in this solution.

Given: $[Ba(OH)_2(aq)] = 0.025$ mol/L

Required: $[H^+(aq)]$ and $[OH^-(aq)]$

Solution:

Since $Ba(OH)_2(aq)$ is a strong base, it dissociates completely into its ions. First write the dissociation equation:

$$Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2\ OH^-(aq)$$

Since every mole of $Ba(OH)_2(aq)$ produces 1 mol of $Ba^{2+}(aq)$ and 2 mol of $OH^-(aq)$,

$$[OH^-(aq)] = 2(0.025\ \text{mol/L})$$
$$[OH^-(aq)] = 0.050\ \text{mol/L}$$

While the autoionization of water produces hydroxide ions, this contribution is insignificant when compared to the 0.050 mol/L of ions produced by the dissociation of $Ba(OH)_2(aq)$. Also, since $Ba(OH)_2$ is a strong base, you may assume that the $Ba^{2+}(aq)$ ions do not affect the acid–base properties of the solution. In general, you may ignore the presence of the cations of all ionic hydroxides when determining acid–base properties of solutions.

Since $Ba(OH)_2(aq)$ is a strong base, it dissociates completely. The only equilibrium system that you need to consider in this problem is the autoionization of water. This reaction is important because it produces $H^+(aq)$, which affects pH.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad K_w = 1.0 \times 10^{-14}$$

The additional OH^- (aq) ions produced shift this equilibrium to the left, reducing the $[H^+(aq)]$ and thus raising the pH. Use the K_w equation to determine $[H^+(aq)]$:

$$K_w = [H^+(aq)][OH^-(aq)]$$
$$[H^+(aq)] = \frac{K_w}{[OH^-(aq)]}$$
$$= \frac{1.0 \times 10^{-14}}{0.050}$$
$$[H^+(aq)] = 2.0 \times 10^{-13}\ \text{mol/L}$$

Notice that the $[OH^-(aq)]$ used was 0.050 mol/L. Although some $OH^-(aq)$ ions react with $H^+(aq)$ ions to form $H_2O(l)$ when the equilibrium shifts to the left, the amount of $OH^-(aq)$ ions that react is so small that the $[OH^-(aq)]$ essentially remains at 0.050 mol/L.

Statement: The concentration of hydrogen ions in the barium hydroxide solution is 2.0×10^{-13} mol/L. The concentration of hydroxide ions is 0.050 mol/L.

Sample Problem 2: Calculating pH from Solution Concentration

Determine the pH of a 500.0 mL solution produced by dissolving 2.6 g of sodium hydroxide, NaOH(s), in water.

Given: $m_{\text{NaOH}} = 2.6$ g; $V = 500.0$ mL

Required: pH

Solution:

Step 1. Write the balanced equation for the dissociation of the base.

$$\text{NaOH(aq)} \rightarrow \text{Na}^+\text{(aq)} + \text{OH}^-\text{(aq)}$$

Step 2. Identify the major entities in solution at equilibrium.

The major entities in solution are Na^+(aq), OH^-(aq), and H_2O(l).

Step 3. Determine $[OH^-(aq)]$.

Use the mass of NaOH(s) and the volume of the solution to calculate the concentration of the base before dissociation.

$$m_{\text{NaOH}} = 2.6 \text{ g}$$

$$M_{\text{NaOH}} = 40.00 \text{ g/mol}$$

$$n_{\text{NaOH}} = 2.6 \cancel{\text{g}} \times \frac{1 \text{ mol}}{40.00 \cancel{\text{g}}}$$

$$n_{\text{NaOH}} = 0.065 \text{ mol}$$

$$c_{\text{NaOH}} = \frac{0.065 \text{ mol}}{0.5000 \text{ L}}$$

$$c_{\text{NaOH}} = 0.13 \text{ mol/L}$$

From the balanced equation, note that every mole of sodium hydroxide dissociates into 1 mol of Na^+(aq) and 1 mol of OH^-(aq). Therefore, after dissociation,

$$[\text{OH}^-\text{(aq)}] = 0.13 \text{ mol/L}$$

Step 4. Determine $[H^+(aq)]$.

Use the K_w equation and your value of $[OH^-(aq)]$ to find $[H^+(aq)]$.

$$K_w = [\text{H}^+\text{(aq)}][\text{OH}^-\text{(aq)}]$$

$$[\text{H}^+\text{(aq)}] = \frac{K_w}{[\text{OH}^-\text{(aq)}]}$$

$$= \frac{1.0 \times 10^{-14}}{0.13} \text{ mol/L}$$

$$[\text{H}^+\text{(aq)}] = 7.7 \times 10^{-14} \text{ mol/L}$$

Step 5. Determine pH.

$$\text{pH} = -\log[\text{H}^+\text{(aq)}]$$

$$= -\log(7.7 \times 10^{-14})$$

$$\text{pH} = 13.11$$

Statement: The pH of the solution is 13.11.

Practice

1. Calculate the $[H^+(aq)]$ and $[OH^-(aq)]$ in a 0.00100 mol/L solution of potassium hydroxide, KOH(aq). K/U [ans: $[OH^-(aq)] = 0.00100$ mol/L; $[H^+(aq)] = 1.00 \times 10^{-11}$ mol/L]
2. Calculate the pH of a 2.00 L solution prepared by dissolving 0.042 mol of strontium hydroxide, $Sr(OH)_2$, in water. K/U [ans: 3.92]

Calculations Involving Solutions of Weak Bases

In Section 8.4 you used the acid ionization constant, K_a, with pH and $[H^+(aq)]$ in calculations involving weak acids. In much the same way, you may use the base ionization constant, K_b, with pOH and $[OH^-(aq)]$ in calculations involving weak bases.

When solving problems involving weak bases, you will need to know the value of K_b for the base in question. In Section 8.2 you learned how to find the K_b value of a base when given the K_a value of its conjugate acid. Sometimes, however, you may not be given either value. In this situation you may find the K_a value in a table (Table 1 in Appendix B5), and then calculate K_b.

Tutorial 2 Calculating K_b and pH for a Weak Base

This tutorial outlines how to find the K_b value for a base when the K_a value of the conjugate acid is not given, and to use this value to determine pH.

Sample Problem 1: Determining K_b from K_a and pH from Concentration

Highly concentrated ammonia solutions used by industry are sometimes called "liquor ammonia." These solutions must be handled carefully as they are corrosive and toxic (**Figure 1**). Calculate the pH of a 15.0 mol/L solution of ammonia, NH_3(aq).

Figure 1 This industrial facility in Saskatchewan produces both ammonia and urea for use as fertilizers and in other applications.

Given: $[NH_3(aq)] = 15.0$ mol/L

Required: pH

Solution:

Step 1. Determine the formula of the base's conjugate acid.

The conjugate acid of ammonia is the ammonium ion, $NH_4^+(aq)$.

Step 2. Look up the conjugate acid's K_a value (Table 1, Appendix B5).

K_a for $NH_4^+(aq)$ is 5.8×10^{-10}.

Step 3. Rearrange the equation $K_aK_b = K_w$ to solve for K_b. Then, substitute in the values for K_a and K_w, noting that $K_w = 1.0 \times 10^{-14}$, and solve the equation.

$$\begin{aligned} K_b &= \frac{K_w}{K_a} \\ &= \frac{1.0 \times 10^{-14}}{5.8 \times 10^{-10}} \\ K_b &= 1.724 \times 10^{-5} \text{ (2 extra digits carried)} \end{aligned}$$

Step 4. Identify the major entities in solution at equilibrium.

Since ammonia is a weak base, most of the dissolved ammonia will remain as $NH_3(aq)$. Thus the major entities in solution are $NH_3(aq)$ and $H_2O(l)$.

Step 5. Identify the primary source of hydroxide ions in solution.

$NH_3(aq)$ and $H_2O(l)$ can produce $OH^-(aq)$, as shown below.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.7 \times 10^{-5}$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.0 \times 10^{-14}$$

Since $K_b >> K_w$, the contribution of water to $[OH^-(aq)]$ can be ignored.

Step 6. Write the equilibrium constant equation for the reaction that is the primary source of $OH^-(aq)$ ions:

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

$$1.724 \times 10^{-5} = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

Step 7. Determine initial and equilibrium concentrations.

Set up an ICE table for the ionization of $NH_3(aq)$ (**Table 1**).

Table 1 ICE Table for the Ionization of $NH_3(aq)$

	$NH_3(aq)$	$\rightleftharpoons$	$OH^-(aq)$	+	$NH_4^+(aq)$
I	15.0		0		0
C	$-x$		$+x$		$+x$
E	$15.0 - x$		x		x

Step 8. Substitute values from the ICE table into the equilibrium constant equation:

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

$$K_b = \frac{(x)(x)}{15.0 - x}$$

Step 9. Use the hundred rule to determine whether any simplifying assumptions may be made.

$$\frac{[NH_3(aq)_{initial}]}{K_b} = \frac{15.0}{1.724 \times 10^{-5}}$$

$$\frac{[NH_3(aq)_{initial}]}{K_b} = 8.7 \times 10^5$$

Since the $\frac{[NH_3(aq)_{initial}]}{K_b}$ ratio is much greater than 100, you may assume that

$15.0 - x \approx 15.0$

Thus, the equilibrium equation is

$$1.724 \times 10^{-5} \approx \frac{x^2}{15.0}$$

Step 10. Solve for *x*.

$$\begin{aligned} 1.724 \times 10^{-5} &\approx \frac{x^2}{15.0} \\ x^2 &\approx (1.724 \times 10^{-5})(15.0) \\ x^2 &\approx 2.6 \times 10^{-4} \\ x &\approx \sqrt{2.6 \times 10^{-4}} \\ x &\approx 1.612 \times 10^{-2} \end{aligned}$$

Step 11. Use the 5 % rule to check your result.

$$\frac{x}{[NH_3(aq)]} \times 100\ \% = \frac{1.724 \times 10^{-5}}{15.0} \times 100\ \%$$

$$\frac{x}{[NH_3(aq)]} \times 100\ \% = 0.00011\ \%$$

Since 0.00011 % < 5 %, the error in this result is acceptable.

Step 12. Determine the $[OH^-(aq)]$ at equilibrium, then calculate pOH and pH.

Since $[OH^-(aq)] = x$ (from the ICE table) and $x \approx 1.612 \times 10^{-2}$

$$\begin{aligned} [OH^-(aq)] &\approx 1.612 \times 10^{-2}\ \text{mol/L} \\ \text{pOH} &= -\log[OH^-(aq)] \\ &\approx -\log(1.612 \times 10^{-2}) \\ \text{pOH} &\approx 1.79 \\ \text{pH} + \text{pOH} &= 14 \\ \text{pH} &= 14 - \text{pOH} \\ &\approx 14 - 1.79 \\ \text{pH} &\approx 12.21 \end{aligned}$$

Statement: The pH of the ammonia solution is 12.21.

Practice

1. Determine K_b for
   (a) the ethanoate ion, $C_2H_3O_2^-(aq)$ [ans: 5.6×10^{-10}]
   (b) the borate ion, $H_2BO_3^-(aq)$ K/U [ans: 1.7×10^{-5}]
2. Calculate the pH of a 0.20 mol/L solution of a base, where $K_b = 3.82 \times 10^{-10}$. K/U [ans: 8.94]
3. Determine the pH of a 4.5 mol/L solution of hydrazine, $N_2H_4(aq)$. Look up the K_b value for hydrazine. K/U [ans: 11.44]

UNIT TASK **BOOKMARK**

If the consumer product that you have chosen for the Unit Task on page 582 is a base, how does the high pH affect its function?

8.5 Review

Summary

- Calculations to determine solution characteristics of weak bases are generally similar to those for determining the characteristics of weak acid solutions.
- The value for K_a can often be found in a reference table. The value for K_b can then be calculated from K_a.

Questions

1. Calculate the pH of each of the following solutions. If necessary, look up the K_b values in Table 3, Appendix B5. K/U
   (a) sodium hydroxide, $NaOH(aq)$; $[NaOH(aq)] = 0.0030$ mol/L
   (b) barium hydroxide, $Ba(OH)_2(aq)$; $[Ba(OH)_2(aq)] = 0.0020$ mol/L
   (c) dimethylamine, $(CH_3)_2NH(aq)$; $[(CH_3)_2NH(aq)] = 0.010$ mol/L
   (d) hydrazine, $N_2H_4(aq)$; $[N_2H_4(aq)] = 0.0250$ mol/L
2. Determine the K_b value for each of the following substances. (For some of them you will have to first look up the K_a values in Table 1 in Appendix B5.) K/U
   (a) hydrogen sulfide ion, $HS^-(aq)$
   (b) nitrite ion, $NO_2^-(aq)$; $K_a = 7.2 \times 10^{-4}$
   (c) cyanide ion, $CN^-(aq)$
   (d) fluoride ion, $F^-(aq)$
3. Calculate the pH of the following solutions at SATP: K/U
   (a) morphine, $C_{17}H_{19}NO_3(aq)$; $[C_{17}H_{19}NO_3(aq)] = 0.01$ mol/L; $K_b = 7.5 \times 10^{-7}$
   (b) strychnine, $C_{21}H_{22}N_2O_2(aq)$; $[C_{21}H_{22}N_2O_2(aq)] = 0.001$ mol/L; $K_b = 1.0 \times 10^{-6}$
4. For a 0.20 mol/L solution of each of the following bases, calculate the hydroxide ion concentration, hydrogen ion concentration, and pH: K/U
   (a) *N,N*-diethylethanamine, $(C_2H_5)_3N(aq)$; $K_b = 4.0 \times 10^{-4}$
   (b) hydroxylamine, $HONH_2(aq)$; $K_b = 1.1 \times 10^{-8}$
5. Calculate $[OH^-(aq)]$, pOH, and pH for a 0.000 40 mol/L solution of calcium hydroxide, $Ca(OH)_2(aq)$; $K_b = 5.0 \times 10^{-11}$ K/U
6. Calculate $[OH^-(aq)]$, pOH, and pH for each of the following aqueous solutions: K/U
   (a) 25 g potassium hydroxide, $KOH(aq)$, per litre
   (b) 150.0 g sodium hydroxide, $NaOH(aq)$, per litre
7. Ammonia is the most common and well-known weak base. A sample of household ammonia has a pH of 11.80. Determine its concentration. K/U A
8. Find an online MSDS for ammonia. Prepare a list of precautions that should be taken while working with ammonia. C A
9. Methanoate ion, $HCO_2^-(aq)$, is the conjugate base of methanoic (formic) acid, $HCO_2H(aq)$. K/U
   (a) Write the K_b equation for the ionization of the methanoate ion.
   (b) Write the K_a equation for the ionization of methanoic acid.
   (c) Use the equations from (a) and (b) to show that $K_aK_b = K_w$.
10. Methylamine, $CH_3NH_2(aq)$, is a weak base ($K_b = 4.4 \times 10^{-4}$). It is used in the pharmaceutical industry to synthesize ephedrine, which is a stimulant, decongestant, and appetite suppressant. T/I C A
   (a) A pharmaceutical company requires a solution of 0.25 mol/L methylamine for its reactions. One of the chemists onsite was unsure if the methylamine supplied was of the correct concentration. He tested the pH and determined it was 11.2. Did this sample of methylamine have the concentration required for their reaction? Show your evidence.
   (b) If you determined that the solution was not the correct concentration, was it too concentrated or too dilute?
   (c) Ephedrine is one of the main ingredients in a "Coast Guard cocktail." Research why ephedrine is used in this application, and the possible health effects of its use.

WEB LINK

Acid–Base Properties of Salt Solutions

8.6

Salts are ionic compounds that are solid at SATP. A salt contains cations (positively charged ions) and anions (negatively charged ions) arranged in a repeating crystalline pattern. Many salts are highly soluble in water and easily dissociate into ions that may or may not affect the pH of the solution.

Investigation **8.6.1**

The Acidity of Salt Solutions (page 570)

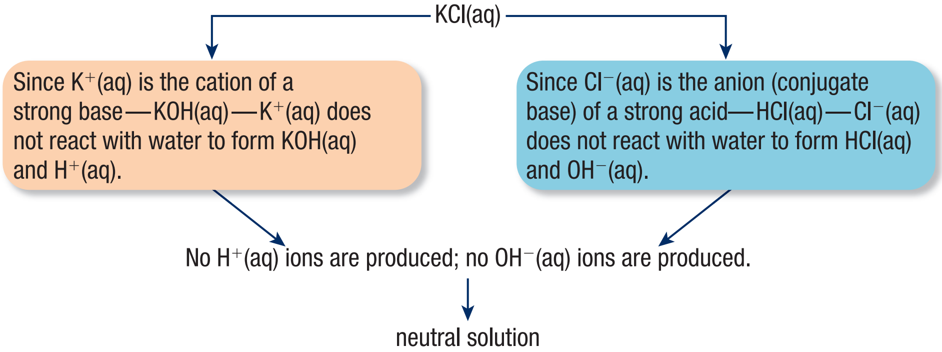
In this controlled experiment you will write and test a hypothesis regarding the pH of common salt solutions.

Salts in Solution

A pure substance that dissociates into ions when it dissolves in water is called an electrolyte. Salts are electrolytes. Salts can be acidic, basic, or neutral. An acidic salt is one that, when it dissolves in water, increases the concentration of hydrogen ions and thus forms an acidic solution. A basic salt increases the concentration of hydroxide ions and thus forms a basic solution in water. A neutral salt produces neither hydrogen ions nor hydroxide ions and thus forms a neutral solution in water.

Salts That Produce Neutral Solutions

When you test a solution of sodium chloride with a pH meter, the reading is 7, or neutral. How may we explain this result? Recall that the anion of a strong acid (the acid's conjugate base) has virtually no affinity for hydrogen ions. Similarly, the cation of a strong base has almost no affinity for hydroxide ions. When sodium chloride dissolves in water, therefore, the dissociated ions do not react with water and thus do not change the concentration of hydrogen ions or hydroxide ions: the solution remains neutral (pH = 7). Examples of common neutral salts are sodium nitrate, $NaNO_3(s)$, and potassium chloride, $KCl(s)$ (**Figure 1**).



$KCl(aq)$

Since $K^+(aq)$ is the cation of a strong base—$KOH(aq)$—$K^+(aq)$ does not react with water to form $KOH(aq)$ and $H^+(aq)$.

Since $Cl^-(aq)$ is the anion (conjugate base) of a strong acid—$HCl(aq)$—$Cl^-(aq)$ does not react with water to form $HCl(aq)$ and $OH^-(aq)$.

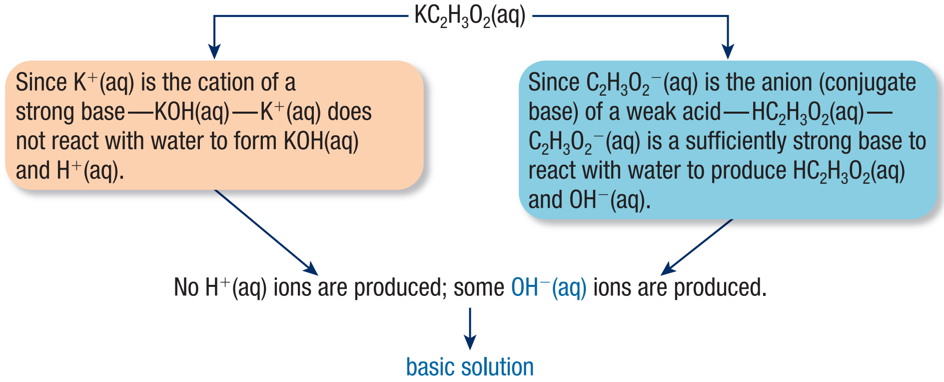
No $H^+(aq)$ ions are produced; no $OH^-(aq)$ ions are produced.

neutral solution

Figure 1 Explaining why potassium chloride produces a neutral solution

Salts That Produce Basic Solutions

Potassium ethanoate, $KC_2H_3O_2(s)$, is another highly soluble salt. In aqueous solution the major entities are potassium ions, $K^+(aq)$, ethanoate ions, $C_2H_3O_2^-(aq)$, and water molecules, $H_2O(l)$. Experimental evidence shows that the pH is basic (**Figure 2**).



$KC_2H_3O_2(aq)$

Since $K^+(aq)$ is the cation of a strong base—$KOH(aq)$—$K^+(aq)$ does not react with water to form $KOH(aq)$ and $H^+(aq)$.

Since $C_2H_3O_2^-(aq)$ is the anion (conjugate base) of a weak acid—$HC_2H_3O_2(aq)$—$C_2H_3O_2^-(aq)$ is a sufficiently strong base to react with water to produce $HC_2H_3O_2(aq)$ and $OH^-(aq)$.

No $H^+(aq)$ ions are produced; some $OH^-(aq)$ ions are produced.

basic solution

Figure 2 Explaining why potassium ethanoate produces a basic solution

As in the example of potassium chloride solution (Figure 1), the potassium ion does not act as a Brønsted–Lowry acid. The basic character of ethanoate solutions results from the ethanoate ion. We can explain this using the Brønsted–Lowry theory. A Brønsted–Lowry base acts as a proton acceptor, and may remove a proton from water to form hydroxide ions in solution. The ethanoate ion is a base, and reacts with the best hydrogen ion donor in the solution. In this case, water is the only hydrogen ion donor present. Thus the ethanoate ion reacts with water to produce ethanoic acid and hydroxide ions.

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$$

Note that this reaction involves a base reacting with water to produce the conjugate acid (ethanoic acid) and a hydroxide ion. The water molecule is split apart during this reaction. This splitting is known as **hydrolysis** (from the Greek words *hydro*, meaning "water," and *lysis*, meaning "splitting").

hydrolysis a chemical reaction of an ion with water to produce an acidic or basic solution by the production of hydronium or hydroxide ions

As these two examples show, Group 1 cations do not react with water to change the pH of a solution. Therefore, all aqueous salt solutions of Group 1 chlorides are neutral.

As you saw in Section 8.2, we can use the K_a value of a weak acid to calculate the K_b value of its conjugate base and, hence, its pH.

LEARNING **TIP**

Hydrolysis
Do not confuse the definition of hydrolysis as it applies to acid–base chemistry with the meaning of the term presented in Chapter 1. In acid–base chemistry it means the reaction of an ion with water to produce aqueous hydrogen ions or hydroxide ions (an acidic or basic solution). In your study of organic chemistry you used the same term to mean "the breaking of a covalent bond in a molecule by the addition of the elements of water (hydrogen and oxygen)."

Tutorial **1** Determining the pH of a Basic Salt Solution

In this tutorial, you will use K_a to determine the pH of a salt solution.

Sample Problem 1: Determining the pH of a Salt Solution

Calculate the pH of a 0.30 mol/L sodium nitrite solution, $NaNO_2(aq)$.

Given: 0.30 mol/L

Required: pH

Solution:

Step 1. Determine the major entities in the solution.

The major entities in this solution are $H_2O(l)$, $NaNO_2(aq)$, $Na^+(aq)$, and $NO_2^-(aq)$.

Step 2. Determine whether any of the ions react with water.

Since nitrous acid is a weak acid, the nitrite ion must have a significant affinity for hydrogen ions. Thus, $NO_2^-(aq)$ may cause hydrolysis with water.

Since sodium hydroxide is a strong base, dissociating completely in water, the sodium ion does not have a significant affinity for hydroxide ions. Thus, $Na^+(aq)$ does not cause hydrolysis.

Step 3. Write the equilibrium reaction equation for the dominant reaction in the solution and identify the conjugate acid produced.

The dominant reaction in the solution is the reaction between $NO_2^-(aq)$ and water. The equilibrium reaction equation for this reaction is

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq)$$

Since $NO_2^-(aq)$ may cause hydrolysis with water and accept a proton, the nitrite ion is a base. Its conjugate acid is nitrous acid, $HNO_2(aq)$.

Step 4. Write the equilibrium constant equation.

The equilibrium constant (K_b) equation is

$$K_b = \frac{[HNO_2(aq)][OH^-(aq)]}{[NO_2^-(aq)]}$$

Step 5. Look up the value of K_a and determine the value of the equilibrium constant.

You need to find the equilibrium constant of the base, $NO_2^-(aq)$. You can determine this value from the equilibrium constant of the acid, $HNO_2(aq)$. According to Table 1 in Appendix B5, $K_a = 4.6 \times 10^{-4}$ for $HNO_2(aq)$.

Next, calculate the value of K_b from K_w and K_a:

$$K_w = K_aK_b$$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}}$$

$$K_b = 2.174 \times 10^{-11} \text{ (2 extra digits carried)}$$

Step 6. Determine the initial and equilibrium concentrations.

You know that the initial concentration of nitrite ions in solution is 0.30 mol/L. Set up an ICE table for the hydrolysis equilibrium (**Table 1**).

Table 1 ICE Table for the Hydrolysis Reaction of Nitrite with Water

	$NO_2^-(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$HNO_2(aq)$ +	$OH^-(aq)$
I	0.30	—	0	≈ 0
C	$-x$	—	$+x$	$+x$
E	$0.30 - x$	—	x	x

Step 7. Substitute the value of the equilibrium constant and equilibrium concentrations (from the ICE table) into the equilibrium constant equation.

$$2.174 \times 10^{-11} = \frac{[HNO_2(aq)][OH^-(aq)]}{[NO_2^-(aq)]}$$

$$2.174 \times 10^{-11} = \frac{(x)(x)}{0.30 - x}$$

Step 8. Use the hundred rule to determine whether any simplifying assumptions may be made.

$$\text{Since } \frac{[NO_2^-(aq)_{\text{initial}}]}{K_a} = \frac{0.30}{2.174 \times 10^{-11}}$$

$$\frac{[NO_2^-(aq)_{\text{initial}}]}{K_a} = 1.380 \times 10^{10}$$

Since the $\frac{[HNO_2(aq)_{\text{initial}}]}{K_a}$ ratio is much greater than 100, you may assume that

$$0.30 - x \approx 0.30$$

Thus, the equilibrium equation is

$$2.174 \times 10^{-11} = \frac{x^2}{0.30}$$

Step 9. Solve for x.

$$2.174 \times 10^{-11} \approx \frac{x^2}{0.30}$$

$$x^2 \approx (2.174 \times 10^{-11})(0.30)$$

$$x^2 \approx 6.522 \times 10^{-12}$$

$$x \approx \sqrt{6.522 \times 10^{-12}}$$

$$x \approx 2.554 \times 10^{-6} \text{ (Note that only the positive root is realistic.)}$$

Step 10. Use the 5 % rule to check your result.

$$\frac{x}{[\text{NO}_2^-(\text{aq})]} \times 100\ \% = \frac{2.554 \times 10^{-6}}{0.30} \times 100\ \%$$

$$\frac{x}{[\text{NO}_2^-(\text{aq})]} \times 100\ \% = 0.00085\ \%$$

Since 0.000 85 % < 5 %, the error in this result is acceptable.

Step 11. Determine $[\text{H}^+(\text{aq})]$ or $[\text{OH}^-(\text{aq})]$ at equilibrium and calculate pH.

$$[\text{OH}^-(\text{aq})] = x$$
$$[\text{OH}^-(\text{aq})] = 2.554 \times 10^{-6}\ \text{mol/L}$$
$$\text{pOH} = -\log[\text{OH}^-(\text{aq})]$$
$$\text{pOH} = -\log(2.554 \times 10^{-6}]$$
$$\text{pOH} = 5.59$$
$$\text{pH} = 14.00 - 5.59$$
$$\text{pH} = 8.41$$

Statement: The pH of a 0.30 mol/L solution of sodium nitrite is 8.41, which is basic, as expected.

Practice

1. Calculate the pH of a 0.35 mol/L solution of sodium methanoate, NaCHO_2(aq). K/U [ans: 8.64]
2. Calculate the pH of a 0.85 mol/L solution of sodium hypochlorite, NaClO(aq). K/U [ans: 10.69]

Salts That Produce Acidic Solutions

Some salts produce acidic solutions when dissolved in water. For example, when solid ammonium chloride, NH_4Cl(s), dissolves, ammonium ions behave as a weak acid:

$$\text{NH}_4^+(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}^+(\text{aq})$$

In general, if a salt contains a cation that is the conjugate acid of a weak base (such as the ammonium ion, NH_4^+(aq)) and an anion that is not a base (such as the chloride ion, Cl^-(aq)), the salt forms an acidic solution (**Figure 3**).

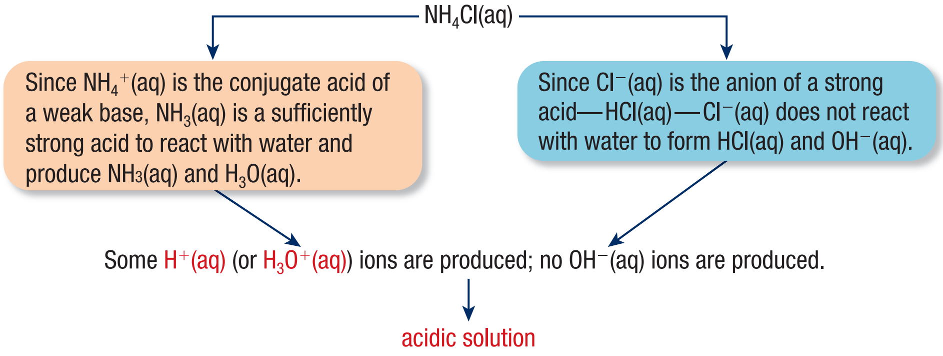


Figure 3 Explaining why ammonium chloride produces an acidic solution

Tutorial 2 Determining the pH of an Acidic Salt Solution

You will use a problem-solving method to determine the pH of an acidic salt solution similar to the one you used for basic salt solutions, except that you will use K_b rather than K_a.

Sample Problem 1: Determining the pH of a Solution

Calculate the pH of a 0.10 mol/L NH_4Cl(aq) solution.

Given: $[\text{NH}_4\text{Cl}(\text{aq})] = 0.10$ mol/L

Required: pH

Solution:

Step 1. Determine the major entities in the solution.

The major entities in this solution are $H_2O(l)$, $NH_4^+(aq)$, and $Cl^-(aq)$.

Step 2. Determine whether any of the ions may react with water.

Since $Cl^-(aq)$ is the conjugate base of a strong acid ($HCl(aq)$), $Cl^-(aq)$ ions cannot cause hydrolysis.

Step 3. Write the equilibrium reaction equation for the dominant reaction in the solution and identify the conjugate base produced.

$NH_4^+(aq)$ ions may react with water to form hydronium ions (hydrogen ions) as follows:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

As before, this equation may be simplified to

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

The conjugate base of the ammonium ion is therefore ammonia, $NH_3(aq)$.

Step 4. Write the equilibrium constant equation.

$$K_a = \frac{[NH_3(aq)][H^+(aq)]}{[NH_4^+(aq)]}$$

Step 5. Look up the value of K_b and determine the value of the equilibrium constant.

Since $NH_3(aq)$ is the conjugate base of $NH_4^+(aq)$, you need to find the equilibrium constant, K_b, of $NH_3(aq)$. According to Table 3 in Appendix B5, $K_b = 1.8 \times 10^{-5}$ for $NH_3(aq)$.

Next, use this value and the equation $K_w = K_aK_b$ to determine the value of K_a for $NH_4^+(aq)$.

$$K_w = K_aK_b$$

$$K_a = \frac{K_w}{K_b}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_a = 5.556 \times 10^{-10}$$

Thus, the equilibrium constant equation is

$$5.556 \times 10^{-10} = \frac{[NH_3(aq)][H^+(aq)]}{[NH_4^+(aq)]}$$

Step 6. Determine the initial and equilibrium concentrations.

Although ammonium, $NH_4^+(aq)$, is a very weak acid, the value of its equilibrium constant (5.556×10^{-10}) is much greater than that of water ($K_w = 1.0 \times 10^{-14}$). The $NH_4^+(aq)$ equilibrium will therefore dominate in the production of $H^+(aq)$ ions. Thus, focus on the $NH_4^+(aq)$ equilibrium to calculate pH.

Set up an ICE table (**Table 2**).

Table 2 ICE Table for the Reaction of Ammonium Ions with Water

	$NH_4^+(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$NH_3(aq)$
I	0.10		≈ 0		0
C	$-x$		$+x$		$+x$
E	$0.10 - x$		x		x

Step 7. Substitute the value of the equilibrium constant and equilibrium concentrations (from the ICE table) into the equilibrium constant equation.

$$5.556 \times 10^{-10} = \frac{[H^+(aq)][NH_3(aq)]}{[NH_4^+(aq)]}$$

$$= \frac{(x)(x)}{0.10 - x}$$

$$5.556 \times 10^{-10} = \frac{x^2}{0.10 - x}$$

Step 8. Use the hundred rule to determine whether any simplifying assumptions may be made.

$$\text{Since } \frac{[NH_4^+(aq)_{\text{initial}}]}{K_a} = \frac{0.10}{5.556 \times 10^{-10}}$$

$$\frac{[NH_4^+(aq)_{\text{initial}}]}{K_a} = 1.8 \times 10^8$$

Since the $\frac{[NH_4^+(aq)_{\text{initial}}]}{K_a}$ ratio is much greater than 100, you may assume that

$0.10 - x \approx 0.10$

Thus, the equilibrium equation is

$$5.556 \times 10^{-10} \approx \frac{x^2}{0.10}$$

Step 9. Solve for *x*.

$$5.556 \times 10^{-10} \approx \frac{x^2}{0.10}$$

$$x^2 \approx 5.556 \times 10^{-11}$$

$$x \approx \sqrt{5.556 \times 10^{-11}}$$

$$x \approx 7.454 \times 10^{-6}$$

Step 10. Use the 5 % rule to check your result.

The error in the result is acceptable. (Check this yourself.)

Step 11. Determine $[H^+(aq)]$ or $[OH^-(aq)]$ at equilibrium and calculate pH.

$$[H^+(aq)] = x$$

$$[H^+(aq)] = 7.454 \times 10^{-6} \text{mol/L}$$

$$\text{pH} = -\log(7.454 \times 10^{-6})$$

$$\text{pH} = 5.13$$

Statement: The pH of a 0.10 mol/L solution of ammonium chloride is 5.13, which is acidic.

Practice

1. Calculate the pH of a 0.525 mol/L solution of ammonium chloride, $NH_4Cl(aq)$. (The K_b value for ammonia, $NH_3(aq)$, is 1.8×10^{-5}). K/U [ans: 4.77]
2. Codeine is an organic base ($K_b = 1.62 \times 10^{-6}$) represented by the symbol D. What is the pH of a 0.0250 mol/L solution of codeine hydrochloride, DHCl(aq)? K/U [ans: 4.91]

In aqueous solutions of salts such as ammonium ethanoate, $NH_4C_2H_3O_2(aq)$, both ions may affect the pH of the solution. Since the equilibrium calculations for these cases can be quite complicated, we will only consider such problems qualitatively. We can predict whether the solution will be basic, acidic, or neutral by comparing the K_a value for the acidic ion with the K_b value for the basic ion (**Table 3**).

- If the K_a value for the acidic ion is larger than the K_b value for the basic ion, the solution will be acidic.
- If the K_b value is larger than the K_a value, the solution will be basic.
- Equal K_a and K_b values result in a neutral solution.

Table 3 Acid–Base Properties of Various Types of Salts

Type of salt	Examples	Comment	pH of solution
Cation of a Group 1 or Group 2 element, other than Be; anion is from strong acid	KCl(aq), NaCl(aq), $NaNO_3$(aq)	Neither of the ions acts as an acid or a base	neutral
Cation of a Group 1 or Group 2 element, other than Be; anion is from weak acid	$NaC_2H_3O_2$(aq), KCN(aq), NaF(aq)	Anion acts as a base; cation has no effect on pH	basic
Cation is conjugate acid of weak base; anion is from strong acid	NH_4Cl(aq), NH_4NO_3(aq)	Cation acts as an acid; anion has no effect on pH	acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	$NH_4C_2H_3O_2$(aq), NH_4CN(aq)	Cation acts as an acid; anion acts as a base	acidic if $K_a > K_b$ basic if $K_b > K_a$ neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	$Al(NO_3)_3$(aq), $FeCl_3$(aq)	Hydrated cation acts as an acid; anion has no effect on pH	acidic

Another type of salt that produces an acidic solution is one that contains a highly charged metal ion. For example, a solution of aluminum chloride, $AlCl_3(s)$, is significantly acidic. Although the $Al^{3+}(aq)$ ion is not itself a Brønsted–Lowry acid, the hydrated ion, $Al(H_2O)_6{}^{3+}(aq)$, that forms in water is a weak acid:

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+(aq)$$

Many metal ions form acidic solutions to varying degrees (**Table 4**).

Table 4 Acid Ionization Constants for Some Metal Cations (K_a at SATP)*

Metal cation*	K_a
Zr^{4+}(aq)	2.1
Sn^{2+}(aq)	2.0×10^{-2}
Fe^{3+}(aq)	1.5×10^{-3}
Cr^{3+}(aq)	1.0×10^{-4}
Al^{3+}(aq)	9.8×10^{-6}
Be^{2+}(aq)	3.2×10^{-7}
Fe^{2+}(aq)	1.8×10^{-7}
Pb^{2+}(aq)	1.6×10^{-8}
Cu^{2+}(aq)	1.0×10^{-8}

*Aqueous metal cations are hydrated complex ions (for example, $Cu(H_2O)_4{}^{2+}$(aq)) but they are usually written without the water molecules.

Hydrolysis of Amphiprotic (Amphoteric) Ions

As you learned in Section 8.1, amphiprotic compounds can act as Brønsted–Lowry acids or bases. Water is amphiprotic; so are polyatomic ions that include hydrogen, H, at the beginning of the formula. Let us consider an example of a compound that produces amphiprotic ions. An aqueous solution of sodium hydrogen sulfate, $NaHSO_4(aq)$, dissociates to produce sodium ions, $Na^+(aq)$, and hydrogen sulfate ions, $HSO_4{}^-(aq)$. The $HSO_4{}^-(aq)$ ions are amphiprotic: they may hydrolyze in two different ways. One way forms sulfate ions, $SO_4{}^{2-}$ (aq), and hydronium ions, $H_3O^+(aq)$, thereby creating an acidic solution. The other hydrolysis reaction forms $OH^-(aq)$ and $H_2SO_4(aq)$ ions, thereby forming a basic solution:

$$NaHSO_4(aq) \rightarrow Na^+(aq) + HSO_4{}^-(aq)$$
(dissociation)

$$HSO_4{}^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$
(acid hydrolysis)

$$HSO_4{}^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2SO_4(aq) \quad K_b = \text{very small}$$
(base hydrolysis)

Whether a solution of sodium hydrogen sulfate is acidic or basic depends on the relative size of the K_a of the acid hydrolysis equilibrium and the K_b of the base hydrolysis equilibrium.

Sodium hydrogen sulfate may act as either an acid or a base but you can see from this example that one equilibrium dominates. In this case, the resulting solution is acidic. For other salts, such as sodium hydrogen carbonate, the solution is basic. By comparing K_a and K_b values you can predict which equilibrium will dominate.

Hydrolysis of Metallic and Non-metallic Oxides

When calcium oxide, a metallic oxide, dissolves in water it produces a basic solution. However, when carbon dioxide, a non-metallic oxide, dissolves in water it forms an acidic solution. This is a general result: metallic oxides form basic solutions and non-metallic oxides form acidic solutions. How can we explain this observation? Oxides are only slightly soluble in water. However, these compounds react with water molecules to affect the pH of the resulting solutions.

Metallic Oxides

Calcium oxide reacts with water to produce calcium ions and hydroxide ions:

$$CaO(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq)$$

This reaction increases $[OH^-(aq)]$ and thus increases the pH.

Metallic oxides, such as those of the Group 1 and Group 2 metals, produce basic solutions in water. As a result, these oxides are sometimes called basic oxides.

Non-metallic Oxides

Non-metallic oxides (such as dinitrogen monoxide, $N_2O(aq)$, and sulfur dioxide, $SO_2(aq)$), increase the concentration of hydronium ions (hydrogen ions) in water. Thus the pH decreases and the resulting solution is acidic. This acidity affects many natural processes including weathering, tooth decay, and nutrient absorption by plants. Oxides of sulfur and nitrogen released into the atmosphere contribute to acid precipitation that can acidify lakes and rivers. Even atmospheric carbon dioxide makes rain slightly acidic.

Carbon dioxide gas reacts with water in a two-step process:

$$\begin{aligned}
&CO_2(g) + H_2O(l) \rightleftharpoons \cancel{H_2CO_3(aq)}\\
&\underline{\cancel{H_2CO_3(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)}\\
&CO_2(g) + 2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad \text{(net equation)}
\end{aligned}$$

The net reaction increases the concentration of hydronium ions in solution and thus decreases the pH. A non-metallic oxide, such as $CO_2(g)$, that dissolves in water to form an acidic solution is sometimes called an acidic oxide.

Tutorial 3 Predicting Properties of Oxide Solutions

In this tutorial, you will learn how to predict the acidity of a solution of an oxide by examining its cation.

Sample Problem 1: Acidity of a Metallic Oxide Solution

A chemist prepares a solution of magnesium oxide, $MgO(aq)$. Write the hydrolysis reaction equation and predict whether the resulting solution will be acidic, basic, or neutral.

Solution

First, identify the oxide as a metallic oxide or a non-metallic oxide.

Magnesium is a metal, so magnesium oxide is a metallic oxide.

Next, write the hydrolysis equation for the oxide.

Metal oxides react with water to form basic solutions. So, magnesium oxide will react with water to form a basic solution as follows:

$$MgO(aq) + H_2O(l) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$$

Practice

1. Predict whether a solution of copper(II) oxide, $CuO(aq)$, will be acidic, basic, or neutral. Write a hydrolysis equation to support your answer. K/U
2. A solution is made by bubbling nitrogen dioxide gas, $NO_2(g)$, into water. Predict whether the solution will be acidic, basic, or neutral. Explain your answer. K/U

8.6 Review

Summary

- For a salt solution in which the anion is the conjugate base of a weak acid, and the cation does not react with water, the aqueous solution is basic.
- For a salt solution in which the cation is the conjugate acid of a weak base, and the anion does not react with water, the aqueous solution is acidic.
- If neither the anion nor the cation is a conjugate base or acid, the ions will not affect the pH of the aqueous solution.
- If the salt has an anion and a cation that can both hydrolyze water, look at the K_b and K_a values of the anion and cation. If $K_a > K_b$, the solution will become more acidic. If $K_a < K_b$, the solution will become more basic. If $K_a = K_b$, the solution will be neutral.
- Metallic oxides form basic solutions and non-metallic oxides form acidic solutions.

Questions

1. Create flow charts similar to Figures 1, 2, and 3 for the following compounds. Specify whether each solution will be acidic, basic, or neutral. (If necessary, look up the relevant K_a and K_b values in Appendix B5.) K/U C
   (a) lithium chloride, $LiCl(aq)$
   (b) lithium fluoride, $LiF(aq)$
   (c) ammonium chloride, $NH_4(aq)$
2. Predict whether each of the following solutions will have a $pH < 7$, $pH = 7$, or $pH > 7$. Explain your answer. K/U
   (a) sodium sulfite, $Na_2SO_3(aq)$
   (b) ammonium methanoate, $NH_4CHO_2(aq)$
   (c) magnesium sulfate, $MgSO_4(aq)$
3. Create a table to summarize what types of salts result in acidic, basic, or neutral aqueous solutions. K/U C
4. Calculate the pH of each of the following solutions: K/U
   (a) 0.30 mol/L ammonium nitrate solution, $NH_4Cl(aq)$
   (b) 0.30 mol/L solution of calcium chloride solution, $CaCl_2(aq)$
   (c) 1.45 mol/L calcium sulfate solution, $CaSO_4(aq)$
   (d) 2.61 mol/L ammonium hydrogen sulfate solution, $NH_4HSO_4(aq)$
   (e) 2.80 mol/L sodium ethanoate solution, $NaC_2H_3O_2(aq)$
   (f) household bleach: 0.91 mol/L $NaClO(aq)$ solution
5. Aniline hydrochloride, $C_6H_5NH_3Cl(s)$, is a crystalline powder that is used in industry to synthesize dyes. Once the dye has been produced, the remaining solution should be neutralized. K/U A
   (a) Determine the pH of a 0.10 mol/L solution of aniline hydrochloride. (K_b for aniline is 4.1×10^{-10}.)
   (b) Would a dilute solution of calcium oxide or nitrogen oxide be the best to use to neutralize the excess aniline hydrochloride? Explain your reasoning.
   (c) Why would an oxide solution be used to neutralize the solution, rather than hydrochloric acid or sodium hydroxide?
6. **Experimental Design**: Small samples of zinc, carbon, phosphorus, and iron will be burned in air. The resulting product will be mixed with water and tested with red and blue litmus paper. K/U T/I C
   (a) Write equations that predict each element's reaction with oxygen, and then the reaction of the oxide with water.
   (b) Predict what will be observed when the solutions are tested with red and blue litmus paper. Record you predictions in a table.
7. Saltwater fish are very sensitive to the pH of their water. K/U T/I A
   (a) Research the optimum pH for a saltwater fish tank.
   (b) What salts do you think could be used to safely adjust the pH of a fish tank? Explain your reasoning.
   (c) The pH in a fish tank will change over time. What substances may affect the pH? What should you do to counteract any change?

WEB LINK

8.7 Acid–Base Titration

titration the addition of precise volumes of a solution in a burette to a measured volume of a sample solution; often used to determine the concentration of a substance in the sample

sample the solution being analyzed in a titration

titrant the solution in a burette during a titration

burette a calibrated tube used to deliver variable known volumes of a liquid during a titration

A food technologist working for a soft-drink company needs to know the concentration of citric acid in a new fruit-flavoured drink. To determine the concentration of the acid, the chemist adds a basic solution, such as sodium hydroxide, of known concentration until the base exactly neutralizes the acid. Knowing the volume of drink used, and the volume and concentration of the basic solution added, the chemist can calculate the concentration of the acid in the drink. The process of analyzing various characteristics of a solution (such as concentration and pH) by the progressive reaction of the solution with another solution is called **titration**. CAREER LINK

In a typical titration, the **sample** is placed in a receiving flask, usually an Erlenmeyer flask. Drops of a solution, called the **titrant**, are then added slowly from a **burette** into the sample (**Figure 1**). Knowing the volume of the titrant and the sample, and the concentration of one of these solutions, we can determine the quantity and concentration of the chemical entity of interest. We can also determine the pH of the solution in the receiving flask at various points in the titration.

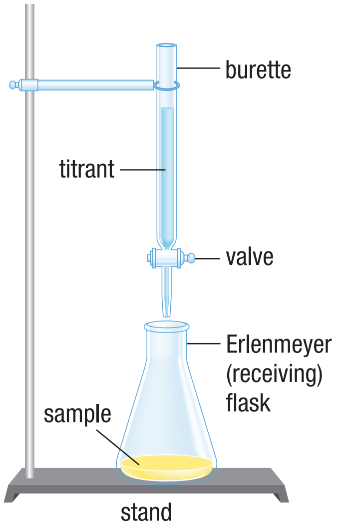


Figure 1 The burette contains the titrant. The Erlenmeyer flask contains the sample.

In an acid–base titration, the sample in the receiving flask may be an acid or a base. If the sample is a base, the titrant used is an acid, and vice versa. By delivering a measured volume of titrant into the sample, we can calculate various characteristics of the sample. These calculations are based on the stoichiometry of the reaction between entities in the titrant and entities in the sample. It is therefore important to know the amount concentration of the titrant to a high degree of accuracy and precision.

standard solution a solution whose concentration is accurately and precisely known

primary standard a highly pure and stable chemical used to determine the precise concentration of acids or bases

equivalence point the point in a titration when neutralization is complete

endpoint the point in a titration at which a sharp change in a measurable and characteristic property occurs (for example, a colour change in an acid–base indicator)

Thus, we usually first determine the concentration of the titrant by a titration procedure called standardization. In a standardization procedure, the solution that will be a titrant in an investigation is titrated into a **standard solution** made by dissolving a compound called a **primary standard** in distilled water. A primary standard must be very pure and the amount present (in moles) must be known to a high degree of accuracy and precision. Common primary standards include the base, sodium carbonate, $Na_2CO_3(s)$, for standardizing acid titrants. The weak acid, potassium hydrogen phthalate, $KHC_8H_4O_4(s)$, is commonly used for standardizing basic titrants. This process accurately determines the concentration of the titrant in the burette.

Some strong acids and bases that are commonly available are not used as primary standards because they absorb water from the air. Sodium hydroxide is an example. Other strong acids and bases degrade or decompose. For example, at high concentrations, hydrochloric acid vaporizes to produce hydrogen chloride gas, $HCl(g)$. Such unpredictable changes reduce the accuracy of measurements.

For most titrations, the titrant is slowly added from a burette into a known volume of sample solution in a receiving flask. The titrant is added just until all the reactant in the sample is consumed. This point is called the **equivalence point** or the stoichiometric point. At the equivalence point, the amount of titrant used is calculated from the volume and concentration added.

In most cases, titrant and sample solutions are clear and colourless, as are the products of their reaction. This makes it impossible to see when the equivalence point is reached. Thus, before beginning an acid–base titration, we mix an appropriate acid–base indicator with the sample. An indicator is a solution of a weak acid or base that changes colour at a certain pH, visually "indicating" when the equivalence point is reached and the titration is complete. The **endpoint** of a titration occurs just as the indicator changes colour. At the endpoint we stop the titration. The volume of titrant in the burette is recorded both before and after the titration. The difference between these readings gives the volume of titrant used.

Titrations are rarely 100 % accurate or precise because there are many opportunities for error. Achieving precision in the laboratory can be challenging. That is why titrations are usually repeated a few times and the titration volumes are averaged.

Titrations and pH Curves

Acid-base titrations may be used to analyze a variety of characteristics of acids and bases. In some cases, the titration is used to determine the amount or concentration of a solute in a sample (as in the case of the food technologist). In other cases, titration may be used to monitor the pH changes that occur during neutralization.

Titrations Involving Strong Acids and Strong Bases

Recall from earlier Chemistry courses that the products of the reaction between a strong acid and a strong base are a salt and water. We will illustrate the titration of a strong acid by a strong base (a strong acid–strong base titration) by considering a specific example. In this example the sample is 50.0 mL of 0.200 mol/L nitric acid, $HNO_3(aq)$, and the titrant is 0.100 mol/L sodium hydroxide solution, $NaOH(aq)$ (**Figure 2**). We will calculate the pH of the solution at five selected points (stages) during the titration, at which specific volumes of the titrant have been added.

Investigation **8.7.1**

Acid–Base Titration (page 571)
In this investigation you will first standardize the titrant using a primary standard, then use the titrant to determine the concentration of hydrogen ions in an unknown solution.

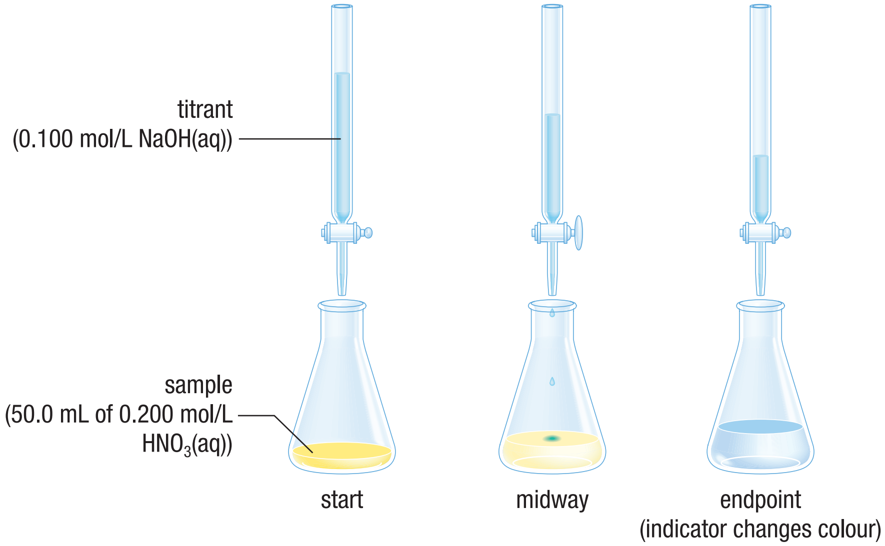


Figure 2 A typical titration of a strong acid with a strong base. The chosen indicator is yellow in an acidic solution and becomes blue in a basic solution.

STAGE 1: BEFORE TITRANT IS ADDED TO THE SAMPLE

Since nitric acid, $HNO_3(aq)$, is a strong acid (it is completely ionized in aqueous solution), the initial sample solution contains the following entities:

$H^+(aq)$, $NO_3^-(aq)$, and $H_2O(l)$

Since a 0.200 mol/L nitric acid solution contains hydrogen ions at a concentration of 0.200 mol/L,

$$\begin{aligned}[H^+(aq)] &= 0.200 \text{ mol/L} \\ pH &= -\log[H^+(aq)] \\ &= -\log(0.200) \\ pH &= 0.699\end{aligned}$$

STAGE 2: AFTER 10.0 mL OF TITRANT IS ADDED TO THE SAMPLE

In this titration, the sample contains the following entities:

$H^+(aq)$, $NO_3^-(aq)$, and $H_2O(l)$

The titrant, NaOH(aq), adds the following entities:

$Na^+(aq)$, $OH^-(aq)$, and $H_2O(l)$

Before any reaction occurs between the entities of the titrant and the entities of the sample, the solution in the receiving flask contains the following entities:

$H^+(aq)$, $NO_3^-(aq)$, $Na^+(aq)$, $OH^-(aq)$, and $H_2O(l)$

Soon after the addition of the titrant to the sample, the following net ionic reaction will occur between hydrogen ions and hydroxide ions:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

This reaction reduces the concentrations of hydrogen ions and hydroxide ions in the solution. **Table 1** shows the amounts of hydrogen ions and hydroxide ions in the receiving flask before and after the reaction. Note that hydrogen ions react with hydroxide ions in a 1:1 molar ratio.

Table 1 Amounts of $H^+(aq)$ and $OH^-(aq)$ in the Flask After 10.0 mL of Titrant Is Added

	$H^+(aq)$ +	$OH^-(aq)$ →	$H_2O(l)$
Amount before reaction	50.0 mL × 0.200 mol/L = 10.0 mmol	10.0 mL × 0.100 mol/L = 1.00 mmol	
Amount after reaction	10.0 mmol − 1.00 mmol = 9.00 mmol	1.00 mmol − 1.00 mmol = 0 mmol	

After the reaction, the solution in the receiving flask contains $H^+(aq)$, $NO_3{}^-(aq)$, $Na^+(aq)$, and $H_2O(l)$. (The $OH^-(aq)$ ions have been consumed). The sodium ion, $Na^+(aq)$, has no acid or base properties. The nitrate ion, $NO_3{}^-(aq)$, is the conjugate base of the strong acid $HNO_3(aq)$ and is therefore only a very weak base. Consequently, neither $NO_3{}^-(aq)$ nor $Na^+(aq)$ ions affect the solution's pH. The pH will be determined by the concentration of hydrogen ions remaining, as follows:

$$[H^+(aq)] = \frac{n_{H^+}}{V}$$

n_{H^+} = amount of H^+ (aq) ions remaining (mmol)

V = volume of solution in receiving flask (mL)

$$[H^+(aq)] = \frac{9.0\ \cancel{m}\text{mol}}{(50.0 + 10.0)\ \cancel{m}\text{L}}$$

$$[H^+(aq)] = 0.15\ \text{mol/L}$$

$$\text{pH} = -\log(0.15)$$
$$\text{pH} = 0.82$$

The pH of the solution after 10.0 mL of titrant is added is 0.82. Note that the volume of the solution in the receiving flask (60.0 mL) is the sum of the original volume of the sample (50.0 mL) and the volume of titrant added (10.0 mL).

STAGE 3: AFTER 50.0 mL OF TITRANT IS ADDED TO THE SAMPLE

We will now calculate the pH of the solution in the receiving flask after 50.0 mL of the titrant has been added to the sample. Note that we do not base these calculations on the contents of the receiving flask at the end of Stage 2. Instead, we treat the situation as though we have added 50.0 mL of titrant to the original 50.0 mL sample of nitric acid (**Table 2**).

Proceeding exactly as we did in Stage 2, we can determine that when 50.0 mL of sodium hydroxide solution has been added to the 50.0 mL sample of nitric acid, the solution in the receiving flask has a pH of 1.30.

UNIT TASK BOOKMARK

You may find this information on titration useful if you need to perform this procedure as part of the Unit Task, which is outlined on page 582.

Table 2 Amounts of H^+(aq) and OH^-(aq) in the Flask After 50.0 mL of Titrant Is Added

	$H^+(aq)$ +	$OH^-(aq)$ →	$H_2O(l)$
Amount before reaction	50.0 mL × 0.200 mol/L = 10.0 mmol	50.0 mL × 0.100 mol/L = 5.00 mmol	
Amount after reaction	10.0 mmol − 5.00 mmol = 5.0 mmol	5.00 mmol − 5.00 mmol = 0 mmol	

STAGE 4: AFTER 100.0 mL OF TITRANT IS ADDED TO THE SAMPLE: THE EQUIVALENCE POINT

In this titration, the equivalence point—the point at which the amount of base added reacts completely with all the acid originally present—is achieved when 100 mL of titrant has been added to the sample (**Table 3**).

Table 3 Amounts of H^+(aq) and OH^-(aq) in the Flask After 100.0 mL of Titrant Is Added

	$H^+(aq)$ +	$OH^-(aq)$ →	$H_2O(l)$
Amount before reaction	50.0 mL × 0.200 mol/L = 10.0 mmol	100.0 mL × 0.100 mol/L = 10.00 mmol	
Amount after reaction	10.0 mmol − 10.00 mmol = 0 mmol	10.00 mmol − 10.00 mmol = 0 mmol	

As Table 3 shows, enough hydroxide ions have been added to react exactly with all of the hydrogen ions in the sample of nitric acid. After this reaction, the entities in solution are $Na^+(aq)$, $NO_3^-(aq)$, and $H_2O(l)$. As mentioned earlier, $Na^+(aq)$ and $NO_3^-(aq)$ do not affect the pH of the solution. Thus, only the $H^+(aq)$ ions produced by the autoionization of water determine the pH of the solution in the receiving flask. Since $[H^+(aq)] = 1.00 \times 10^{-7}$ mol/L, pH = 7.00: neutral.

STAGE 5: AFTER 150.0 mL OF TITRANT IS ADDED TO THE SAMPLE

The calculation in **Table 4** shows how the addition of 150 mL of sodium hydroxide solution to the original sample of nitric acid affects the pH of the solution in the receiving flask. At this stage, excess hydroxide ions have been added.

Table 4 Amounts of H^+(aq) and OH^-(aq) in the Flask After 150.0 mL of Titrant Is Added

	$H^+(aq)$ +	$OH^-(aq)$ →	$H_2O(l)$
Amount before reaction	50.0 mL × 0.200 mol/L = 10.0 mmol	150.0 mL × 0.100 mol/L = 15.0 mmol	
Amount after reaction	10.0 mmol − 10.0 mmol = 0 mmol	15.0 mmol − 10.0 mmol = 5.0 mmol	

In this case, an excess of hydroxide ions has been added to the receiving flask. Thus, these ions will determine the pH of the resulting solution.

$$[OH^-(aq)] = \frac{n_{OH^-}}{V}$$

$$n_{OH^-} = \text{amount of } OH^-(aq) \text{ in excess (mmol)}$$

$$V = \text{volume of solution (mL)}$$

$$[OH^-(aq)] = \frac{5.0\ \cancel{m}\text{mol}}{(50.0 + 150.0)\ \cancel{m}\text{L}}$$

$$= \frac{5.0 \text{ mmol}}{200.0 \text{ mL}}$$

$$[OH^-(aq)] = 0.025 \text{ mol/L}$$

Since $[H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$
we can determine $[H^+(aq)]$ and hence the pH of the solution:

$$\begin{aligned}[H^+(aq)] &= \frac{1.0 \times 10^{-14}}{[OH^-(aq)]} \\ &= \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-2}} \\ [H^+(aq)] &= 4.0 \times 10^{-13}\ \text{mol/L} \\ \text{pH} &= -\log[H^+(aq)] \\ &= -\log(4.0 \times 10^{-13}) \\ \text{pH} &= 12.40\end{aligned}$$

The pH of the solution in the receiving flask is 12.40.

pH CURVES FOR STRONG ACID–STRONG BASE TITRATIONS

pH curve a graph of pH plotted against volume of titrant added in an acid–base titration; titration curve

The results of these calculations may be illustrated in a graph of pH plotted against volume of titrant added. Such a graph is called a **pH curve**, or a titration curve. **Figure 3** shows the pH curve for the above calculations. The centre of the vertical region of the pH curve indicates the equivalence point. This graph, with its equivalence point at pH 7, is typical of a strong acid–strong base titration.

LEARNING **TIP**

pH Curves

pH curves provide a wealth of information:

- equivalence points
- initial pH of solution
- number of quantitative reactions
- pH endpoints
- transition points for selecting indicators

pH curves can also be plotted using empirical data measured with a pH meter. pH readings are taken frequently throughout the titration, and plotted against the volume of titrant added.

Note that the pH changes very gradually until the titration is close to the equivalence point, where a dramatic change occurs. We can explain this observation as follows: Early in the titration there is a relatively large concentration of hydrogen ions in the solution, and the addition of a given amount of hydroxide ions thus produces only a small change in pH. However, near the equivalence point the concentration of hydrogen ions is relatively small, and the addition of hydroxide ions produces a large pH change.

When you calculate pH values at different points in a titration, you must consider whether hydrogen or hydroxide ions are in excess during each part of the titration. Let us first consider the titration of a strong acid with a strong base:

- Before the equivalence point, you may calculate $[H^+(aq)]$ (and hence the pH) by dividing the remaining amount of hydrogen ions (in millimoles) by the total volume of the solution in the receiving flask (in millilitres).
- At the equivalence point, the pH is always equal to 7. (Note that this is only true for titrations involving a strong acid and a strong base. You will learn about the equivalence point pH values for other titrations shortly.)
- After the equivalence point, you may calculate $[OH^-(aq)]$ by dividing the amount of excess hydroxide ions by the total volume of the solution in the receiving flask. Then obtain $[H^+(aq)]$ from K_w, and calculate pH.

The titration of a strong base with a strong acid requires reasoning very similar to that used above, except, of course, that hydroxide ions are in excess before the equivalence point and hydrogen ions are in excess after the equivalence point. **Table 5** and **Figure 4** show the data and pH curve for the titration of 100.0 mL of 0.500 mol/L sodium hydroxide solution with 1.000 mol/L hydrochloric acid. The curve has the opposite shape to that in Figure 3, as you might expect. The equivalence point occurs when 50.00 mL of the acid has been added, since at this point 5.00 mmol of hydrogen ions has been added to react with the original 5.00 mmol of hydroxide ions.

Table 5 Changes in pH during a Titration of 100.0 mL of 0.500 mol/L NaOH(aq) with 1.000 mol/L HCl(aq)

Initial volume of NaOH(aq) (mL)	Initial amount of NaOH(aq) (mmol)	Volume of 1.000 mol/L HCl(aq) added (mL)	Amount of added HCl(aq) (mmol)	Amount of excess reagent remaining (mmol)	Total volume of solution (mL)	Concentration of ion in excess (mmol/mL)	pH
100.0	50.00	0	0	50.0 OH^-(aq)	100.0	0.500 OH^-(aq)	13.700
100.0	50.00	40.0	40.0	10.0 OH^-(aq)	140.0	0.0714 OH^-(aq)	12.854
100.0	50.00	45.0	45.0	5.0 OH^-(aq)	145.0	0.034 OH^-(aq)	12.54
100.0	50.00	48.0	48.0	2.0 OH^-(aq)	148.0	0.014 OH^-(aq)	12.13
100.0	50.00	49.0	49.0	1.0 OH^-(aq)	149.0	0.0067 OH^-(aq)	11.83
100.0	50.00	49.5	49.5	0.5 OH^-(aq)	149.5	0.003 OH^-(aq)	11.5
100.0	50.00	50.0	50.0	0	150.0	0	7.0
100.0	50.00	50.5	50.5	0.5 H^+(aq)	150.5	0.003 H^+(aq)	2.5
100.0	50.00	51.0	51.0	1.0 H^+(aq)	151.0	0.0066 H^+(aq)	2.18
100.0	50.00	52.0	52.0	2.0 H^+(aq)	152.0	0.013 H^+(aq)	1.88
100.0	50.00	55.0	55.0	5.0 H^+(aq)	155.0	0.032 H^+(aq)	1.49
100.0	50.00	60.0	60.0	10.0 H^+(aq)	160.0	0.0625 H^+(aq)	1.204
100.0	50.00	100.0	100.0	50.0 H^+(aq)	200.0	0.250 H^+(aq)	0.602

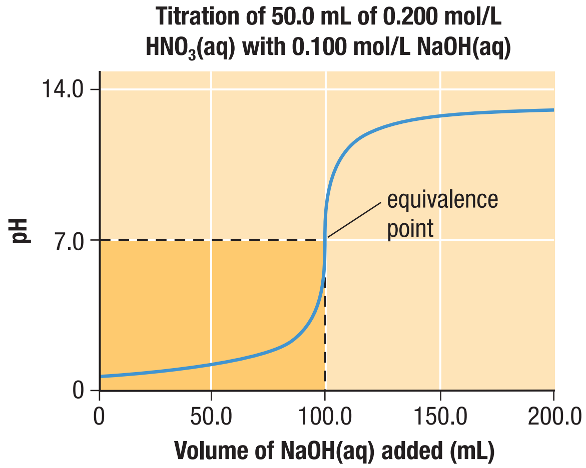


Figure 3 The pH curve for the titration of nitric acid with sodium hydroxide solution. Note that the equivalence point occurs when 100.0 mL NaOH(aq) has been added, the point where there is exactly enough OH^-(aq) to react with all the H^+(aq) originally present.

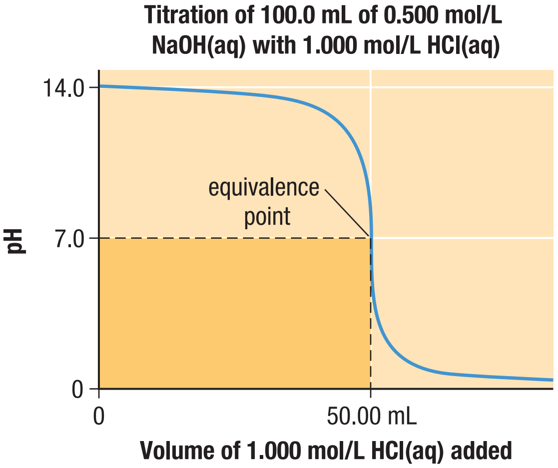


Figure 4 The pH curve for the titration of sodium hydroxide solution with hydrochloric acid.

Tutorial 1 Titrations Involving Strong Acids and Strong Bases

In this tutorial, you will be reminded how to determine the volume of titrant that must be added to a sample to reach the equivalence point in a strong base–strong acid titration. You will then learn how to determine the concentration of hydrogen ions and the pH of the solution after some strong base has been added during a strong acid–strong base titration.

Sample Problem 1: Determining the Volume of Titrant Required to Reach the Equivalence Point

What volume of 3.00 mol/L hydroiodic acid, HI(aq), must be added to a 15.0 mL sample of a 2.50 mol/L potassium hydroxide solution to reach the equivalence point?

Given: [HI(aq)] = 3.00 mol/L; V_{KOH} = 15.0 mL; [KOH(aq)] = 2.50 mol/L

Required: V_{HI} needed to reach the equivalence point

Solution:

Step 1. Determine the amount of OH^-(aq) in the sample before titration.

KOH(s) will completely dissociate into K^+(aq) and OH^-(aq) ions. Thus, 15.0 mL of a 2.50 mmol/mL solution of KOH(aq) contains 2.50 mmol/mL OH^-(aq). The amount of OH^-(aq) in 15.0 mL of this solution is

$$\begin{aligned} n_{\text{OH}^-} &= c_{\text{OH}^-} \times V_{\text{OH}^-} \\ &= (2.50\ \text{mmol}/\cancel{\text{mL}})(15.0\cancel{\text{mL}}) \\ n_{\text{OH}^-} &= 37.5\ \text{mmol} \end{aligned}$$

Step 2. Determine the volume of acid needed to react with all of the base in the sample.

HI(aq) will be completely ionized into H^+(aq) and I^-(aq) ions. The concentration of H^+(aq) will be equal to the concentration of HI(aq). Thus, in a 3.00 mol/L HI(aq) solution, the concentration of H^+(aq) is 3.00 mol/L. The H^+(aq) ions supplied by the titrant will neutralize the OH^-(aq) ions in the sample:

$\text{H}^+\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{H}_2\text{O(l)}$

Since H^+(aq) reacts with OH^-(aq) in a 1:1 molar ratio, 37.5 mmol of OH^-(aq) will require 37.5 mmol of H^+(aq) to reach the equivalence point.

The volume of 3.00 mol/L HI(aq) containing 37.5 mmol of H^+(aq) is

$$\begin{aligned} V_{\text{HI}} &= \frac{n_{\text{HI}}}{[\text{HI(aq)}]} \\ &= \frac{(37.5\ \cancel{\text{mmol}})}{(3.00\ \cancel{\text{mmol}}/\text{mL})} \\ V_{\text{HI}} &= 12.5\ \text{mL} \end{aligned}$$

Statement: 12.5 mL of 3.50 mol/L hydroiodic acid must be added to 25.0 mL of 2.50 mol/L potassium hydroxide to reach the equivalence point.

Sample Problem 2: Determining [H^+(aq)] and pH

In a titration, a 25.00 mL sample of 0.350 mol/L hydrochloric acid is titrated with standardized 0.500 mol/L sodium hydroxide solution. Determine the amount of unreacted hydrogen ions and the pH of the sample after 10.00 mL of NaOH(aq) is added.

Given: V_{HCl} = 25.00 mL; c_{HCl} = 0.350 mol/L; V_{NaOH} = 10.00 mL; c_{NaOH} = 0.500 mol/L

Required: n_{H^+}; pH

Solution: Hydrochloric acid is a strong acid and sodium hydroxide is a strong base.

Step 1. Determine the amount of H^+(aq) in the sample before titration.

Since HCl(aq) is a strong acid, a 0.350 mmol/mL solution of HCl(aq) contains 0.350 mmol/mL H^+(aq) and 0.350 mmol/mL Cl^-(aq) ions. The amount of H^+(aq) in 25.00 mL of this solution is

$$\begin{aligned} n_{\text{H}^+} &= c_{\text{H}^+} \times V_{\text{H}^+} \\ &= (0.350\ \text{mmol}/\cancel{\text{mL}})(25.00\ \cancel{\text{mL}}) \\ n_{\text{H}^+} &= 8.75\ \text{mmol} \end{aligned}$$

There is 8.75 mmol of H^+(aq) in the sample before titration.

Step 2. Determine the amount of OH^-(aq) added to the sample by the titrant.

Since NaOH(s) is a strong base, a 0.500 mmol/mL solution of NaOH(aq) contains 0.500 mmol/mL OH^-(aq). The amount of OH^-(aq) in 10.00 mL of this solution is

$$\begin{aligned} n_{OH^-} &= [OH^-(aq)] \times V_{OH^-} \\ &= (0.500\ \text{mmol}/\cancel{\text{mL}})(10.00\ \cancel{\text{mL}}) \\ n_{OH^-} &= 5.00\ \text{mmol} \end{aligned}$$

There is 5.00 mmol of OH^-(aq) in the sample solution.

Step 3. Determine the amounts of H^+(aq) and OH^-(aq) in the receiving flask after reaction. The calculation is shown in **Table 6**.

Table 6 Amounts of H^+(aq) and OH^-(aq) in the Flask After 10.0 mL of Titrant Is Added

	H^+(aq) +	OH^-(aq) →	H_2O(l)
Amount before reaction	8.75 mmol	5.00 mmol	
Amount after reaction	8.75 mmol – 5.00 mmol = 3.75 mmol	5.00 mmol – 5.00 mmol = 0 mmol	

There is 3.75 mmol of H^+(aq) and no OH^-(aq) in the receiving flask after reaction.

Step 4. Determine the concentration of any excess H^+(aq) or OH^-(aq) in the receiving flask and calculate pH.

Since there is 3.75 mmol excess H^+(aq) in the solution in the receiving flask,

$$\begin{aligned} c_{H^+} &= \frac{n_{H^+}}{V_{\text{solution}}} \\ &= \frac{3.75\ \text{mmol}}{(25.00 + 10.00)\ \text{mL}} \\ &= \frac{3.75\ \cancel{\text{m}}\text{mol}}{35.00\ \cancel{\text{m}}\text{L}} \\ c_{H^+} &= 0.107\ \text{mol/L} \end{aligned}$$

$$\begin{aligned} \text{pH} &= -\log\,[H^+(aq)] \\ &= -\log\,(0.107) \\ \text{pH} &= 0.971 \end{aligned}$$

Statement: The pH of the solution is 0.971 and the sample contains 3.75 mmol H^+(aq).

Practice

1. Calculate the volume of titrant needed to reach the equivalence point in the titration of a 25.0 mL sample of 0.50 mol/L NaOH(aq) by 0.10 mol/L HCl(aq). K/U [ans: 0.12 L]
2. For the titration in Sample Problem 2,
   (a) what is the concentration of unreacted H^+(aq) and the pH of the solution after 5.0 mL of the sodium hydroxide solution, NaOH(aq), has been added?
   (b) what is the amount (in moles) of unreacted H^+(aq) and the pH of the solution after 20.0 mL of the sodium hydroxide solution has been added? K/U
   [ans: (a) $[H^+(aq)] = 0.208$ mol/L; pH = 0.681 (b) 0 mmol H^+(aq); pH = 12.398]

Titrations Involving Weak Acids and Strong Bases

You have seen that, since strong acids are completely ionized in aqueous solution and strong bases are completely dissociated, the calculations used to determine the pH for titrations involving strong acids and strong bases are quite straightforward. However, when a weak acid is being titrated with a strong base, there is a major difference: to calculate the concentration of hydrogen ions, $[H^+(aq)]$, and pH after a certain amount of strong base has been added, we must deal with the weak acid ionization equilibrium. In performing these calculations it is very important to remember that even though the acid is weak, it *reacts essentially to completion* with the hydroxide ion. In other words, at the equivalence point, all of the acid in the flask has reacted.

In the following tutorial, you will learn how the concentration of a weak acid solution may be determined by titrating it with a strong base. The sample problems demonstrate a problem-solving strategy for analyzing the changes in hydrogen ion concentration and pH that occur at different stages during the titration.

Tutorial 2 Titrations Involving Weak Acids and Strong Bases

In Sample Problem 1, you will learn how to determine the concentration of a weak acid solution by titration with a strong base. In Sample Problem 2, you will analyze the titration of a weak acid by a strong base by determining the amount of unreacted acid that remains in the solution in the receiving flask at three different points in the titration. You will also calculate the pH of the solution at these three points.

Sample Problem 1: Determining the Concentration of a Weak Acid Solution by Titration with a Strong Base

A 25.0 mL sample of hydrofluoric acid, HF(aq), is titrated with 0.400 mol/L standardized sodium hydroxide solution, NaOH(aq). Determine the concentration of the acid if 60.5 mL of titrant is required to reach the equivalence point.

Given: V_{HF} = 25.0 mL; V_{NaOH} = 60.5 mL; c_{NaOH} = 0.400 mol/L

Required: [HF(aq)]

Solution: In this titration, hydrofluoric acid solution is the sample and sodium hydroxide solution is the titrant.

Step 1. Determine the amount of OH^-(aq) ions required to reach the equivalence point.

The equivalence point is reached after 60.5 mL of sodium hydroxide solution has been added to the sample. Thus,

$$\begin{aligned} n_{NaOH} &= c_{NaOH} \times V_{NaOH} \\ &= (0.400\ \text{mmol}/\cancel{\text{mL}})(60.5\ \cancel{\text{mL}}) \\ n_{NaOH} &= 24.2\ \text{mmol} \end{aligned}$$

The equivalence point is reached when 24.2 mmol of NaOH(aq) has been added to the sample.

Step 2. Determine the concentration of the HF(aq) solution.

Since HF(aq) is a weak acid, the following equilibrium exists in the receiving flask before titration begins:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

The equilibrium position of this reaction lies far to the left. Before any NaOH(aq) titrant is added, only a very small number of HF(aq) molecules have ionized to form H^+(aq) and F^-(aq) ions. The OH^-(aq) ions introduced by the titrant will react with the H^+(aq) ions in the sample:

$$\underset{\text{(from HF(aq))}}{H^+(aq)} + \underset{\text{(from NaOH(aq))}}{OH^-(aq)} \rightarrow H_2O(l)$$

As additional OH^-(aq) ions are added, they react with the H^+(aq) ions in the sample, continually shifting the acid ionization equilibrium to the right. The equivalence point is reached when all of the HF(aq) molecules have ionized to form H^+(aq) and F^-(aq) ions, and the H^+(aq) ions have all reacted with OH^-(aq) ions to form H_2O(l). Since 24.2 mmol of OH^-(aq) is required to reach the equivalence point, there must have been 24.2 mmol of HF(aq) molecules in the original sample.

Thus,

$$c_{\mathrm{HF}} = \frac{n_{\mathrm{HF}}}{V_{\mathrm{HF}}}$$

$$= \frac{24.2\ \cancel{\mathrm{m}}\mathrm{mol}}{25.0\ \cancel{\mathrm{m}}\mathrm{L}}$$

$$c_{\mathrm{HF}} = 0.968\ \mathrm{mol/L}$$

Statement: The concentration of the hydrofluoric acid solution is 0.968 mol/L.

Sample Problem 2: Determining [H^+(aq)] and pH in a Weak Acid–Strong Base Titration

A quality-control technician places a 20.00 mL sample of 0.600 mol/L ethanoic acid, $HC_2H_3O_2$(aq) (a weak acid), in an Erlenmeyer flask. She titrates this sample with a standardized 0.300 mol/L solution of sodium hydroxide, NaOH(aq) (a strong base). Predict the amount of unreacted ethanoic acid and the pH of the solution

(a) before titration begins
(b) at the equivalence point when 40.00 mL of NaOH(aq) has been added
(c) beyond the equivalence point when a total of 60.00 mL of NaOH(aq) has been added

As in Sample Problem 1, this is a titration of a weak acid, $HC_2H_3O_2$(aq), by a strong base, NaOH(aq). The following equilibrium exists in the sample before titration begins:

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

Since ethanoic acid is a weak acid, the equilibrium position lies far to the left.

Since sodium hydroxide is a strong base, the titrant contains only Na^+(aq) and OH^-(aq) ions and water. When some titrant is added to the sample, the OH^-(aq) ions in the titrant react with the H^+(aq) ions in the sample according to the following net ionic (neutralization) equation:

$$\underset{(\text{from } HC_2H_3O_2(aq) \text{ equilibrium})}{H^+(aq)} + \underset{(\text{from NaOH(aq)})}{OH^-(aq)} \rightarrow H_2O(l)$$

This reaction reduces the concentration of H^+(aq) ions in the solution and shifts the ethanoic acid equilibrium to the right. The extent of this shift determines the concentrations of $HC_2H_3O_2$(aq), $C_2H_3O_2^-$(aq), and H^+(aq) remaining in the solution, and thus the pH. To determine concentration (and pH) values, you need to perform two separate analyses (**Figure 5**):

1. a *stoichiometry analysis* to determine the concentration of weak acid (ethanoic acid) remaining after a certain amount of strong base titrant is added
2. an *equilibrium analysis* to determine the new position of relevant equilibrium systems in the sample solution and, thus, the solution's pH

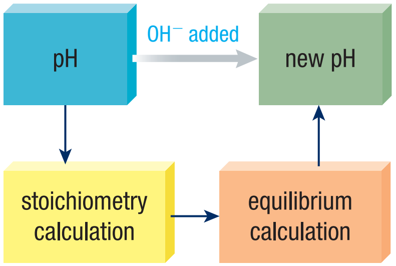


Figure 5 First consider the stoichiometry calculation and then the equilibrium calculation.

(a) Amount of unreacted $HC_2H_3O_2$(aq) and pH of the solution before titration begins

Given: $V_{HC_2H_3O_2} = 20.00$ mL; $c_{HC_2H_3O_2} = 0.600$ mol/L; $c_{\mathrm{NaOH}} = 0.300$ mol/L

Required: $n_{HC_2H_3O_2}$; pH

Solution: Before any titrant is added, the sample in the flask is simply a 0.600 mol/L $HC_2H_3O_2$(aq) solution. Since no reaction with NaOH(aq) has occurred, a stoichiometric analysis is not necessary. You may determine the amount of unreacted ethanoic acid in the sample and its pH by analyzing the ethanoic acid equilibrium only.

Step 1. Determine the amount of unreacted ethanoic acid molecules in the sample before titration begins.

Since ethanoic acid is a weak acid ($K_a = 1.8 \times 10^{-5}$), assume that, before titration, virtually none of the ethanoic acid molecules have ionized. Thus, the major entities in the sample solution are $HC_2H_3O_2$(aq) and H_2O(l).

The amount of $HC_2H_3O_2(aq)$ is calculated as follows:

$$\begin{aligned} n_{HC_2H_3O_2} &= c_{HC_2H_3O_2} \times V_{HC_2H_3O_2} \\ &= (0.600\ \text{mmol}/\cancel{\text{mL}})(20.00\ \cancel{\text{mL}}) \\ n_{NaOH} &= 12.0\ \text{mmol} \end{aligned}$$

The amount of unreacted ethanoic acid is 12.0 mmol.

Step 2. Determine the pH of the sample solution using the equilibrium calculation outlined in Section 8.6, Tutorial 2.

The major entities in solution (before ionization occurs) are $HC_2H_3O_2(aq)$ and $H_2O(l)$.

Set up an ICE table for the equilibrium reaction (**Table 7**).

Table 7 ICE Table for the Ionization of Ethanoic Acid, $HC_2H_3O_2(aq)$

	$HC_2H_3O_2(aq) \rightleftharpoons$	$H^+(aq)$ +	$C_2H_3O_2^-(aq)$
I	0.600	0	0
C	$-x$	$+x$	$+x$
E	$0.600 - x$	$+x$	$+x$

Step 3. Substitute the equilibrium concentration values into the K_a equation for this equilibrium, and solve for x:

$$K_a = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

From Appendix B5, $K_a = 1.8 \times 10^{-5}$:

$$1.8 \times 10^{-5} = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.600 - x}$$

Assuming that $0.600 - x \approx 0.600$ (use the hundred rule), the equilibrium expression becomes

$$\begin{aligned} 1.8 \times 10^{-5} &\approx \frac{x^2}{0.600} \\ x^2 &\approx 0.600 \times 1.8 \times 10^{-5} \\ x^2 &\approx 1.08 \times 10^{-5} \\ x &\approx \sqrt{1.08 \times 10^{-5}} \\ x &\approx 3.286 \times 10^{-3} \end{aligned}$$

The error in this result is 5 % or less. (Check this yourself.)

Step 4. Use the ICE table and the value of x to determine the hydrogen ion concentration at equilibrium and then calculate pH.

Since $[H^+(aq)] = x$ (from the ICE table)

$$\begin{aligned} \text{and } x &\approx 3.286 \times 10^{-3} \\ [H^+(aq)] &\approx 3.286 \times 10^{-3}\ \text{mol/L} \\ \text{pH} &= -\log[H^+(aq)] \\ \text{pH} &\approx -\log(3.286 \times 10^{-3}) \\ \text{pH} &\approx 2.48 \end{aligned}$$

Before titration begins, the pH of the sample is 2.48.

Statement: Before titration begins, the amount of unreacted $HC_2H_3O_2(aq)$ is 12.00 mmol and the pH of the sample is 2.48.

(b) Amount of unreacted ethanoic acid and pH of the solution at the equivalence point when 40.00 mL of NaOH(aq) has been added

Given: $V_{HC_2H_3O_2} = 20.00$ mL; $[HC_2H_3O_2(aq)] = 0.600$ mol/L; $V_{NaOH} = 40.00$ mL; $c_{NaOH(aq)} = 0.600$ mol/L

Required: Amount of $HC_2H_3O_2$(aq) at the equivalence point, $n_{HC_2H_3O_2}$; pH

Solution: Since a reaction between the ethanoic acid solution and the sodium hydroxide solution has occurred and the ethanoic acid equilibrium has been shifted to the right, two analyses are necessary: a stoichiometry analysis to determine the concentrations of unreacted ethanoic acid and ethanoate ions remaining, and an equilibrium analysis to determine the pH of the solution.

I. Stoichiometry Analysis

Step 1. List the major entities in the sample at the equivalence point.

As hydroxide ions from the titrant react with the hydrogen ions of the ethanoic acid equilibrium, the equilibrium continually shifts to the right. This continues until all $HC_2H_3O_2$(aq) molecules have ionized and the concentration of non-ionized $HC_2H_3O_2$(aq) molecules is reduced to zero. At this point (the equivalence point), all hydrogen ions have joined with hydroxide ions to form water. What remains is a salt (sodium ethanoate) solution containing the following major entities: Na^+(aq), $C_2H_3O_2^-$(aq), and H_2O(l).

Step 2. Determine whether any of the major entities are able to cause hydrolysis.

Na^+(aq) does not affect the pH of the solution. $C_2H_3O_2^-$(aq) is the conjugate base of a weak acid (ethanoic acid), and *does* hydrolyze. The pH of the solution will therefore be determined by the extent of this hydrolysis reaction.

Step 3. Write reaction equations for any hydrolysis reactions and their associated equilibrium constant equations:

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$$

The related ionization constant equation is

$$K_b = \frac{[HC_2H_3O_2(aq)][OH^-(aq)]}{[C_2H_3O_2^-(aq)]}$$

The value of K_b for $C_2H_3O_2^-$(aq) can be determined from the K_a of its conjugate acid, $HC_2H_3O_2$(aq), and K_w, as follows:

$$K_a = 1.8 \times 10^{-5};\ K_w = 1.0 \times 10^{-14}$$

$$K_w = K_a K_b$$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_b = 5.556 \times 10^{-10}$$

Therefore, $5.556 \times 10^{-10} = \dfrac{[HC_2H_3O_2(aq)][OH^-(aq)]}{[C_2H_3O_2^-(aq)]}$.

Step 4. Determine the initial concentration of any ions that cause hydrolysis.

To reach the equivalence point, 40.00 mL of NaOH(aq) was added to the original 20.00 mL of solution. At the equivalence point, the total volume of the solution is 60.00 mL. Since there was initially 12.00 mmol of $HC_2H_3O_2$(aq), the final amount will be 12.00 mmol of $C_2H_3O_2^-$(aq) at the equivalence point. This amount of $C_2H_3O_2^-$(aq) is dissolved in 60.00 mL of solution:

$$[C_2H_3O_2^-(aq)] = \frac{12.00\ \cancel{m}mol}{60.00\ \cancel{m}L}$$

$$[C_2H_3O_2^-(aq)] = 0.200\ mol/L$$

This is the concentration of ethanoate ions in the sample solution before hydrolysis reactions begin and the $C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$ equilibrium is established. Use this as the initial concentration of ethanoate ions in the equilibrium analysis below.

II. Equilibrium Analysis

Step 5. Set up an ICE table (**Table 8**).

Table 8 ICE Table for the Hydrolysis Reaction of $C_2H_3O_2^-(aq)$

	$C_2H_3O_2^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$OH^-(aq)$	+	$HC_2H_3O_2(aq)$
I	0.200		—		0		0
C	$-x$		—		$+x$		$+x$
E	$0.200 - x$		—		$+x$		$+x$

Step 6. Substitute the equilibrium concentration values into the equilibrium constant equation and solve for *x*.

$$\frac{[HC_2H_3O_2(aq)][OH^-(aq)]}{[C_2H_3O_2^-(aq)]} = K_b$$

$$\frac{x^2}{(0.200 - x)} = 5.556 \times 10^{-10}$$

Assuming that $0.200 - x \approx 0.200$ (using the hundred rule)

$$\frac{x^2}{0.200} \approx 5.555 \times 10^{-10}$$

$$x^2 \approx 1.111 \times 10^{-10}$$

$$x \approx 1.054 \times 10^{-5}$$

The error in the result is 5 % or less. (Check this yourself.)

$$[OH^-(aq)] \approx 1.054 \times 10^{-5}\ mol/L$$

$$pOH \approx -\log(1.054 \times 10^{-5})$$

$$pOH \approx 4.98$$

Since

$$pH + pOH = 14.00$$

$$pH = 14.00 - pOH$$

$$= 14.00 - 4.98$$

$$pH = 9.02$$

Statement: The pH of the solution at the equivalence point is 9.025 and there are no ethanoic acid molecules left in solution.

You can see that the equivalence point does not necessarily mean the point at which the sample has a pH of 7. While all strong acid–strong base titrations *do* have a pH of 7 at the equivalence point, the same may not be true of other titrations. Rather, the equivalence point is the point at which equivalent amounts of reactants have reacted, according to the balanced chemical equation. At the equivalence point, there may still be ions in solution that affect the pH. As you might predict, the titration of any weak acid with a strong base results in a basic solution with a pH greater than 7.

(c) Amount of unreacted $HC_2H_3O_2(aq)$ and pH of the sample solution beyond the equivalence point when a total of 60.00 mL of NaOH(aq) has been added

Once you pass the equivalence point and continue adding titrant, the concentration of hydroxide ions in the sample will rise sharply since there are no more ethanoic acid molecules to provide hydrogen ions for neutralization. Thus, the $[OH^-(aq)]$ may be calculated from the volume of NaOH(aq) added, the concentration of NaOH(aq) (0.300 mol/L), and the total volume of the solution after the addition. You may then use the $[OH^-(aq)]$ to calculate the pH of the solution. Notice that the ethanoate ion hydrolysis equilibrium that you analyzed in (b) still exists in the sample solution:

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$$

However, the K_b of this equilibrium is so low ($K_b = 5.6 \times 10^{-10}$) that its contribution of $OH^-(aq)$ ions is insignificant when compared to the relatively large amount contributed by the drop of titrant added to the solution.

Given: $V_{HC_2H_3O_2} = 20.00$ mL; $[HC_2H_3O_2(aq)] = 0.600$ mol/L; $V_{NaOH} = 60.00$ mL; $[NaOH(aq)] = 0.300$ mol/L

Required: Amount of $HC_2H_3O_2(aq)$ beyond the equivalence point, $n_{HC_2H_3O_2}$; pH

Solution: At the equivalence point and beyond, no unreacted ethanoic acid remains in the solution. The acid has completely ionized and all the $H^+(aq)$ ions have reacted.

Step 1. Identify the major entities in the solution:

$Na^+(aq)$; $OH^-(aq)$; $C_2H_3O_2^-(aq)$; $H_2O(l)$

Step 2. Identify any ions that may cause hydrolysis.

Ethanoate ions may cause hydrolysis; sodium ions do not. As already mentioned, ethanoate ion hydrolysis produces a very small amount of $OH^-(aq)$ ions compared to the much larger amount of $OH^-(aq)$ introduced by the titrant.

Step 3. Determine the $[OH^-(aq)]$, pOH, and pH of the solution.

As you remember from (b) of this sample problem, it takes 40.00 mL of titrant for the sample to reach the equivalence point. At or beyond this point in the titration, there are no unreacted $HC_2H_3O_2(aq)$ molecules in the sample solution. Any titrant added to the solution after the equivalence point adds excess $OH^-(aq)$ to the solution. These excess $OH^-(aq)$ ions will determine the pH of the solution. The volume of excess NaOH(aq) added to the sample ($V_{\text{NaOH added}}$) is

$$V_{\text{NaOH added}} = 60.00 \text{ mL} - 40.00 \text{ mL}$$

$$V_{\text{NaOH added}} = 20.00 \text{ mL}$$

You may now use the volume of excess NaOH(aq) added to the sample solution to calculate the amount of excess NaOH(aq) added:

$$\begin{aligned} n_{\text{NaOH added}} &= V_{\text{NaOH added}} \times c_{\text{NaOH added}} \\ &= 20.00 \cancel{\text{mL}} \times 0.300 \text{ mmol}/\cancel{\text{mL}} \\ n_{\text{NaOH added}} &= 6.00 \text{ mmol} \end{aligned}$$

Since NaOH is a strong base, the amount of $OH^-(aq)$ ions added to the sample is equal to the amount of NaOH(aq) added. Thus,

$$n_{OH^- \text{ added}} = 6.00 \text{ mmol}$$

There is 6.00 mmol of $OH^-(aq)$ ions in the sample solution. Calculate the concentration of $OH^-(aq)$ ions in the sample solution using the amount of $OH^-(aq)$ in the solution ($n_{OH^- \text{ in solution}}$) and the volume of the solution after the addition (V_{solution}).

The volume of solution in the flask after the addition of 60 mL of NaOH(aq) is

$$\underset{\text{(total volume of solution)}}{V_{\text{solution}}} = \underset{\text{(sample volume)}}{20.00 \text{ mL}} + \underset{\text{(volume of titrant added)}}{60.00 \text{ mL}}$$

$$V_{\text{solution}} = 80.00 \text{ mL}$$

Calculate the concentration of $OH^-(aq)$ ions in the sample solution, $[OH^-(aq)]_{\text{in solution}}$, using the amount of $OH^-(aq)$ ions in the solution ($n_{OH^- \text{ in solution}}$) and the total volume of the solution (V_{solution}):

$$\begin{aligned} c_{OH^- \text{ in solution}} &= \frac{n_{OH^- \text{ in solution}}}{V_{\text{soultion}}} \\ &= \frac{6.0 \text{ mmol}}{80 \text{ mL}} \\ c_{OH^- \text{ in solution}} &= 0.075 \text{ mol/L} \end{aligned}$$

Use the concentration of $OH^-(aq)$ ions in the sample solution to calculate the pOH of the solution and then use the formula pH + pOH = 14 to calculate the solution's pH.

$$\begin{aligned} \text{pOH} &= -\log[OH^-(aq)] \\ &= -\log(0.075) \\ \text{pOH} &= 1.12 \\ \text{pH} + \text{pOH} &= 14 \\ \text{pH} &= 14 - \text{pOH} \\ &= 14 - 1.12 \\ \text{pH} &= 12.88 \end{aligned}$$

Statement: There are no unreacted $HC_2H_3O_2(aq)$ molecules in the sample solution and the pH of the sample solution is 12.88.

Practice

1. In the titration in Sample Problem 2, what is the amount of unreacted ethanoic acid and the pH of the solution during titration
   (a) when 10.00 mL of 0.300 mol/L NaOH(aq) is added? [ans: 9 mmol; pH = 4.267]
   (b) when 18.00 mL of 0.300 mol/L NaOH(aq) is added? K/U [ans: 7 mmol; pH = 4.656]
2. A 25.00 mL sample of a weak acid, hypochlorous acid, HClO(aq), is titrated with 0.100 mol/L potassium hydroxide solution, KOH(aq). The equivalence point is reached when 19.3 mL of the base has been added. K/U
   (a) What is the concentration of the acid? [ans: 0.0772 mol/L]
   (b) Determine the pH at the equivalence point ($K_a = 3.5 \times 10^{-8}$). [ans: 10.05]

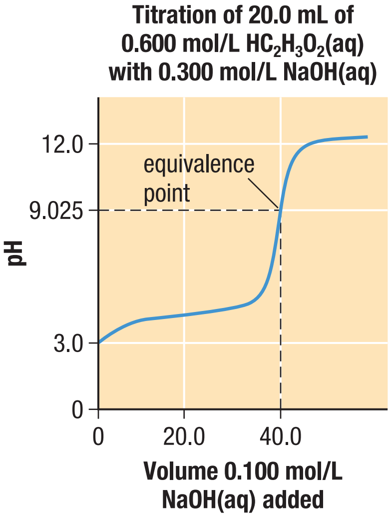


Figure 6 The pH curve for the titration of ethanoic acid, $HC_2H_3O_2(aq)$, with sodium hydroxide solution. Note that the equivalence point occurs at 40.0 mL of NaOH(aq) added, where the amount of added hydroxide ions exactly equals the original amount of acid.

pH CURVES FOR WEAK ACID–STRONG BASE TITRATIONS

Figure 6 illustrates the titration curve for the titration in Tutorial 2. The pH at the equivalence point is greater than 7.0 because the ethanoate ion, $C_2H_3O_2^-(aq)$, present at this point is a base and reacts with water to produce $OH^-(aq)$.

The strength of a weak acid affects the shape of the pH curve of a titration. **Figure 7** shows pH curves for 50 mL samples of 0.10 mol/L solutions of six different acids titrated with 0.10 mol/L sodium hydroxide solution, NaOH(aq). Note that the equivalence point occurs in each case when the same volume of 0.10 mol/L NaOH(aq) has been added but that the shapes of the curves differ. The weaker the acid, the higher the pH value at the equivalence point. In particular, note that the vertical region of the curve becomes shorter as the acid becomes weaker. The choice of an indicator is particularly important for such a titration. WEB LINK

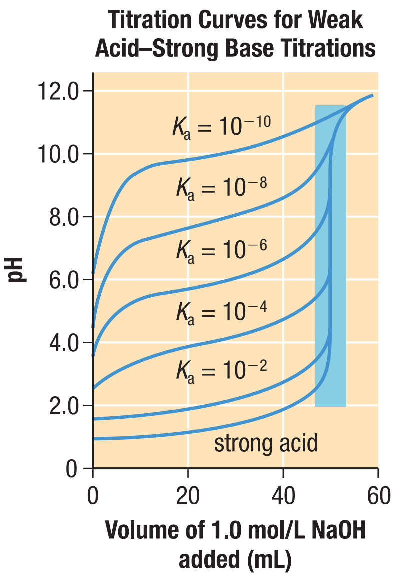


Figure 7 The pH curves for the titrations of 50.0 mL samples of 0.10 mol/L acids with various K_a values with 0.10 mol/L sodium hydroxide, NaOH(aq).

Titrations Involving Weak Bases and Strong Acids

The calculations for titrations in which a weak base is titrated with a strong acid are similar to those in which a weak acid is titrated with a strong base. The major difference is that in a weak base–strong acid titration, the strong acid titrant is completely ionized and we have to consider the equilibrium of the weak base sample. Remember that even though the base is weak, it *reacts essentially to completion* with the hydrogen ions provided by the strong acid titrant. We will not analyze weak base–strong acid titrations in sample problems because the concepts and calculations are similar to those involved in weak acid–strong base titrations. In general, determine the pH in weak base–strong acid titrations as follows:

- Before titration begins, calculate the pH of the sample using the K_b of the weak base.
- At the equivalence point, hydrogen ions in the solution are the result of hydrolysis caused by the conjugate acid of the weak base. Calculate the pH using the K_a of the conjugate acid. The solution will be acidic: pH will be less than 7.
- Beyond the equivalence point, determine the pH of the solution by the amount of excess strong acid provided by the titrant. Determine the pH from the $[H^+(aq)]$ produced by the ionization of the strong acid.

Acid–Base Indicators

We can make the equivalence point of an acid–base titration more visible by adding a few drops of a solution called an acid–base indicator to the sample. There are many different acid–base indicators that change colour (have endpoints) at different pH levels. For example, the indicator called phenolphthalein starts to change from colourless to pink at a pH of 8.2. Ideally, we want the endpoint of a titration to coincide with the equivalence point, thus alerting us that the equivalence point has been reached.

The most common acid–base indicators are complex molecules that are themselves weak acids (represented by HIn). They exhibit one colour in their acid form and a different colour in their conjugate base form. For example, phenolphthalein is colourless in its HIn form and pink in its In^-, or basic, form (**Figure 8**). Indicators have K_a or K_b values as well; for example, the K_a of phenolphthalein is around 10^{-10} and the K_a of methyl orange is 6.3×10^{-6} (**Figure 9**).

UNIT TASK BOOKMARK

What indicator will you choose to test your consumer product in the Unit Task (page 582)? The information in this section might help you decide.

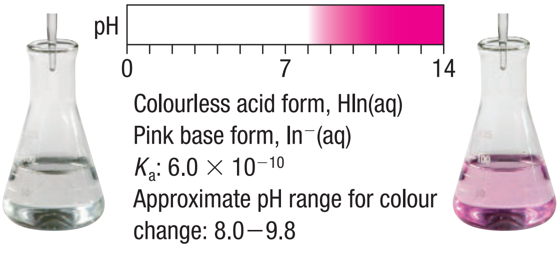


Figure 8 In an acid solution phenolphthalein indicator, HIn(aq), is colourless. When hydrogen ions are removed to give the base form, $In^-(aq)$, the colour changes to pink.

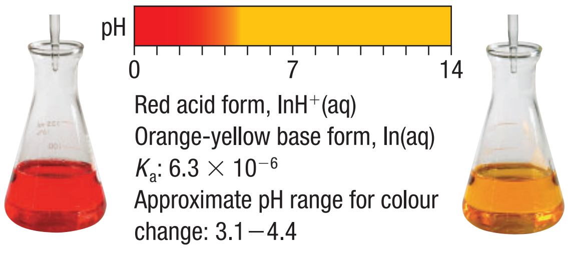


Figure 9 Methyl orange indicator is red in highly acidic solution.

Figure 10 shows the pH ranges of several commonly used acid–base indicators.

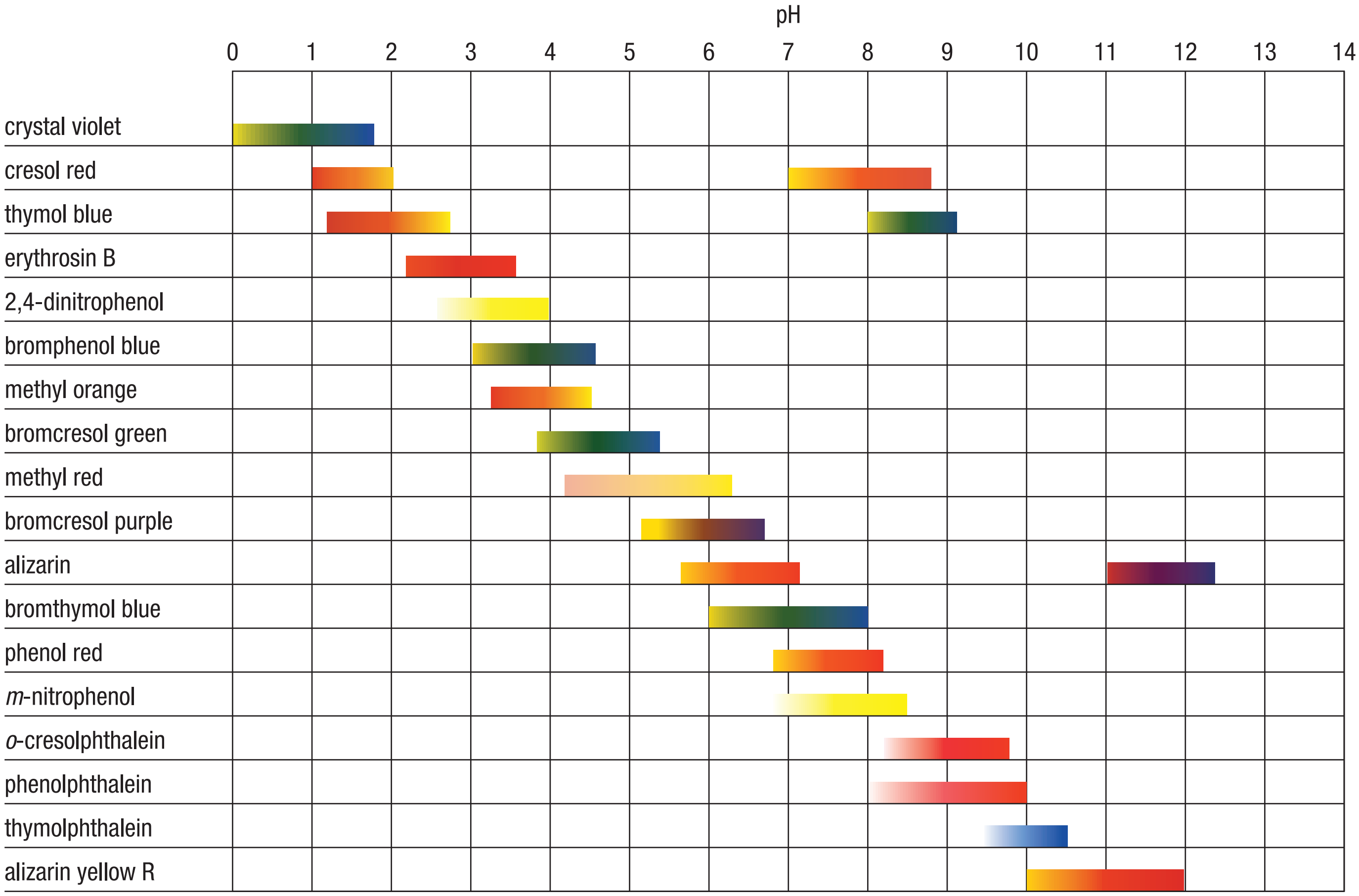


Figure 10 The useful pH ranges for several common indicators

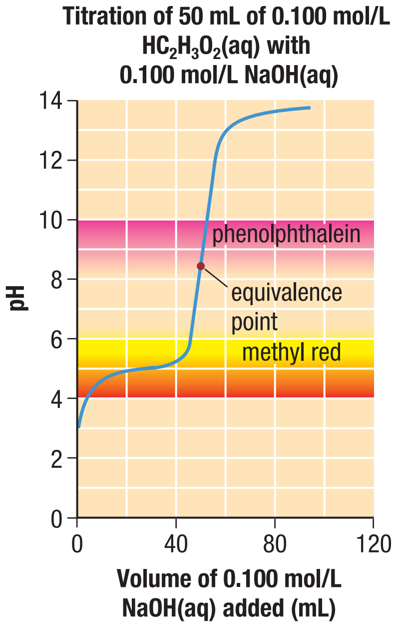


Figure 11 Phenolphthalein changes colour at a pH very close to the equivalence point of this titration. Methyl red changes colour too soon.

Selecting an Indicator

As mentioned earlier, when we select an indicator for a titration, we want the indicator endpoint and the titration equivalence point to be as close as possible. Choosing an indicator is easier if there is a large change in pH near the equivalence point of the titration. When we titrate a strong acid with a strong base there is a very rapid change from a low pH to a high pH around the equivalence point. Any indicator that changes colour anywhere along this pH range is suitable. The same is true when we titrate a strong base with a strong acid.

When we are titrating weak acids, however, the change in pH near the equivalence point is much smaller than for a strong acid. Figure 7 showed that the weaker the acid being titrated, the smaller the vertical area around the equivalence point. This allows much less flexibility in choosing the indicator. We must choose an indicator whose useful pH range has a midpoint as close as possible to the pH at the equivalence point. For example, in the titration of 0.1 mol/L ethanoic acid, $HC_2H_3O_2(aq)$, with 0.1 mol/L sodium hydroxide solution, the pH at the equivalence point is 8.7 (**Figure 11**). A good indicator choice would be phenolphthalein, since its useful pH range is 8 to 10. Methyl red, however, would change colour well before the equivalence point so the endpoint would be very different from the equivalence point. Thus, methyl red would not be a suitable indicator for this titration.

8.7 Review

Summary

- The progress of a titration is represented by plotting a pH curve showing the pH of the solution against the volume of titrant added.
- Strong acid–strong base titrations show a sharp change in pH near the equivalence point.
- In strong acid–strong base titrations, pH = 7 at the equivalence point because the pH is determined solely by the autoionization of water: $[H^+(aq)] = 1.0 \times 10^{-7}$ mol/L.
- In weak acid–strong base titrations, pH > 7 at the equivalence point because of hydrolysis caused by the conjugate base of the weak acid.
- In weak base–strong acid titrations, pH < 7 at the equivalence point because of hydrolysis caused by the conjugate acid of the weak base.
- When calculating pH values for a strong base–weak acid titration, perform stoichiometry first and then equilibrium.
- Indicators are often used to mark the equivalence point of an acid–base titration. An indicator changes colour at its endpoint. The goal is to have the endpoint and the equivalence point be as close as possible.

Questions

1. A 25.0 mL sample of hydrochloric acid, HCl(aq), is titrated with 67.2 mL of 0.125 mol/L potassium hydroxide solution, KOH(aq). What is the concentration of the acid? K/U
2. In a titration, 15.00 mL of hydrochloric acid, HCl(aq), is titrated with standardized sodium hydroxide solution, NaOH(aq). The amount concentration of each solution is 0.250 mol/L. K/U
   (a) What is the amount of $H^+(aq)$ and the pH of the sample before NaOH(aq) is added?
   (b) What is the amount of $H^+(aq)$ and the pH of the solution after 10.0 mL of NaOH(aq) is added?
   (c) What is the pH at the equivalence point?
3. A student titrates 40.0 mL of household ammonia solution, $NH_3(aq)$, with 25.0 mL of 0.50 mol/L hydrochloric acid, HCl(aq). K/U
   (a) What is the concentration of the ammonia solution?
   (b) What is the pH at the equivalence point?
4. Acetysalicylic acid (ASA) is the pain reliever in Aspirin. ASA is a weak acid with $K_a = 3.2 \times 10^{-4}$. One Aspirin tablet was ground up and dissolved in 25.0 mL of water. It was titrated using 0.15 mol/L sodium hydroxide. To reach the endpoint, 98.3 mL of base was required. K/U
   (a) Determine the concentration of the ASA solution.
   (b) What amount of ASA was present in the tablet?
   (c) What was the pH at the equivalence point?
5. A 50.00 mL sample of 0.30 mol/L methanoic acid, $HCO_2H(aq)$, is titrated with 0.30 mol/L sodium hydroxide solution, NaOH(aq). K/U
   (a) What volume of base is required to reach the endpoint?
   (b) What is the pH before titration begins?
   (c) What is the pH of the solution at the equivalence point?
6. If 10.0 mL of 0.500 mol/L sodium hydroxide solution, NaOH(aq), is added to 30.0 mL of 0.340 mol/L hydrocyanic acid, HCN(aq), what is the pH of the solution? K/U
7. Would cresol red be a good indicator for a titration of a strong acid with a strong base? Explain. K/U T/I
8. In a titration, 50.00 mL of 0.100 mol/L ethanoic acid, $HC_2H_3O_2(aq)$, is titrated with standardized 0.100 mol/L potassium hydroxide solution, KOH(aq). K/U T/I
   (a) What is the amount of unreacted $HC_2H_3O_2(aq)$ and the pH of the sample before titration?
   (b) What is the amount of unreacted ethanoic acid and the pH of the solution after 10.0 mL of base is added?
   (c) What is the pH when 30.0 mL of base is added?
   (d) What amount and volume of titrant must be added to reach the equivalence point?
   (e) What is a good indicator for this titration? Why?
9. Research a "digital titrator." Create an illustrated report to compare its advantages and disadvantages to the traditional titration setup. 🌐 K/U C A

WEB LINK

8.8 Buffer Systems

buffer an aqueous solution containing a conjugate acid–base pair that maintains a nearly constant pH when an acid or base is added

Much important chemistry, including almost all the chemistry of the natural world, occurs in aqueous solution. Living systems usually require a relatively narrow pH range for survival. Because of this, they depend on solutions that are resistant to changes in pH. Such a solution is called a **buffer**, or buffer solution: an aqueous solution that resists changes in pH upon the addition of an acid or base. A buffer contains a weak acid and its conjugate base (or a weak base and its conjugate acid) in an equilibrium mixture. Buffers may be prepared in a lab setting or they may be naturally occurring. Buffers can be created to maintain almost any pH value. In this section, we explore why buffers are important, their characteristics, and how they work.

Buffers in Action

Buffers may contain different acids, bases, and ions, but buffers all serve one purpose: to keep the pH of a solution constant when small quantities of acid or base are added to the solution.

Many biological processes include chemical reactions that must occur in a specific range of pH; buffers function to maintain this pH range. Gas exchange, muscle activity, and many other biological processes are sensitive to pH. Enzymes function at an optimal pH range. CAREER LINK

Although human blood contains many chemical components that help maintain the pH at a constant level, there is one particularly important conjugate acid–base pair: hydrogen carbonate, $HCO_3^-(aq)$, and carbonate, $CO_3^{2-}(aq)$. These ions produce a pH of 7.4 in healthy blood. Since our cells are so sensitive to pH, it is important that this pH be maintained. When reactions occur in our bodies, such as the formation of lactic acid, $HC_3H_5O_3(aq)$, by active muscles, these pH buffers must be capable of neutralizing the effects of this acid to maintain the blood's pH at 7.4. Even small changes in pH may have harmful effects on a person's health.

Buffers are also an important ingredient in many foods, drinks, and medicines. Buffers are useful to maintain the pH at a desired level. Sodium citrate, for example, is a common additive in products that contain fruit, such as jams and preserves (**Figure 1**). The citrate ion combines with the weak acids in fruit to form a buffer system that resists pH changes in the product. This helps to stabilize the properties of the product, including taste. Sodium citrate also acts as a preservative. Aspartame is a common artificial sweetener used in low-calorie soft drinks. The stability of the aspartame molecule is pH dependent. Aspartame decomposes readily unless its pH is maintained within a range of 4 to 5 by the additives in soft drinks. Some medicines use a buffer coating to reduce the risk of stomach upset from the acidic medicinal ingredient.

Figure 1 Buffers help to preserve foods containing fruits or vegetables.

The food industry uses weak acids to change the flavour of food and to improve its shelf life. Citric acid is one of the most commonly used acidic additives in the food industry. It is a natural organic (carboxylic) acid found in many fruits, vegetables, and dairy products. This acid is added to many foods, beverages, and candies. The sour taste of citric acid enhances fruit flavours like citrus and berry. The salt calcium citrate, which tastes sour and salty, contains the conjugate base of citric acid. The use of citric acid and calcium citrate deters bacterial growth and stabilizes pH. You will explore the use of buffers in the food industry in more detail in Section 8.9.

UNIT TASK BOOKMARK

For the Unit Task (page 582), you may ask a testable question regarding the buffering capacity of your consumer product.

Characteristics of a Buffer

A buffer keeps the pH of a solution within a certain narrow range. When an acid or base is added to this solution, the buffer prevents the pH from changing. Buffers always contain a mixture of a weak acid (or base) and its conjugate ion in solution. Living cells contain a phosphate buffer, which includes the conjugate acid–base pair of dihydrogen phosphate, $H_2PO_4^-(aq)$ (a weak acid), and hydrogen phosphate, $HPO_4^{2-}(aq)$ (its conjugate base). This buffer system maintains a neutral pH. Other combinations of an acid (or base) and its conjugate maintain the pH at different pH values.

Acidic Buffers

An acidic buffer includes a weak acid and its conjugate base. Let us consider an acidic buffer system in which ethanoic acid, $HC_2H_3O_2(aq)$, is the weak acid. Its conjugate base is the ethanoate ion, $C_2H_3O_2^-(aq)$. Imagine a titration in which a basic titrant, such as sodium hydroxide solution, is added to the ethanoic acid buffer. The pH is monitored throughout the titration as shown in **Figure 2**. You see that, in the highlighted region, the pH changes very little as $OH^-(aq)$ ions are added. This region, about halfway to the equivalence point, is called the "buffer zone." In the buffer zone there are approximately equal amounts of unreacted ethanoic acid, $HC_2H_3O_2(aq)$, and its conjugate base, $C_2H_3O_2^-(aq)$, in the receiving flask. This mixture of entities prevents large changes in pH as more hydroxide ions are added. The solution in the receiving flask at halfway to the equivalence point is a buffer: the pH of this solution changes very little as more base is added.

In contrast, at or near the equivalence point, the pH changes dramatically when even small amounts of hydroxide ions are added.

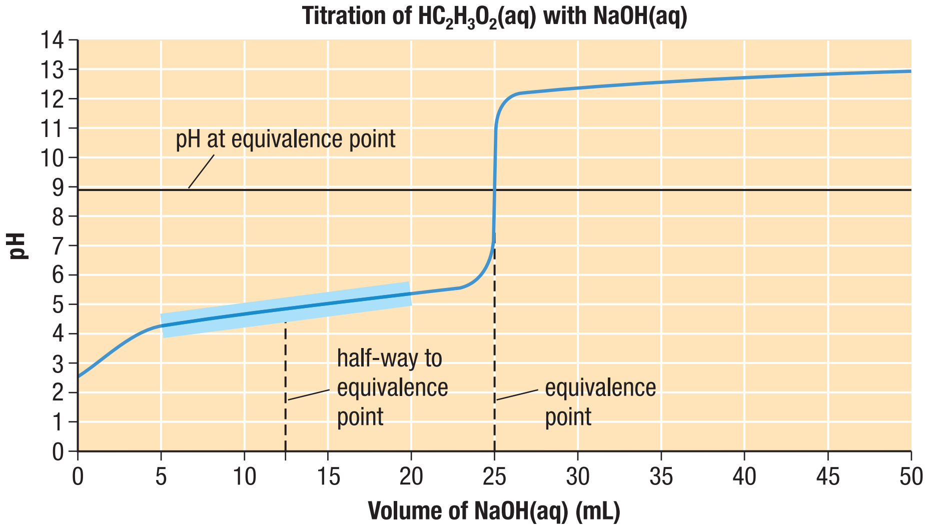


Figure 2 This graph shows the titration of ethanoic acid (a weak acid) with sodium hydroxide (a strong base). Note that, from the addition of 5 to 23 mL of base, the pH of the solution stays relatively constant.

Another example of an acidic buffer is a solution containing hydrofluoric acid, $\mathrm{HF(aq)}$, and sodium fluoride, $\mathrm{NaF(aq)}$. The conjugate base in this case is the fluoride ion, $\mathrm{F^-(aq)}$. As you know, since hydrofluoric acid is a weak acid, a hydrofluoric acid solution has a relatively high concentration of non-ionized HF molecules and relatively low concentrations of $\mathrm{H^+(aq)}$ and $\mathrm{F^-(aq)}$ ions. A solution of hydrofluoric acid alone is not a buffer solution. To change this solution to a buffer, we must increase the concentration of $\mathrm{F^-(aq)}$ ions until it is approximately equal to the concentration of non-ionized $\mathrm{HF(aq)}$ molecules. This is done by adding a soluble salt containing fluoride ions, such as sodium fluoride, $\mathrm{NaF(s)}$.

Buffer solutions are usually prepared by simply mixing a weak acid or base with a soluble salt containing the corresponding conjugate acid or base in approximately equal (molar) amounts.

By mixing appropriate acid–salt or base–salt combinations, we can prepare buffer solutions with virtually any pH. Acidic buffers (those based on a weak acid and a salt containing its conjugate base) generally have their buffering zone at a pH below 7.

Buffers with a higher pH can be made from a weak base and its conjugate acid. An example of a basic buffer is a solution containing ammonia, $\mathrm{NH_3(aq)}$, and a salt. In this case, ammonia is the weak base component and the ammonium ion, $\mathrm{NH_4{}^+(aq)}$, is the conjugate acid component. A soluble salt such as $\mathrm{NH_4Cl(s)}$ could provide the additional $\mathrm{NH_4{}^+(aq)}$ ions necessary to form the buffer.

How Do Buffers Work?

How does a buffer maintain its pH when an acid or a base is added? Suppose a buffer contains relatively large quantities of a weak acid, $\mathrm{HA(aq)}$, and its conjugate base, $\mathrm{A^-(aq)}$. The general equation for the ionization equilibrium is

$$\mathrm{HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)}$$

When hydroxide ions are added to the solution, the non-ionized weak acid molecules react with the hydroxide ions, removing the hydroxide ions from the solution.

$$\mathrm{HA(aq) + OH^-(aq) \rightleftharpoons A^-(aq) + H_2O(aq)}$$

The net result of this reaction is that, when a base is added, $\mathrm{OH^-(aq)}$ ions are not allowed to accumulate but are replaced by $\mathrm{A^-(aq)}$ ions (**Figure 3**).

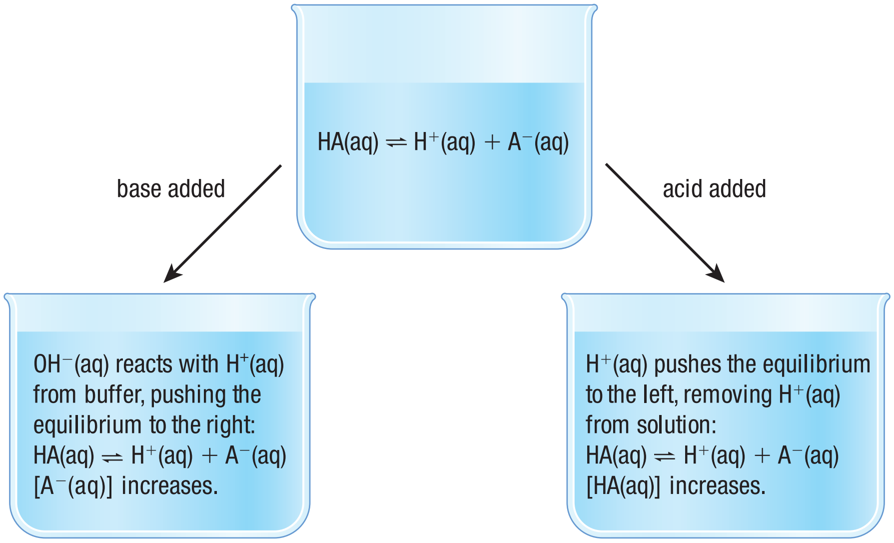


Figure 3 Le Châtelier's principle explains the changes that occur in an acidic buffer solution when a base or an acid is added.

When hydrogen ions are added to the solution, they push the ionization equilibrium to the left, removing the hydrogen ions from the solution and increasing the concentration of the acid molecules.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The pOH (and hence the pH) of the solution thus remains relatively constant regardless of whether an acid or a base is added.

We can understand the stability of the pH under these conditions by examining the equilibrium equation for the ionization of a weak acid, HA(aq):

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

Rearranging this equation to isolate $[H^+(aq)]$ on the left side, we get

$$[H^+(aq)] = K_a \frac{[HA(aq)]}{[A^-(aq)]}$$

This form of the equation tells us that the equilibrium concentration of hydrogen ions, $H^+(aq)$, (and thus the pH) is determined by the ratio $[HA(aq)]/[A^-(aq)]$. When $OH^-(aq)$ ions are added, HA(aq) is converted to $A^-(aq)$, and the $[HA(aq)]/[A^-(aq)]$ ratio decreases. However, if the amounts of HA(aq) and $A^-(aq)$ originally present are very large compared with the amount of $OH^-(aq)$ added (as is the case in buffer solutions), the change in the $[HA(aq)]/[A^-(aq)]$ ratio, and thus the change in pH, will be small.

The essence of buffering is that [HA(aq)] and $[A^-(aq)]$ are large compared with the amount of $OH^-(aq)$ added. Thus, when a small quantity of $OH^-(aq)$ is added, the concentrations of HA(aq) and $A^-(aq)$ change only slightly. Under these conditions, the $[HA(aq)]/[A^-(aq)]$ ratio stays almost the same within the buffering zone. Thus $[H^+(aq)]$ (and pH) remain virtually constant.

Similarly, when hydrogen ions are added to a buffer, they react with $A^-(aq)$ ions to form the weak acid, HA(aq). There will be a net change of $A^-(aq)$ to HA(aq). However, if $[A^-(aq)]$ and [HA(aq)] are large compared with the amount of $H^+(aq)$ added, little change in the pH will occur. **Figure 4** illustrates why a high initial concentration of the buffering entities is very important for them to function effectively.

Concentrated Buffer Solution

Original solution → New solution

$$\frac{[A^+(aq)]}{[HA(aq)]} = \frac{5.00\ mol/L}{5.00\ mol/L} \xrightarrow[\text{added}]{H^+(aq)} \frac{[A^+(aq)]}{[HA(aq)]} = \frac{4.99\ mol/L}{5.01\ mol/L}$$

$$\frac{[A^+(aq)]}{[HA(aq)]} = 1.00 \qquad \frac{[A^+(aq)]}{[HA(aq)]} = 0.996$$

(a)

Dilute Buffer Solution

Original solution → New solution

$$\frac{[A^+(aq)]}{[HA(aq)]} = \frac{0.050\ mol/L}{0.050\ mol/L} \xrightarrow[\text{added}]{H^+(aq)} \frac{[A^+(aq)]}{[HA(aq)]} = \frac{0.040\ mol/L}{0.060\ mol/L}$$

$$\frac{[A^+(aq)]}{[HA(aq)]} = 1.00 \qquad \frac{[A^+(aq)]}{[HA(aq)]} = 0.67$$

(b)

Figure 4 (a) When the initial concentrations of the buffering entities are high, the addition of a small amount of acid has little effect on their ratio. (b) When the initial concentrations are low, the addition of a small amount of acid has a much greater effect on their ratio.

Instructions for mixing buffer solutions can be found in many chemistry resources, including *The CRC Handbook of Chemistry and Physics*.

pH of Buffer Solutions

Buffers are simply solutions of weak acids or bases and their respective soluble salts. The pH calculations for buffers require exactly the same procedures used in studying acids, bases, and acid–base titrations. The problem-solving strategy was introduced in Section 8.4. *This is not a new type of problem.* In Tutorial 1, you will learn how to use this strategy to calculate the pH of buffer solutions.

Investigation 8.8.1

Buffer Systems (page 572)

This observational study compares how pH changes in a buffer solution and in a control solution.

Tutorial 1 The Initial pH of Buffer Solutions

In this tutorial, you will learn how to calculate the pH of an acidic buffer and a basic buffer.

Sample Problem 1: Calculating the pH of an Acidic Buffer

A chemist in a leather-tanning facility is considering using a buffer containing 0.50 mol/L ethanoic acid, $HC_2H_3O_2$(aq) ($K_a = 1.8 \times 10^{-5}$), and 0.50 mol/L sodium ethanoate, $NaC_2H_3O_2$(aq). Calculate the pH of this solution.

Given: 0.50 mol/L ethanoic acid, $K_a = 1.8 \times 10^{-5}$; 0.50 mol/L sodium ethanoate

Required: pH

Solution:

Step 1. Write the formulas of all the entities in solution.

The entities in the solution are

$$\underset{\substack{\text{Weak}\\\text{acid}}}{\underset{\uparrow}{HC_2H_3O_2(aq)}}, \quad \underset{\substack{\text{Neither}\\\text{acid nor}\\\text{base}}}{\underset{\uparrow}{Na^+(aq)}}, \quad \underset{\substack{\text{Weak base}\\\text{(conjugate}\\\text{base of}\\HC_2H_3O_2)}}{\underset{\uparrow}{C_2H_3O_2^-(aq)}}, \quad \text{and} \quad \underset{\substack{\text{Very weak}\\\text{acid or}\\\text{base}}}{\underset{\uparrow}{H_2O(l)}}$$

Step 2. Write the reaction equation and the equilibrium constant equation for the equilibrium that determines the pH of the solution.

To decide which equilibrium reaction determines the pH of the solution, examine the list of entities in solution. The ethanoic acid ionization equilibrium, which involves both $HC_2H_3O_2$(aq) and $C_2H_3O_2^-$(aq), is the relevant reaction:

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

The equilibrium constant equation is

$$K_a = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

$$1.8 \times 10^{-5} = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

Step 3. Determine initial and equilibrium concentrations.

Table 1 shows the ICE table. Note that, before reaction, the initial concentration of $HC_2H_3O_2$(aq) is 0.50 mol/L and the initial concentration of H^+(aq) is essentially 0 mol/L. Also, note that the initial concentration of $C_2H_3O_2^-$(aq) is equal to the concentration of $NaC_2H_3O_2$(aq).

Table 1 ICE Table for the Ethanoic Acid–Sodium Ethanoate Buffer Equilibrium (mol/L)

	$HC_2H_3O_2$(aq)	$\rightleftharpoons$	H^+(aq)	+	$C_2H_3O_2^-$(aq)
I	0.50		≈ 0		0.50
C	$-x$		$+x$		$+x$
E	$0.50 - x$		x		$0.50 + x$

Step 4. Substitute equilibrium concentrations from the ICE table into the equilibrium constant equation.

$$1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$1.8 \times 10^{-5} = \frac{(x)(0.50 + x)}{0.50 - x}$$

Step 5. Use the hundred rule to determine if any simplifying assumptions may be made.

$$\text{Since } \frac{[HC_2H_3O_2(aq)_{\text{initial}}]}{K_a} = \frac{0.50}{1.8 \times 10^{-5}}$$

$$\frac{[HC_2H_3O_2(aq)_{\text{initial}}]}{K_a} = 2.8 \times 10^{4}$$

Since the $\frac{[HC_2H_3O_2(aq)_{\text{initial}}]}{K_a}$ ratio is much greater than 100, you may make an assumption about the equilibrium concentration of $HC_2H_3O_2(aq)$:

$0.50 - x \approx 0.50$

By a similar calculation you may make an assumption about the equilibrium concentration of $C_2H_3O_2^-(aq)$:

$0.50 + x \approx 0.50$

Thus,

$$1.8 \times 10^{-5} \approx \frac{(x)(0.50)}{0.50}$$

$$x \approx 1.8 \times 10^{-5}$$

Step 6. Use the 5 % rule to check your result:

$$\frac{x}{[HC_2H_3O_2(aq)_{\text{initial}}]} \times 100\ \% = \frac{1.8 \times 10^{-5}}{0.5} \times 100\ \%$$

$$\frac{x}{[HC_2H_3O_2(aq)_{\text{initial}}]} \times 100\ \% = 0.0036\ \%$$

Since 0.0036 % < 5 %, the error in the result is acceptable.

A similar calculation shows that the assumption that $0.50 + x \approx 0.50$ is valid.

Step 7. Determine $[H^+(aq)]$ at equilibrium and calculate pH:

$$x \approx 1.8 \times 10^{-5}$$

$$[H^+(aq)] \approx 1.8 \times 10^{-5}$$

$$\text{pH} \approx -\log(1.8 \times 10^{-5})$$

$$\text{pH} \approx 4.74$$

Statement: The pH of the ethanoic acid/sodium ethanoate buffer is 4.74.

Basic buffers are solutions of a weak base and a soluble salt of its conjugate acid in approximately equal concentrations. You can determine the pH of a basic buffer in much the same way as an acidic buffer.

Sample Problem 2: Calculating the pH of a Basic Buffer

Calculate the pH of a buffer made with 0.25 mol/L ammonia solution, $NH_3(aq)$ ($K_b = 1.8 \times 10^{-5}$), and 0.40 mol/L ammonium chloride solution, $NH_4Cl(aq)$.

Given: 0.25 mol/L ammonia solution, $K_b = 1.8 \times 10^{-5}$; 0.40 mol/L ammonium chloride solution

Required: pH

Solution:

Step 1. Write the formulas of all the entities in solution.

The entities in the solution are $NH_3(aq)$, $\underbrace{NH_4^+(aq),\ Cl^-(aq)}_{\text{From the dissolved } NH_4Cl(aq)}$, and $H_2O(l)$.

Step 2. Write the reaction equation and the equilibrium constant equation for the equilibrium that determines the pH of the solution.

Since the chloride ion is such a weak base and water is a weak acid or base, the important equilibrium is

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The equilibrium constant equation is

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

$$1.8 \times 10^{-5} = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

Step 3. Determine initial and equilibrium concentrations (**Table 2**).

Table 2 ICE Table for the Ionization of Ammonia, $NH_3(aq)$ (mol/L)

	$NH_3(aq)$	+ $H_2O(l)$ $\rightleftharpoons$	$NH_4^+(aq)$	+ $OH^-(aq)$
I	0.25	—	0.40	≈ 0
C	$-x$	—	$+x$	$+x$
E	$0.25 - x$	—	$0.40 + x$	x

Step 4. Substitute equilibrium concentrations from the ICE table into the equilibrium constant equation:

$$1.8 \times 10^{-5} = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

$$1.8 \times 10^{-5} = \frac{(0.40 + x)(x)}{0.25 - x}$$

Step 5. Use the hundred rule to determine if any simplifying assumptions may be made.

Assume that $0.25 - x \approx 0.025$ and that $0.40 + x = 0.40$.

$$1.8 \times 10^{-5} \approx \frac{(0.40)(x)}{0.25}$$

$$x \approx 1.1 \times 10^{-5}$$

Step 6. Use the 5 % rule to check your result.

The approximation is valid by the 5 % rule. (Check for yourself.)

Step 7. Determine $[OH^-(aq)]$ at equilibrium and calculate pH.

$$x \approx 1.1 \times 10^{-5}$$

$$[OH^-(aq)] \approx 1.1 \times 10^{-5}$$

$$pOH \approx -\log(1.1 \times 10^{-5})$$

$$pOH \approx 4.96$$

$$\begin{aligned} pH &\approx 14.00 - pOH \\ &\approx 14.00 - 4.96 \\ pH &\approx 9.04 \end{aligned}$$

Statement: The pH of the buffer with 0.25 mol/L $NH_3(aq)$ and 0.40 mol/L $NH_4Cl(aq)$ is 9.04.

Practice

1. A buffer solution contains 2.250 mol/L ethanoic acid, $HC_2H_3O_2(aq)$ ($K_a = 1.8 \times 10^{-5}$), and 2.250 mol/L sodium ethanoate, $NaC_2H_3O_2(aq)$. Calculate the pH of this buffer solution. K/U [ans: 4.74]
2. A buffer contains 0.10 mol/L hydrofluoric acid, HF(aq) ($K_a = 6.6 \times 10^{-4}$), and 0.10 mol/L fluoride ions, $F^-(aq)$. Calculate the pH of this buffer solution. K/U [ans: 3.18]
3. Calculate the pH of a buffer solution containing 0.15 mol/L ammonia $NH_3(aq)$ ($K_b = 1.8 \times 10^{-5}$), and 0.04 mol/L ammonium chloride, $NH_4Cl(aq)$. K/U [ans: 8.83]

Buffers and Equilibria

We can better understand buffers in action if we consider their Brønsted–Lowry equations. For example, when sodium hydroxide is added to a buffer solution of ethanoic acid–ethanoate ions, the following equilibrium occurs:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightleftharpoons C_2H_3O_2^-(aq) + H_2O(l)$$

The hydroxide ions from sodium hydroxide convert ethanoic acid to ethanoate ions. This reduces the ratio of ethanoic acid to ethanoate ions, which results in a slight increase in pH. If there were no buffer present, there would be a large increase in pH. This ethanoic acid–ethanoate buffer can also buffer a strong acid in a similar way, except that added hydrogen ions (from the strong acid) encourage the formation of ethanoic acid:

$$C_2H_3O_2^-(aq) + H^+(aq) \rightleftharpoons HC_2H_3O_2(aq)$$

Investigation 8.8.2

The Effectiveness of an Antacid (page 573)

This investigation involves a back-titration procedure to determine how much acid is neutralized by a crushed antacid tablet. You may compare several brands of tablets.

The ratio of ethanoic acid to ethanoate ions will increase and the pH will decrease slightly. The pH decrease would be much greater if there were no buffer present.

WEB LINK

We can summarize the characteristics of buffers as follows:

- Buffers contain relatively large concentrations of a weak acid and its conjugate base. They can involve a weak acid, HA(aq), and the conjugate base, $A^-(aq)$, or a weak base, B(aq), and the conjugate acid, $BH^+(aq)$.
- When an acid is added to a buffered solution (of either type), the hydrogen ions react essentially to completion with the weak base present:

$$H^+(aq) + A^-(aq) \rightleftharpoons HA(aq) \quad \text{or} \quad H^+(aq) + B(aq) \rightleftharpoons BH^+(aq)$$

- When a base is added to a buffer, the hydroxide ions react essentially to completion with the weak acid present:

$$OH^-(aq) + HA(aq) \rightleftharpoons A^-(aq) + H_2O(l) \quad \text{or}$$

$$OH^-(aq) + BH^+(aq) \rightleftharpoons B(aq) + H_2O(l)$$

The pH of a buffer is determined by the ratio of the concentrations of the weak acid and weak base.

$$\frac{[HA(aq)]}{[A^-(aq)]} \quad \text{or} \quad \frac{[B(aq)]}{[BH^+(aq)]}$$

As long as this ratio remains virtually constant, the pH will remain virtually constant. This will be the case as long as the amounts of the buffering entities (HA(aq) and A^-(aq) or B(aq) and BH^+(aq)) present are large compared with the amounts of H^+(aq) or OH^-(aq) added.

When solving problems involving the addition of a strong acid or base to a buffer, deal first with the stoichiometry of the resulting reaction. A strong acid will dissociate completely and react with the chemical entities present in solution. After the stoichiometric calculations are completed, then consider the equilibrium calculations (**Figure 5**).

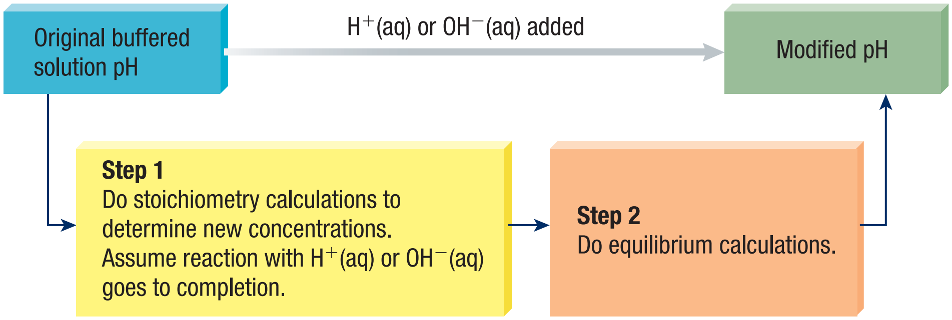


Figure 5 The procedure for solving calculations involving buffers

The Capacity of a Buffer

buffering capacity the ability of a buffer to resist changes in pH by reacting with added hydrogen ions or hydroxide ions

The **buffering capacity** of a buffer solution represents the amount of added hydrogen ions or hydroxide ions that the buffer can absorb without a significant change in pH (**Figure 6**). A buffer with a large capacity contains large concentrations of buffering components and so can absorb a relatively large amount of hydrogen ions or hydroxide ions and show little pH change. The pH of a buffered solution is determined by the [HA(aq)]/[A^-(aq)] ratio. The capacity of a buffered solution is determined by the magnitudes of [HA(aq)] and [A^-(aq)].

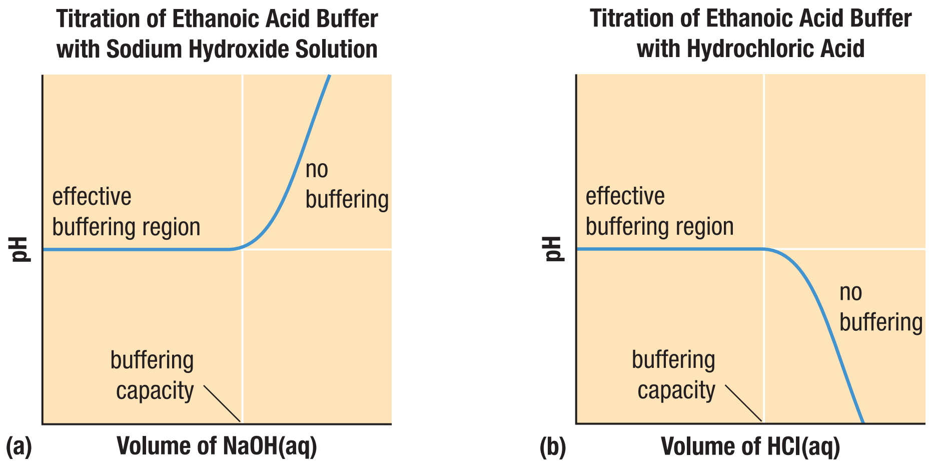


Figure 6 (a) Ethanoic acid buffer with a strong base added (b) Ethanoic acid buffer with a strong acid added. The pH changes quickly once all of the available buffer is depleted.

8.8 Review

Summary

- Buffers contain a weak acid, HA(aq), and a salt of its conjugate base, A^-(aq), or a weak base, B(aq), and a salt of its conjugate acid, BH^+(aq).
- Buffers play an important role in many biological and industrial processes.
- When an acid or a base is added to a buffer, the system resists change in pH by removing OH^-(aq) or H^+(aq) ions from solution until its buffering capacity is exceeded.
- The buffering capacity of a solution containing HA(aq) and A^-(aq) depends on the ratio of [HA(aq)] to [A^-(aq)] (**Figure 7**). Buffering is most efficient when the ratio is close to 1.

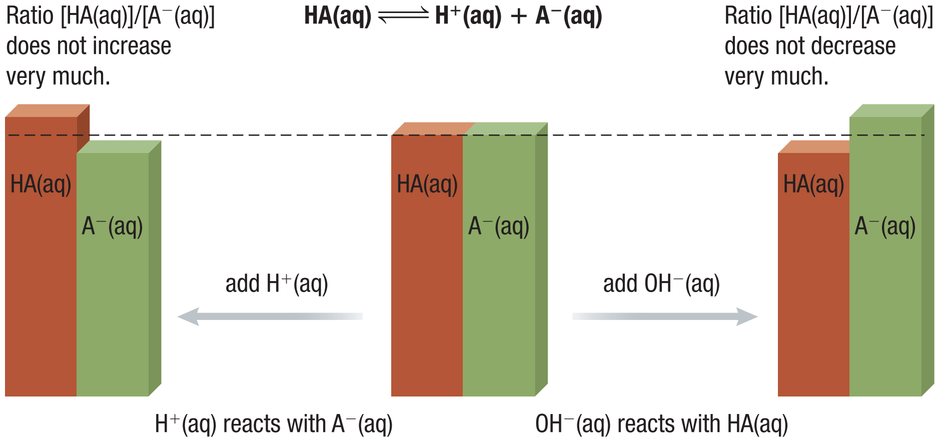


Figure 7 The effect of adding a strong acid or base to a buffer system

Questions

1. Describe the function of a buffer. K/U
2. What compounds make up a buffer? K/U
3. Write the equilibrium reaction equation for each of the following weak acids or bases. Name the conjugate base or acid in each case. K/U
   (a) phosphoric acid, H_3PO_4(aq)
   (b) carbonic acid, H_2CO_3(aq)
   (c) hydrogen sulfite ion, HSO_3^-(aq)
   (d) hypochlorite ion, ClO^-(aq)
4. For each acid or base listed in Question 3, suggest a salt that could be added to form a buffer. K/U
5. How will the equilibrium shift if a small amount of strong acid is added to a basic buffer solution? Write an example of this reaction equation. K/U
6. Explain what occurs in the buffer zone. K/U
7. A buffer contains 2.63 mol/L ethanoic acid, $HC_2H_3O_2$(aq) ($K_a = 1.8 \times 10^{-5}$), and 0.50 mol/L sodium ethanoate, $NaC_2H_3O_2$(aq). Calculate the pH of this solution. K/U
8. Calculate the pH of a buffer with 0.15 mol/L ammonia solution, NH_3(aq) ($K_b = 1.8 \times 10^{-5}$), and 0.04 mol/L ammonium chloride, NH_4Cl(aq). K/U
9. Research two buffer systems in the human body. Present your findings in a format of your choice. Your report should
   - explain why these buffers are important
   - include the equilibrium reaction equations
   - describe how each buffer responds to the addition of hydrogen or hydroxide ions

   🌐 T/I C A

🌐 WEB LINK

Explore an Issue in Acids and Bases

SKILLS MENU

- Defining the Issue
- Researching
- Identifying Alternatives
- Analyzing
- Defending a Decision
- Communicating
- Evaluating

Additives in the Food and Beverage Industry

Acids, bases, and buffers are widely used in the food and beverage industry (**Figure 1**). Acids and bases are artificial flavouring agents, and buffers stabilize the pH of food and beverage products. These substances may also be used to help thicken foods and beverages, maintain colour, and deter bacterial growth.

Citric acid is the acid most commonly added to foods. Others include ethanoic acid, lactic acid, and malic acid. If a salt is also added, containing the conjugate base of the acid, we have a buffer system that operates to keep the pH at a constant level. Typical salts used as food additives are sodium citrate and ammonium malate. Bases are less often added, but those that are used include ammonium hydroxide and calcium carbonate.

Figure 1 Pop commonly includes several acids and buffers.

The Issue

The media have been reporting that chemical additives are not safe. Some are calling for stricter government regulations. The food industry argues that our food supply is highly regulated and safe. They also say that the inclusion of additives such as acids, bases, and buffers enhances taste and reduces spoilage.

You will research and analyze this issue and then pick one of the following stakeholders: community member, journalist, chief financial officer of a food company, government minister, supermarket ordering manager, food scientist, dietitian, health-food advocate, allergist, or environmentalist. You will ultimately present your decision from this person's perspective. CAREER LINK

AUDIENCE

Your teacher and classmates will represent local citizens attending a public inquiry about the use of additives in prepared foods and beverages.

Goal

To promote your position on the use of a specific food additive to the citizens of your community so that they may make informed purchasing decisions.

Research

SKILLS HANDBOOK A5

You should research details related to the additive that you have chosen. Investigate the science behind the chemical: why it is added to food, how it works, possible health or environmental risks that it poses, and any claimed benefits. How widely used is the additive in other countries? Also think about ethical, cultural, and economic considerations with respect to the chemical's use. What financial costs and benefits are associated with using this food additive?

You might also want to explore the following topics:

- Some food ingredients decompose over time if not held at a constant pH. Why is this important?
- *Escherichia coli* is a bacterium that grows in many different environments, including on the surface of foods. The optimal pH for *E. coli* growth is about 6.0 to 7.0 but some strains can survive over a much wider range of pH. Using acidic additives to lower pH kills most of the bacteria. However, there are instances of *E. coli* becoming acid resistant and surviving at lower pHs. Other species of bacteria grow in different pH ranges. How might this affect the decision to use chemicals to modify the pH of a food?
- Buffer systems are used in dry mixes where there will be some variation in the pH of the water used to make the food or beverage. This ensures that the final product is consistent. Read through the ingredients list on a variety of food and beverage packages. Are any of these buffers? What is the most common buffer in your refrigerator or pantry? WEB LINK

Possible Solutions

The following questions might help you to develop a solution that would be appropriate for your stakeholder:

- What are the implications of banning the use of this additive?
- What would happen if it could be used without any restrictions?
- Should the food industry be allowed to self-regulate the use of this additive?
- How might other stakeholders view this issue? What would their arguments be?
- Should Canada adopt another country's approach? If so, which country's?

Decision

Decide what position your stakeholder would hold on the use of the chosen additive. Prepare to present this position, supported with facts and arguments.

Communicate

- Prepare a graphic organizer from the perspective of your role. Your graphic organizer should address both the advantages and disadvantages of your position. Graphic organizers can be t-charts, SWOT (strengths, weaknesses, opportunities, and threats) tables, flow charts, or any other suitable format.

Your graphic organizer should be designed to convince local citizens to support your position. Use persuasive arguments and back them up with researched facts. Be prepared to defend your arguments and answer questions.

- Post your graphic organizer for others to see. Review your classmates' graphic organizers. How did their stated positions differ from yours? Did other people use positions, facts, or arguments that you had not considered?
- Find a partner in your class who chose the opposite position to yours. Cross-question each other. After the discussion, write a one-page reflection focusing on which of you had better arguments.

Plan for **Action**

To help consumers make informed choices about foods containing additives, share your position with the public. You could write a letter to the editor of a food magazine, make a video to share online, create an information poster for a local farmers' market, or compose a blog entry. If you think that government regulations need to be changed, plan a way to get people in your community to side with you and help your voice be heard.

WEB LINK

CHAPTER 8 Investigations

Investigation 8.6.1 CONTROLLED EXPERIMENT

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

The Acidity of Salt Solutions

Many ionic compounds dissolve in water, dissociating to produce ions. These compounds are often called salts. Some salts form neutral solutions when dissolved in water. Others form acidic or basic solutions. Salts dissociate in water and the ions from this dissociation determine the acid–base characteristics of the aqueous solution. This theory will be tested in this experiment.

Testable Question

Write a question, suggested by the introduction and the hypothesis, that this experiment will attempt to answer.

Hypothesis

For each salt listed in the Equipment and Materials section, use your current understanding of acids, bases, and ions to predict whether the aqueous solution of the salt is acidic, basic, or neutral. Provide reasons for your predictions in each case.

Variables

Identify all major variables that will be measured and/or controlled in the experiment. Identify which are the manipulated and which are the responding variables.

Experimental Design

The pH of a variety of salt solutions is measured using pH paper and/or a pH meter.

Equipment and Materials

- lab apron
- chemical safety goggles
- pH paper, pH meter, and/or universal indicator
- containers (small beakers, test tubes, or spot plates)
- beakers for collecting waste solutions
- distilled water
- dropper bottles containing aqueous solutions (0.10 mol/L) of
  - sodium carbonate, $Na_2CO_3(aq)$
  - sodium phosphate, $Na_3PO_4(aq)$
  - aluminum sulfate, $Al_2(SO_4)_3(aq)$
  - sodium chloride, $NaCl(aq)$
  - ammonium chloride, $NH_3Cl(aq)$
  - ammonium ethanoate, $NH_4C_2H_3O_2(aq)$
  - ammonium carbonate, $(NH_4)_2CO_3(aq)$
  - potassium sulfate, $K_2(SO_4)_3(aq)$
  - iron(III) chloride, $FeCl_3(aq)$
  - sodium hydrogen carbonate, $NaHCO_3(aq)$
  - sodium hydrogen sulfate, $NaHSO_4(aq)$

These chemicals may be corrosive, toxic, and/or irritants. Wear a lab apron and chemical safety goggles. Do not touch your eyes. Wash any spills on the skin, in the eyes, or on clothing immediately with plenty of cold water. Report any spills to your teacher.

Procedure

SKILLS HANDBOOK A1, A2.2, B6

1. Write your procedure for this investigation. If you intend to use a pH meter, include the setup instructions and safety precautions that should be followed.
2. Get approval from your teacher and continue with the procedure.

Analyze and Evaluate

(a) What variables were measured/recorded and/or manipulated in this investigation? Which were kept constant? What type of relationship was being tested? T/I

(b) Analyze your observations and use them to answer the testable question. Write your answer in an observation table. T/I C

(c) Compare your answers for (b) to your predictions in your hypothesis. Does the evidence support your predictions? Suggest an explanation for any discrepancies. T/I

Apply and Extend

(d) What conclusions can you make about the pH of salt solutions from your observations? T/I

(e) For each of the solutions tested write the dissociation equation and, if appropriate, the equation for any hydrolysis reaction with water. T/I

(f) How could you predict the pH of a solution with the help of your dissociation equations? K/U T/I

Investigation 8.7.1 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Acid–Base Titration

In this activity, you will standardize a strong base and determine the concentration of an unknown acid. You will use an acid–base indicator to detect the endpoints and then measure the pH with a pH meter.

Equipment and Materials

- lab apron
- chemical safety goggles
- electronic balance
- two 125 mL Erlenmeyer flasks
- 100 mL graduated cylinder
- 10 mL graduated cylinder
- 1 L glass or plastic bottle with stopper
- stirring rod
- burette
- utility stand with burette clamp
- small funnel
- sheet of white paper
- pH meter
- weighing paper
- meniscus finder
- 25 mL pipette with pipette pump
- wash bottle with distilled water (previously boiled)
- sodium hydroxide crystals, $NaOH(s)$
- potassium hydrogen phthalate crystals, $KHC_8H_4O_4(s)$
- dropper bottle of 1 % phenolphthalein indicator
- vinegar, lemon juice, or other acidic solution of unknown concentration

Acids are corrosive and may also be toxic. Solid sodium hydroxide is extremely corrosive, and especially dangerous to eyes and skin. Wear a lab apron and chemical safety goggles. Do not touch your eyes. If sodium hydroxide enters your eye, flush continuously with cold water for 10 min and get immediate medical attention.

Phenolphthalein indicator is flammable. Keep it away from open flames.

Procedure

SKILLS HANDBOOK A1, A2.3, A3

Part A: Standardization of NaOH(aq)

1. Put on your lab apron and safety goggles.
2. Dissolve approximately 1 g of sodium hydroxide crystals in 50 mL of water in an Erlenmeyer flask.
3. In a 1 L bottle, add 10 mL of the sodium hydroxide solution and dilute with 500 mL of distilled water. Stopper the bottle and swirl it but do not shake it.
4. Measure about 0.4 g potassium hydrogen phthalate crystals and record the mass to 2 significant digits.
5. Place the potassium hydrogen phthalate crystals into a clean flask. Add about 50 mL of water and 2–3 drops of phenolphthalein indicator. Swirl to mix.
6. Using the funnel, rinse the inside of the burette with 3–5 mL of the sodium hydroxide solution. Make sure that the solution reaches all of the interior. Open the valve to allow the solution to run out through the tip of the burette. Discard this solution as directed.
7. Fill the rinsed burette with the sodium hydroxide solution. Dislodge any bubbles that might be stuck in the tip of the burette by letting a few drops of the solution run through. Record the burette reading in a table.
8. Place the flask on white paper. Titrate the potassium hydrogen phthalate solution with the sodium hydroxide solution, swirling the flask frequently, until you observe a faint colour change that persists for at least 30 s. This is the endpoint. Record the volume in the burette.
9. Repeat Steps 4, 5, 7, and 8 at least two more times, recording your results each time. Rinse out the flask.

Part B: Determining $[H^+(aq)]$

10. Refill the burette with standardized sodium hydroxide solution.
11. Using the pipette, measure 25.00 mL of an unknown acid solution into a clean, dry flask. Add 2–3 drops of phenolphthalein and swirl gently.
12. Place the flask on white paper. Titrate the acid solution with sodium hydroxide solution until the endpoint is reached. Record your readings.
13. Repeat Steps 11 and 12 until you have three consistent results within 0.5 mL of each other.
14. Using a calibrated pH meter, measure the pH of the solution in the Erlenmeyer flask and record this value.
15. Dispose of all solutions as directed by your teacher. Return equipment and materials to their proper location. Wash your hands with soap and water.

Analyze and Evaluate

(a) Calculate $[NaOH(aq)]$ for each trial in Part A. Average the results. K/U T/I

(b) Calculate the average volume of sodium hydroxide solution used (Step 13) to reach the endpoint. Use this average to determine $[H^+(aq)]$ in the acid. K/U T/I

(c) Use your answer in (b) to determine the pH of the unknown solution. K/U T/I

(d) Compare your calculated pH to the pH value measured in Step 14. Account for any difference. T/I

(e) Evaluate the design, identifying any possible sources of error and suggesting improvements. T/I

Apply and Extend

(f) Predict the shape of the pH curve for the titration of 1.0 mol/L sulfuric acid with 1.0 mol/L sodium hydroxide.

(g) Plan and conduct the titration described in question (f), using a pH meter. Have your teacher approve your design before starting.

Investigation 8.8.1 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Buffer Systems

Phosphate buffers occur naturally in cell cytoplasm, where they maintain a neutral pH, which is ideal for cell functions. In this experiment you will measure the capacity of a buffer over a range of pH levels. The buffer you will investigate is the phosphate buffer, which contains the conjugate acid–base pair $H_2PO_4^-(aq)$–$HPO_4^{2-}(aq)$.

$$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$$

You will make this buffer by mixing solutions of sodium hydroxide and potassium phosphate.

Purpose

To observe change in pH when a strong acid and a strong base are slowly added to different samples of a buffer

Equipment and Materials

- lab apron
- chemical safety goggles
- 100 mL beaker
- 4 small beakers
- glass stirring rod
- two 50 mL graduated cylinders
- glass marking pen
- stoppered bottles containing solutions (0.10 mol/L) of
  - potassium dihydrogen phosphate, $KH_2PO_4(aq)$
  - 29 mL of sodium hydroxide, $NaOH(aq)$
  - sodium chloride, $NaCl(aq)$
- dropper bottles containing
  - bromocresol green indicator
  - hydrochloric acid, $HCl(aq)$ (0.10 mol/L)
  - phenolphthalein indicator
  - sodium hydroxide solution, $NaOH(aq)$ (0.10 mol/L)

Hydrochloric acid is corrosive. Bases and buffers may be corrosive, toxic, and/or irritants. Avoid splashing these solutions on your skin, in your eyes, or on clothing. Immediately rinse any spills with plenty of cold water and inform your teacher.

Phenolphthalein indicator is flammable. Keep it away from open flames.

Procedure

SKILLS HANDBOOK A1, A2.3, B6

1. Put on your lab apron and safety goggles.
2. In separate graduated cylinders, measure 12.6 mL of potassium phosphate solution and 7.4 mL of sodium hydroxide solution. Pour both solutions into a 100 mL beaker. This mixture is the buffer.
3. Label the small beakers 1 through 4. Pour about 10 mL of the buffer into each of beakers 1 and 2.
4. As a control, add the same volume of sodium chloride solution to beakers 3 and 4.
5. Add 2 drops of bromocresol green indicator to beakers 1 and 3.
6. Add drops of hydrochloric acid to beakers 1 and 3, counting each drop, until the colour changes. Between drops, stir the contents of each beaker with the stirring rod. Record the number of drops required in each case.
7. Repeat Steps 5 and 6 in beakers 2 and 4 with phenolphthalein indicator and sodium hydroxide solution.
8. Dispose of all solutions as directed by your teacher. Return equipment and materials to their proper location. Wash your hands with soap and water.

Analyze and Evaluate

(a) Compare the number of drops of acid or base required to cause a colour change in each beaker. Write a statement about the effect of a buffer. T/I

(b) Evaluate the design of this investigation. T/I

Apply and Extend

(c) Examine the ingredients lists of packaged foods to find products containing phosphate salts. Why do these foods contain phosphates? T/I A

(d) Plan a procedure to make 30 mL of an ethanoic acid–ethanoate bufffer using 0.1 mol/L ethanoic acid, $HC_2H_3O_2(aq)$, and solid sodium ethanoate, $NaC_2H_3O_2(s)$. Include a test for your buffer. Proceed with your plan once it is approved by your teacher. T/I

Investigation 8.8.2 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

The Effectiveness of an Antacid

In this activity, you will use a technique known as "back titration" to measure the quantity of hydrochloric acid, HCl(aq), neutralized by an antacid. This simulates the neutralization of stomach acid.

Equipment and Materials

- lab apron
- chemical safety goggles
- mortar and pestle
- weighing paper
- electronic balance
- graduated cylinders
- two 125 mL Erlenmeyer flasks
- 2 burettes, 25 mL or 50 mL
- 2 utility stands with clamps
- stirring rod
- 2 small funnels
- pH paper (low range)
- stoppered bottles containing
  - standardized hydrochloric acid, HCl(aq) (0.1 mol/L)
  - standardized sodium hydroxide solution, NaOH(aq) (0.1 mol/L)
- dropper bottle of bromophenol blue indicator
- various antacid tablets (white, unflavoured)

Hydrochloric acid is corrosive. Sodium hydroxide is corrosive, toxic, and an irritant. Avoid splashing solutions on your skin, in your eyes, or on clothing. Immediately rinse any spills with plenty of cool water and inform your teacher.

Never consume anything in the laboratory or remove it for consuming outside of the laboratory.

To unplug the balance, pull directly on the plug rather than the cord.

Procedure

SKILLS HANDBOOK A1, A2.3, A3.2

1. Put on your lab apron and safety goggles.
2. Crush an antacid tablet using a mortar and pestle.
3. Tare the balance with the weighing paper. Add about 0.4 g of the crushed tablet and measure its mass to 2 decimal places. Transfer the crushed tablet into an Erlenmeyer flask. Record the brand of tablet and the mass of your sample.
4. Label one burette "HCl(aq)." Rinse the burette with hydrochloric acid, clamp it to a utility stand, and then, using the funnel, fill it with the acid.
5. Label the other burette "NaOH(aq)." Rinse this burette with sodium hydroxide solution, clamp it to a utility stand, and then fill it with the base.
6. Dislodge any bubbles that might be stuck in the tips of the burettes by letting a few drops of the solutions run through. Record the burette readings to 0.01 mL.
7. Add about 10.0 mL of hydrochloric acid to the crushed antacid sample and record the final volume of acid in the burette to 0.01 mL.
8. Gently swirl the flask with the antacid tablet to dissolve it as much as possible. Add 2–5 drops of bromophenol blue indicator. The solution should be yellow. If it is blue, continue to add acid slowly until the solution turns yellow and remains yellow after swirling. Again, record the volume of acid remaining in the burette.
9. Titrate the solution with sodium hydroxide solution until the solution in the flask turns blue. Watch carefully because the change may not be obvious. Record the volume of sodium hydroxide solution remaining in the burette.
10. Refill the burettes if needed and repeat Steps 2–3 and 6–9 two more times with other samples of the same type of antacid tablet. Record your results carefully.
11. Repeat the procedure three times using a different brand of tablet.
12. Dispose of waste properly. Clean and rinse all equipment as directed. Wash your hands with soap and water.

Analyze and Evaluate

(a) What was measured in this investigation? T/I

(b) Calculate the amount of hydrochloric acid neutralized by each 1.00 g of antacid tablet. K/U T/I

(c) Why must burettes and flasks be clean and dry? T/I

(d) In Step 8, why is it necessary to make sure the indicator stays yellow before titrating with the base? T/I

(e) Why did the procedure instruct you to first react the tablet with acid, and then *back-titrate* with the base, and not just titrate with the acid? What possible errors does this additional step introduce? Do you think it was a good idea? Why or why not? T/I

Apply and Extend

(f) Compare the effectiveness of different antacids. T/I A

(g) Were you surprised by any of the results? Explain. T/I A

(h) Research the cost per tablet of each type of antacid that you investigated. Compare the cost-effectiveness of the different tablets. T/I A

WEB LINK

CHAPTER 8 SUMMARY

Summary Questions

1. Create a study guide based on the Key Concepts listed on page 486. For each point, create three or four sub-points that provide further information, relevant examples, diagrams, or general equations.
2. Look back at the Starting Points questions on page 486. Answer these questions using what you have learned in this chapter. Compare your latest answers with those that you wrote at the beginning of the chapter. Note how your answers have changed.
3. List the mathematical equations and concepts that you used to solve problems in this chapter. Create a concept map to illustrate the relationships between these equations and concepts.

Vocabulary

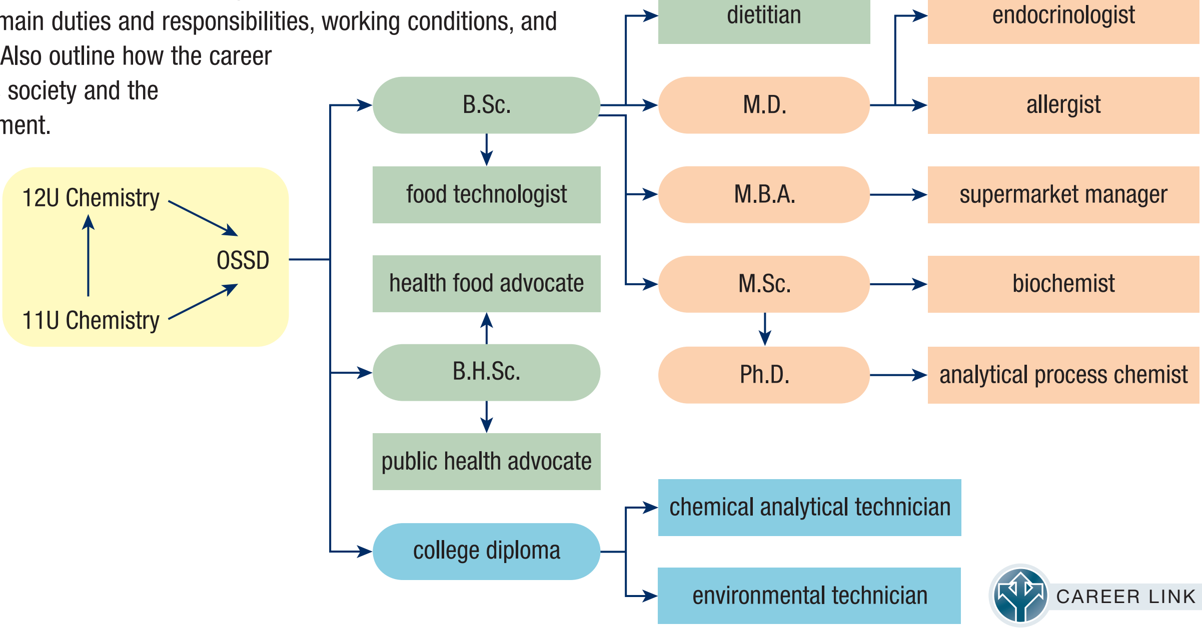
Arrhenius theory (p. 488)
Brønsted–Lowry theory (p. 488)
hydronium ion (p. 489)
conjugate acid (p. 490)
conjugate base (p. 490)
conjugate acid–base pair (p. 490)
amphiprotic (amphoteric) (p. 491)
acid ionization constant (K_a) (p. 492)
strong acid (p. 495)
weak acid (p. 495)
oxyacid (p. 496)
organic acid (p. 497)
strong base (p. 497)
weak base (p. 498)
base ionization constant (K_b) (p. 498)
organic base (p. 499)
autoionization of water (p. 499)
ion-product constant for water (K_w) (p. 500)
pH (p. 502)
pOH (p. 502)
pH meter (p. 505)
acid–base indicator (p. 506)
percentage ionization (p. 514)
monoprotic acid (p. 521)
polyprotic acid (p. 521)
hydrolysis (p. 532)
titration (p. 540)
sample (p. 540)
titrant (p. 540)
burette (p. 540)
standard solution (p. 540)
primary standard (p. 540)
equivalence point (p. 540)
endpoint (p. 540)
pH curve (p. 544)
buffer (p. 558)
buffering capacity (p. 566)

CAREER PATHWAYS

SKILLS HANDBOOK A7

Grade 12 Chemistry can lead to a wide range of careers. Some require a college diploma or a B.Sc. degree. Others require specialized or postgraduate degrees. This graphic organizer shows a few pathways to careers mentioned in this chapter.

1. Select two careers related to Acid–Base Equilibrium that you find interesting. Research the educational pathways that you would need to follow to pursue these careers. What is involved in the required educational programs? Prepare a brief report of your findings.
2. For one of the two careers that you chose above, describe the career, main duties and responsibilities, working conditions, and setting. Also outline how the career benefits society and the environment.



CAREER LINK

CHAPTER 8 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. According to the Arrhenius theory, when acids dissolve in water they
   (a) produce $H^+(aq)$
   (b) produce $OH^-(aq)$
   (c) accept $H^+(aq)$
   (d) accept $OH^-(aq)$ (8.1) K/U
2. Which of the following is the conjugate base of phosphoric acid, $H_3PO_4(aq)$? (8.1) K/U
   (a) $H_2PO_4(aq)$ (c) $H_2PO_4{}^-(aq)$
   (b) $H_3PO_3(aq)$ (d) $HPO_4{}^{2-}(aq)$
3. Which of the following is true of a strong acid? (8.2) K/U
   (a) The K_a value is small.
   (b) The acid exists primarily in the form of molecules in solution.
   (c) Its molecules ionize completely in aqueous solution.
   (d) The ionization equilibrium lies far to the left.
4. Perchloric acid, $HClO_4(aq)$, is a strong acid used in the preparation of ammonium perchlorate, a rocket propellant. Determine the pH of a 0.00450 mol/L perchloric acid solution. (8.2) K/U
   (a) 0.45 (c) 3.00
   (b) 2.35 (d) 4.50
5. Determine the K_a value of a 0.100 mol/L weak acid solution that has a pH of 5.98. (8.3) K/U
   (a) 1.10×10^{-12} (c) 1.04×10^{-6}
   (b) 1.10×10^{-11} (d) -5.98
6. Which of the following salts will form a basic solution when dissolved in water? (8.6) K/U
   (a) potassium nitrate, $KNO_3(s)$
   (b) calcium chloride, $CaCl_2(s)$
   (c) sodium carbonate, $Na_2CO_3(s)$
   (d) ammonium chloride, $NH_4Cl(s)$
7. Which of the following acids would be most appropriate for preparing a buffer solution with a pH of 4.15? (8.8) K/U
   (a) hydrofluoric acid, $K_a = 6.6 \times 10^{-4}$
   (b) methanoic acid, $K_a = 1.8 \times 10^{-4}$
   (c) ascorbic acid, $K_a = 7.9 \times 10^{-5}$
   (d) carbonic acid, $K_a = 4.3 \times 10^{-7}$
8. The pH values of four different samples before and after the addition of a strong base are shown in **Table 1**. Which sample is a buffered solution? (8.8) K/U

Table 1 Sample pH Changes

	Initial pH before addition	Final pH after addition
(a) Sample A	2.3	9.8
(b) Sample B	4.5	7.0
(c) Sample C	3.4	7.0
(d) Sample D	1.2	1.4

9. Why does the food industry often add acids to foods? (8.9) K/U
   (a) to remove unwanted flavours
   (b) to cause colour change
   (c) to deter bacterial growth
   (d) all of the above

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

10. A Brønsted–Lowry acid accepts protons. (8.1) K/U
11. An amphoteric substance can behave as either an acid or a base. (8.1) K/U
12. The acid ionization constant, K_a, is the equilibrium constant for the reaction of an acid with water to form the conjugate base and hydroxide ions. (8.1) K/U
13. Oxyacids always contain carbon and oxygen. (8.2) K/U
14. A solution with pH 2 has a $[H^+(aq)]$ that is 1000 times that of a solution with pH 3. (8.2) K/U
15. The production of sulfuric acid proceeds best at low temperatures because the reaction is endothermic. (8.3) K/U
16. A strong acid reacts with a strong base to produce an acidic salt and water. (8.4) K/U
17. Hydrolysis is the splitting of a water molecule. (8.6) K/U
18. The transition point in a titration is the point at which chemically equivalent amounts of titrant and sample have reacted. (8.7) K/U
19. A buffer solution contains a mixture of a weak acid and a weak base. (8.8) K/U
20. Using buffers destabilizes pH, which can help preserve food and beverages. (8.8) K/U
21. Adding acid to food products to lower the pH helps deter bacterial growth. (8.9) K/U

Go to Nelson Science for an online self-quiz.
WEB LINK

Knowledge

For each question, select the best answer from the four alternatives.

1. Which of the following is a characteristic of a base? (8.1) K/U
   (a) tastes sour
   (b) feels slippery
   (c) turns blue litmus pink
   (d) all of the above
2. According to the Arrhenius theory, bases in aqueous solution
   (a) produce $H^+(aq)$
   (b) produce $OH^-(aq)$
   (c) accept $H^+(aq)$
   (d) accept $OH^-(aq)$ (8.1) K/U
3. Which of the following is a base according to the Brønsted–Lowry theory, but not according to the Arrhenius theory? (8.1) K/U
   (a) ammonia, $NH_3(aq)$
   (b) sodium hydroxide, NaOH(aq)
   (c) phenol, $HC_6H_5O(aq)$
   (d) hydrochloric acid, HCl(aq)
4. A conjugate acid–base pair consists of two entities that
   (a) differ by one oxygen atom
   (b) differ by one hydrogen ion
   (c) neutralize each other in aqueous solution
   (d) produce hydroxide ions in solution (8.1) K/U
5. Which of the following is the conjugate acid of water? (8.1) K/U
   (a) $H_2O_2(aq)$
   (b) $OH^-(aq)$
   (c) $HCHO_2(aq)$
   (d) $H_3O^+(aq)$
6. Which of the following is a property of a strong acid? (8.2) K/U
   (a) K_a is small.
   (b) It exists primarily in the form of molecules in solution.
   (c) It ionizes completely in aqueous solution.
   (d) Its ionization equilibrium lies far to the left.
7. Determine the pH of a 0.032 mol/L solution of NaOH(aq), a strong base. (8.2) K/U
   (a) 2.49
   (b) 3.20
   (c) 11.51
   (d) 14.00
8. Which of the following substances is the first to be produced in the sulfuric acid manufacturing process? (8.3) K/U
   (a) oleum, $H_2S_2O_7(aq)$
   (b) water, $H_2O(l)$
   (c) sulfur trioxide, $SO_3(g)$
   (d) sulfur dioxide, $SO_2(g)$
9. Which of the following salts forms a basic solution when dissolved in water? (8.6) K/U
   (a) potassium chloride, KCl(s)
   (b) sodium nitrate, $NaNO_3(s)$
   (c) potassium cyanide, KCN(s)
   (d) lithium sulfate, $Li_2SO_4(s)$
10. Which of the following terms describes substances that have different colours in solutions of different pH? (8.2, 8.7) K/U
    (a) amphiprotic
    (b) indicators
    (c) polyprotic
    (d) electrolytes
11. Which of the following statements correctly describes the process of titration? (8.7) K/U
    (a) The titrant is added slowly from a burette into the sample until the equivalence point is observed.
    (b) The sample is added slowly from a burette into the titrant until the equivalence point is observed.
    (c) The sample is added slowly from a burette into the titrant until the endpoint is observed.
    (d) The titrant is added slowly from a burette into the sample until the endpoint is observed.
12. Which of the following best describes the components of a buffer solution? (8.8) K/U
    (a) a weak acid and a strong base in water
    (b) a weak acid and its conjugate base in water
    (c) a strong acid and a weak base in water
    (d) a neutral salt in water
13. Which of the following statements correctly explains why weak acids, rather than strong acids, are used as food additives? (8.8) K/U
    (a) Weak acids can only be used in low concentrations.
    (b) Weak acids have a buffering effect.
    (c) Weak acids have a lower pH.
    (d) Weak acids react to produce basic salts.

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

14. A weak acid completely ionizes in solution. (8.2) K/U
15. The autoionization of water involves the transfer of a proton from one water molecule to another to produce a hydroxide ion and a hydronium ion. (8.2) K/U
16. The hydrogen ion concentration of a solution with a pH of 3.0 is 3.33×10^{-3} mol/L. (8.2) K/U
17. A strong acid exists primarily in the form of molecules in solution. (8.2) K/U
18. A diprotic acid has 2 ionizable hydrogen atoms. (8.4) K/U
19. The reaction of a weak acid with a strong base produces a neutral salt. (8.6) K/U
20. The endpoint in a titration is the point at which an indicator starts to change colour permanently. (8.7) K/U
21. The endpoint of a strong acid–strong base titration occurs at a pH near 5. (8.7) K/U
22. The colour of an acid–base indicator depends on the pH of the solution. (8.7) K/U
23. A buffer solution can absorb any amount of acid or base without a significant change in pH. (8.8) K/U
24. The sour taste of citric acid enhances fruit flavours. (8.9) K/U

Match each term in the first list ((a) to (k)) with the most appropriate definition in the second list ((i) to (xi)).

25. (a) conjugate acid
    (b) sample
    (c) weak
    (d) concentrated
    (e) K_a
    (f) polyprotic
    (g) strong acid
    (h) organic acid
    (i) dilute
    (j) acid titrant
    (k) monoprotic

    (i) containing relatively few entities per unit volume
    (ii) used to titrate a base
    (iii) only partially ionized in water
    (iv) acid ionization constant
    (v) having only one ionizable hydrogen atom
    (vi) entity formed when a base gains a hydrogen ion
    (vii) the solution in the flask during a titration
    (viii) an acid based on the elements C, H, and O
    (ix) having 2 or more ionizable hydrogen atoms
    (x) an acid that ionizes almost completely in water
    (xi) containing many entities per unit volume (8.1, 8.2, 8.4, 8.7) K/U

Write a short answer to each question.

26. How did Arrhenius describe acids and bases? (8.1) K/U
27. Identify whether water behaves as an acid or a base in each of the following reactions: (8.1) K/U
    (a) $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$
    (b) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
    (c) $HBr(aq) + H_2O(l) \rightleftharpoons Br^-(aq) + H_3O^+(aq)$
    (d) $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$
28. Identify the conjugate acid–base pairs in each of the reactions shown in question 27. (8.1) K/U
29. Write the name and formula for
    (a) the conjugate base of HF
    (b) the conjugate acid of H_2O
    (c) the conjugate base of H_2O
    (d) the conjugate acid of NH_3 (8.1) K/U
30. Write equations to show how the hydrogen sulfate ion, $HSO_4^-(aq)$, is amphiprotic. (8.1) K/U
31. Calculate the pH of each of the following strong acid or base solutions: (8.2) T/I
    (a) 0.004 mol/L hydrochloric acid
    (b) a 3.5×10^{-8} mol/L solution of potassium hydroxide
    (c) 7.3×10^{-6} mol/L nitric acid, $HNO_3(aq)$
    (d) 0.25 mol/L hydrobromic acid, HBr(aq)
    (e) a 0.45 mol/L solution of sodium hydroxide
    (f) a 6.1×10^{-5} mol/L solution of barium hydroxide, $Ba(OH)_2(aq)$
    (g) a 0.006 mol/L solution of potassium hydroxide, KOH(aq)
32. Write the equation used to calculate pOH from pH. (8.2) K/U
33. Write the chemical equation that represents the autoionization of water. (8.2) K/U
34. What is the hydroxide ion concentration of a solution with a pH of 8.0? (8.2) K/U
35. What is the difference between a strong acid and a weak acid? (8.2) K/U
36. Would you expect hydrochloric acid to have a large or small K_a? Explain. (8.2) K/U
37. Calculate the K_a value of a 0.1000 mol/L solution of an acid that is only partially ionized: $[H^+(aq)] = 1.34 \times 10^{-3}$ mol/L. (8.2) K/U T/I

38. Copy **Table 1** into your notebook and fill in the missing information. (8.2) K/U T/I

Table 1 Characteristics of Four Solutions

Solution	pH	pOH	$[H^+(aq)]$	$[OH^-(aq)]$	Acidic, basic, or neutral?
A	6.88				
B				8.4×10^{-14} mol/L	
C		3.11			
D			1.0×10^{-7} mol/L		

39. What is the pH of a substance with a pOH of 7.6? (8.2) K/U T/I

40. Calculate the hydroxide ion concentration of each of the following solutions at 25 °C. Identify each solution as neutral, acidic, or basic. (8.2) K/U T/I
   (a) $[H^+(aq)] = 1.0 \times 10^{-7}$ mol/L
   (b) $[H^+(aq)] = 8.3 \times 10^{-6}$ mol/L
   (c) $[H^+(aq)] = 1.0 \times 10^{-12}$ mol/L
   (d) $[H^+(aq)] = 5.4 \times 10^{-5}$ mol/L

41. What is the hydroxide ion concentration of a solution with a pH of 4.0? (8.2) K/U T/I

42. State whether the ionization of each of the following favours the reactants or the products: (8.2) T/I
   (a) H_2SO_4
   (b) HCO_3^-
   (c) HF

43. Use the information in **Table 2** to answer the following questions. (8.2) K/U T/I

Table 2 K_w Values at Various Temperatures

Temperature (°C)	K_w
0	1.14×10^{-15}
25	1.00×10^{-14}
35	2.09×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}

   (a) Is the autoionization of water exothermic or endothermic? Explain your answer.
   (b) Calculate $[H^+(aq)]$ and $[OH^-(aq)]$ in a neutral solution at 50 °C.

44. Describe a solution for which each of the following mathematical expressions would be true. Give an example in each case. $[HA(aq)_{initial}]$ and $[A^-(aq)_{initial}]$ represent the initial concentrations of an acid and its conjugate base. (8.2, 8.4) K/U T/I
   (a) $[OH^-(aq)] = [A^-(aq)_{initial}]$
   (b) $[H^+(aq)] = 2\,[HA(aq)_{initial}]$

45. Calculate the percentage ionization of 0.050 mol/L hydrofluoric acid, HF(aq). ($K_a = 6.6 \times 10^{-4}$) (8.4) K/U T/I

46. Determine the concentrations of the ions present in a beverage that contains 0.050 mol/L carbonic acid, $H_2CO_3(aq)$. (Use information from Table 4 in Section 8.4.) (8.4) K/U T/I

47. Methanoic acid (formic acid) is a colourless solution used in making textiles. Calculate the value of K_a for a 0.100 mol/L methanoic acid solution in which $[H^+(aq)] = 1.34 \times 10^{-3}$. (8.4) K/U

48. Calculate the pH of 0.10 mol/L ethanoic acid, $HC_2H_3O_2(aq)$. ($K_a = 1.8 \times 10^{-5}$) (8.4) T/I

49. Will an aqueous solution of each of the following salts will be acidic, basic, or neutral? (8.6) T/I
   (a) sodium nitrate, $NaNO_3(s)$
   (b) ammonium bromide, $NH_4Br(s)$
   (c) sodium fluoride, NaF(s)

50. An acid–base titration starts at pH 3.4 and reaches an endpoint at pH 8.5. Describe the type of sample and titrant being used in the titration. (8.7) K/U T/I

51. Consider the titration that gives the titration curve shown in **Figure 1**.

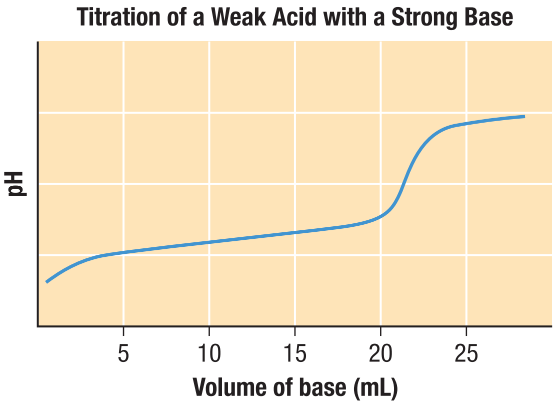


Figure 1

Copy the titration curve into your notebook. On your curve, indicate the points that correspond to the following: (8.7) T/I
   (a) the stoichiometric (equivalence) point
   (b) the region corresponding to the buffering action of the weak acid
   (c) the endpoint of the titration

52. If the pH of a solution is 4.8, what is the colour of each of the following indicators in this solution? (8.7) T/I
    (a) phenolphthalein
    (b) bromocresol green
    (c) phenol red

53. Sodium lactate is the sodium salt of lactic acid. What is the pH of a solution that contains 0.75 mol/L lactic acid, $HC_3H_5O_3(aq)$ ($K_a = 1.4 \times 10^{-4}$), and 0.25 mol/L sodium lactate, $NaC_3H_5O_3(aq)$? (8.8) T/I

54. Calculate the volume of 0.10 mol/L sodium methanoate solution that must be added to 1.00 L of 0.1 mol/L methanoic acid to give a buffer solution with a pH of 3.5. (The pK_a value for methanoic acid is 3.75.) (8.8) T/I

55. A buffer solution contains aqueous ammonia and ammonium chloride. K/U
    (a) Write an equation for the equilibrium system.
    (b) In which direction does the equilibrium shift if hydrochloric acid is added? Why?

56. What is the conjugate base of citric acid? (8.9) T/I

57. Summarize the use of citric acid as an additive in the food industry. (8.9) K/U

Understanding

58. Explain why nitric acid, $HNO_3(aq)$, is an Arrhenius acid. (8.1) K/U

59. Explain why ammonia, NH_3, is a base according to the Brønsted–Lowry theory, but not according to the Arrhenius theory. (8.1) K/U

60. Explain why water, $H_2O(l)$, is not included in the equilibrium constant equation for an acid ionizing in water. (8.1) K/U

61. Two monoprotic acids have K_a values of 1.0×10^{-4} and 1.0×10^{-6}, respectively. Which acid produces a 1.0 mol/L solution with the highest pH? Why? (8.1) K/U

62. Why does doubling the concentration of a hydrochloric acid solution not cause the pH of the solution to decrease by a factor of two? (8.2) K/U

63. Show that the pH of pure water at 25 °C is 7. (8.2) K/U

64. Explain how a sample of an acid can be both weak and concentrated. (8.2) K/U

65. In the production of sulfuric acid, increased pressure favours the forward reaction, forming more products. Use Le Châtelier's principle to explain why. (8.3) K/U

66. Which acid has the larger percentage ionization: hydrofluoric acid or ethanoic acid. Explain. (8.4) K/U

67. Rank K_{a1}, K_{a2}, and K_{a3} for a triprotic acid, $H_3A(aq)$, in order of decreasing magnitude. Justify your order. (8.4) K/U

68. Does water act as a diprotic acid? Explain. (8.4) T/I

69. An acid, HA(aq), is a very weak acid. (8.4) K/U
    (a) How does the strength of the conjugate base, $A^-(aq)$, compare to that of water?
    (b) How do the relative concentrations of $H^+(aq)$ and HA(aq) compare at equilibrium?

70. Explain why aqueous solutions of salts may be either acidic, basic, or neutral. (8.6) K/U

71. Create a flow chart or concept map that can be used to determine the type of solution (acidic, basic, or neutral) that will form when different types of salts are dissolved in water. (8.6) K/U C

72. Consider the titration of 100.0 mL of 0.200 mol/L ethanoic acid, $HC_2H_3O_2(aq)$ ($K_a = 1.8 \times 10^{-5}$), by 0.100 mol/L potassium hydroxide solution, KOH(aq). Calculate the pH of the resulting solution after each of the following volumes of potassium hydroxide solution has been added: (8.7) T/I
    (a) 0.0 mL
    (b) 50.0 mL
    (c) 100.0 mL
    (d) 150.0 mL
    (e) 200.0 mL
    (f) 250.0 mL

73. Describe how you would choose an indicator for the titration of a strong acid with a strong base. (8.7) T/I

74. Which is the better indicator for the titration of a weak acid with a strong base: methyl yellow or thymol blue? Why? (Use Figure 10 in Section 8.7.) (8.7) T/I

75. Use equations to show how a buffer system works. (8.8) K/U T/I C

76. Would a solution made from combining hydrochloric acid and sodium chloride make a good buffer? Explain your answer. (8.8) T/I

77. A solution is 0.40 mol/L hydrazine, $H_2NNH_2(aq)$ ($K_b = 1.7 \times 10^{-6}$), and 0.80 mol/L hydrazinium nitrate, $H_2NNH_3NO_3(aq)$. (8.8) T/I
    (a) Calculate the pH of the solution.
    (b) Describe, using words or chemical equilibrium equations, what happens when hydrochloric acid and sodium hydroxide are added to two different samples of the original solution.

Analysis and Application

78. Hemoglobin (abbreviated to Hb) is a protein that is responsible for transporting oxygen in the blood of mammals. The binding of oxygen to hemoglobin is pH dependent. The relevant equilibrium reaction is

$$HbH_4^{4+}(aq) + 4\,O_2(g) \rightleftharpoons Hb(O_2)_4(aq) + 4\,H^+(aq)$$

Use Le Châtelier's principle to answer the following questions: (8.2) K/U T/I
    (a) What form of hemoglobin, $HbH_4^{4+}(aq)$ or $Hb(O_2)_4(aq)$, is favoured in the lungs? What form is favoured in the cells?

(b) When a person hyperventilates, the concentration of carbon dioxide in the blood falls. How does this affect the oxygen-binding equilibrium? How does breathing into a paper bag help?

(c) When a person has suffered a cardiac arrest, injection of a sodium hydrogen carbonate solution is given. Why is this necessary? (*Hint*: [CO_2(aq)] in blood increases during cardiac arrest.)

79. Vitamin C (ascorbic acid) is a weak diprotic acid with the molecular formula $C_6H_8O_6$ ($K_{a1} = 7.9 \times 10^{-5}$; $K_{a2} = 1.6 \times 10^{-12}$). (8.4) T/I A

(a) Determine [H^+(aq)] and the pH of a solution made by dissolving a 0.500 g tablet of vitamin C in 250 mL of water.

(b) Stomach fluids have a pH ≈ 1.0 due to the presence of hydrochloric acid. What fraction of the vitamin in a 0.500 g tablet will ionize if the volume of fluid in the stomach is 200 mL?

80. Fossil fuels contain trace amounts of nitrogen and sulfur. Burning fossil fuels therefore produces nitrogen dioxide and sulfur dioxide, which may be released into the atmosphere. (8.6) K/U A

(a) Write the chemical reactions showing how these oxides react with water in the atmosphere. Will acidic or basic solutions be produced?

(b) The solutions formed may fall as precipitation and be washed into rivers and lakes. Lakes on lime. stone bedrock are less affected by these solutions than are many other lakes. Explain why this may be the case.

81. When a diprotic acid, H_2A(aq), is titrated with sodium hydroxide, NaOH(aq), the resulting graph is essentially two titration curves (**Figure 2**). (8.7) T/I

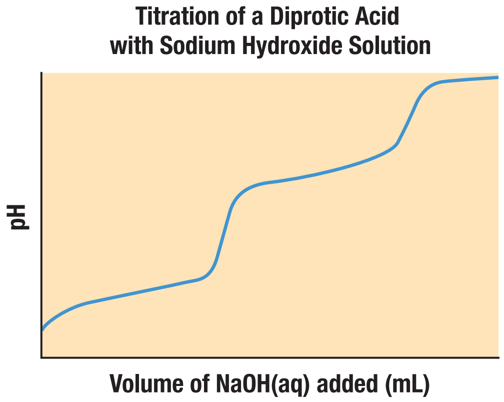


Figure 2

(a) If the first equivalence point occurs at 100 mL NaOH(aq) added, approximately what volume of sodium hydroxide solution has been added at the second equivalence point?

(b) For the following volumes of sodium hydroxide solution added, list the major entities present after the hydroxide ions react completely:

(i) 0 mL NaOH(aq) added

(ii) between 0 and 100 mL NaOH(aq) added

(iii) 100 mL NaOH(aq) added

(iv) between 100 and 200 mL NaOH(aq) added

(v) 200 mL NaOH(aq) added

(vi) more than 200 mL NaOH(aq) added

(c) When 50.0 mL of sodium hydroxide solution has been added, the pH is 4.0. When 150 mL of sodium hydroxide solution has been added, the pH is 8.0. Determine the values of K_{a1} and K_{a2} for the diprotic acid.

82. A natural indicator is an indicator that is either a naturally occurring substance or produced from a naturally occurring substance. Summarize the procedure for an investigation designed to determine the pH range of a homemade indicator. The indicator may be made from cabbage juice, turmeric, or hydrangea flowers. (8.7) T/I C A

83. Write a procedure for a colour change trick using acids, bases, and indicators. (8.7) T/I C A

84. Write a procedure for preparing an acidic buffer solution. (8.8) T/I C A

85. Design an investigation to determine the buffering capacity of a buffer solution. (8.8) T/I C A

86. **Table 3** lists four solids and four solutions that are available to you. What combinations of reactants would you use to prepare buffers with each of the following pH values? (8.8) T/I

(a) 3.0

(b) 4.0

(c) 5.0

(d) 7.0

Table 3 Available Reactants

Solids	Solutions	K_a of acid
potassium fluoride	5.0 mol/L hydrofluoric acid	6.6×10^{-4}
sodium ethanoate	1.0 mol/L ethanoic acid	1.8×10^{-5}
sodium benzoate	2.6 mol/L benzoic acid	6.3×10^{-5}
potassium dihydrogen phosphate	1.0 mol/L phosphoric acid, H_3PO_4(aq)	7.1×10^{-3}

87. Create a concept map linking the main ideas in this chapter. Use "acid–base equilibria" as the central concept. Include the key terms introduced in this chapter. (8.1, 8.2, 8.4, 8.5, 8.6, 8.7, 8.8) K/U T/I C

Evaluation

88. Evaluate the cost-effectiveness of the active ingredient in four different antacids. Locate four brands at a drugstore and record the cost of each package and the quantity of antacid per package. Calculate the cost of a single dose from each package. Prepare a spreadsheet to summarize the information. (8.1) T/I C A
89. A chemistry student is selecting an appropriate indicator to use for the titration of 0.10 mol/L sodium borate, $NaB_4O_7(aq)$, with 0.10 mol/L hydrochloric acid, $HCl(aq)$. The pH at the equivalence point for this titration is 5.22. Is phenolphthalein an appropriate choice? Explain your answer and, if appropriate, recommend a better choice. (8.7) T/I A
90. Is a titration of a weak acid with a weak base feasible? Give your reasons. If you feel that the titration could be done, what type of titration curve would you expect to see? (8.7) T/I A

Reflect on Your Learning

91. Think about the various examples of acids and bases that were discussed in this chapter. Do you think there may be more examples of acids and bases in the substances you use every day? How could you explore this possibility? What equipment would you use to search for examples of acids and bases? K/U T/I A
92. How did your study of pH indicators change how you think about substances that change colour? For example, if you observe an item that loses its colour (becomes colourless), how could you explain this change? How does this relate to your thinking about how stain removers might work? K/U T/I A
93. How has your understanding of the role of acids, bases, and buffers in food changed since you began studying this chapter? K/U T/I A

Research

WEB LINK

94. Many recently published books and documents are printed on paper that has a high acid content. This paper deteriorates quite quickly. Research the methods used to save existing books and prevent them from deteriorating. Present your research in a poster. K/U T/I A
95. Use Internet research to collect information about the Arabic discovery of the alkali hydroxides. Use an innovative way to communicate what you learn to other chemistry students. T/I C
96. The Richter scale is used to measure the strength of earthquakes. Construct a Venn diagram comparing and contrasting the Richter scale with the pH scale. T/I C A
97. Research factors that are responsible for acid rain. Present your findings in the form of a mystery story or investigative report. Begin with the observed results of acid rain and then use detective work to determine the culprits responsible. T/I C A
98. How does the concept of pH apply to the process of home canning of foods? Prepare a brochure that could be used to educate the general public about safe canning methods and why they are used. T/I C A
99. How is limestone used to moderate the effects of acid precipitation on lakes and streams? Prepare a slideshow that could be used at a visitors' centre in a natural area for educating the public about environmental issues. T/I C A
100. Use Internet resources to research Svante Arrhenius's role in the history of chemistry. Make a poster that presents your information in a creative, visual way. C A
101. Research the topic of acid indigestion or acid reflux, and the medicines manufactured to reduce the symptoms. What are the properties of these medicines, and how to they work? Present your findings in a format that a doctor could share with patients. T/I C A
102. Research medicines that include a buffer. Why are buffers added? Present your answer as though you were a chemist working for a pharmaceutical company and you must convince company officials of the benefits of adding a buffer to a new medication under development. T/I C A
103. Use your knowledge of acid–base chemistry to evaluate the effectiveness of the ingredients in toothpastes in preventing tooth decay. Start by researching the ingredients and identify which ones are intended to prevent tooth decay. Share your findings in the form of a pamphlet or electronic communication aimed at consumers choosing a toothpaste. T/I C A
104. List at least four occupations in which people need to measure pH on a regular basis. For each occupation, describe the techniques used to measure pH and how the pH measurements are used. C A
105. Sodium hydroxide is a strong base that is used to clear clogged drains. Hydrochloric acid is a strong acid used to clean stone and metal surfaces. Conduct research to identify two more bases and two more acids used for household purposes or hobbies. Prepare an informational pamphlet that can be distributed to homeowners explaining the safe use and disposal of the four substances you find. C A
106. Conduct research to determine the minerals used by farmers to maintain soil pH within an acceptable range and how these substances function. Present the results of your findings in either a poster or pamphlet. T/I C A

Testing Consumer Product Claims

Many of the foods, beverages, and other products we use in everyday life contain acids or bases. In many cases, these products contain weak acids or bases that form equilibrium systems in aqueous solution. The pH of these solutions gives these products many of their desirable properties. Analytical chemists use quantitative measurements to monitor the quality of the products, and one of the many factors monitored is the concentration of hydrogen ions and pH. As we have learned in this unit, this is one of the purposes of an acid–base titration.

Companies' ad campaigns often make claims concerning the properties of their products. A company may claim that its antacid "consumes twice its weight in stomach acid." A painkiller may be "buffered" to be "gentle on your stomach." Shampoo may be "pH balanced" and a "no-name" product may claim to be as effective as a national brand (**Figure 1**). Are these claims true? Analytical chemists can test these claims.

Your task is to choose a consumer product that is acidic or basic, and to ask and explore a question related to that product's acidic or basic characteristics. Your teacher may give you a list of products to choose from, and will supply the necessary substances for you to test.

Figure 1 Is there really a big difference between products?

Part 1: Research and Preparation

1. Working in a small group, brainstorm a list of consumer products that are acids or bases, or that have acids or bases as a major active ingredient.
2. Research the reasons why the products are acidic or basic. Find the connection between the product's use and its pH.
3. Choose one of these products and, when your teacher has approved your choice, research in detail the role that pH plays in its function. Determine the acid or base in your substance, its formula, and its K_a or K_b value.
4. Use your research to develop a testable question about your product that can be answered through laboratory investigation. You may wish to compare two different versions of your chosen product, or two different brands, or the product before and after use. You may also wish to test a consumer claim that a company has made about the product.
5. Write a hypothesis (including both a prediction and an explanation) for your investigation.
6. Using your researched information, write a background section for your investigation. Make sure to include the product and its use, information about the acid or base, the question you are trying to answer, and any other relevant information. WEB LINK

Part 2: Laboratory Investigation

Purpose

To explore a consumer product and, using an acid-base titration, answer a question relating to its acidic or basic properties

Equipment and Materials

- chemical safety goggles
- lab apron
- 10 mL pipette
- pipette bulb
- Erlenmeyer flasks
- beakers (various sizes)
- graduated cylinders (various sizes)
- mortar and pestle
- burette
- retort stand with burette clamp
- small funnel
- meniscus finder
- washer bottle of distilled water

- stoppered bottle containing a standardized dilute solution of sodium hydroxide or hydrochloric acid
- various other materials as determined by your procedure

Do not bring your chosen consumer product(s) to school. Do not do any preliminary tests at home. A sample of your chosen product(s) will be supplied to you by your teacher.

Procedure

SKILLS HANDBOOK A1, A3, B6

Design and write a procedure to test your hypothesis and answer your testable question.

Consider the following questions as you go:

- What variables are involved? What variables do you need to control? What variables will you manipulate and measure?
- What will be the approximate pH of your solution at the equivalence point?
- What would be an appropriate indicator for the titration?
- Is your solution highly coloured? If so, how will this affect your experiment? How could you compensate for this?
- Do you need to dissolve your product first? What would be an effective way to do this?
- What do you expect your product's acid concentration to be? Do you need to dilute the product you are investigating before the titration?
- What is a back titration? Do you need to employ this technique?
- What safety precautions must be taken?

Once you have written your procedure and have had it approved by your teacher, assemble the provided equipment and materials and perform the steps. Record any changes that you make as you proceed, and record all observations.

Analyze and Evaluate

(a) Using your evidence, evaluate your hypothesis from Step 5 in Part 1. T/I

(b) Using your evidence, answer your testable question from Step 4 in Part 1. Show calculations to support your answer. T/I

(c) Describe sources of experimental error and suggest improvements that would help reduce error. T/I

(d) What challenges did you encounter as you followed your procedure? How did you overcome these challenges? T/I

(e) Explain and justify your acid–base indicator choice. T/I

(f) Discuss the impact of your results. Did you confirm or refute a product claim? What was the result of your product comparison? T/I A

Apply and Extend

(g) Comment on how your discoveries, made during this investigation, might affect your purchasing decisions in the future. A

(h) Suggest a follow-up study to your investigation. Write a testable question and hypothesis for this proposal. T/I A

ASSESSMENT **CHECKLIST**

Your completed Unit Task will be assessed according to these criteria:

Knowledge/Understanding

✓ Identify the manipulated and controlled variables.

✓ Identify a chemical reaction, related to the product under investigation, that reaches equilibrium.

Thinking/Investigation

✓ Plan a safe and effective procedure for your investigation.

✓ Conduct the procedure safely and effectively.

✓ Record all changes to the procedure and all observations carefully and in an organized manner.

✓ Analyze the results.

✓ Evaluate the procedure.

Communication

✓ Use units and significant digits appropriately in calculations.

✓ Prepare a suitable lab report that includes the background section, list of equipment and materials, complete procedures, summary of the observations, any necessary analysis, and evaluation.

Application

✓ Analyze the acid–base characteristics of an everyday product.

✓ Apply the information gathered to future purchasing decisions.

UNIT 4 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Which of the following statements correctly describes a characteristic of a reaction that has reached equilibrium? (7.1) K/U
   (a) Product entities are continually being formed from reactant entities.
   (b) Reactant concentrations are continually decreasing and product concentrations are continually increasing.
   (c) The forward reaction has gone to completion.
   (d) none of the above
2. For a chemical reaction system in equilibrium, how do the rates of the forward and reverse reactions compare? (7.1) K/U
   (a) The rate of the forward reaction is less than the rate of the reverse reaction.
   (b) The rate of the forward reaction is equal to the rate of the reverse reaction.
   (c) The rate of the forward reaction is greater than the rate of the reverse reaction.
   (d) Insufficient information is provided to answer the question.
3. What information is provided by the magnitude of the equilibrium constant, K? (7.2) K/U
   (a) the temperature at which the reaction is carried out
   (b) the initial concentrations of the reactants and products
   (c) whether products or reactants are favoured
   (d) an indication of how rapidly equilibrium will be achieved
4. Which of the following is true when the equilibrium constant, K, is equal to 1? (7.2) K/U
   (a) The reaction proceeds to completion.
   (b) The concentrations of the products are much greater than the concentrations of the reactants.
   (c) The concentrations of the products and the concentrations of the reactants are approximately equal.
   (d) The concentrations of the reactants are much greater than the concentrations of the products.
5. Complete the following sentence: A heterogeneous equilibrium involves more than one ____. (7.2) K/U
   (a) phase
   (b) reactant
   (c) product
   (d) catalyst
6. For a chemical system involving a gas, which of the following sets of conditions affects the equilibrium position? (7.4) K/U
   (a) temperature, pressure, and particle size
   (b) pressure, temperature, and concentration
   (c) concentration, temperature, and particle size
   (d) particle size, pressure, and concentration
7. For a chemical system at equilibrium, which of the following changes causes the equilibrium to shift to the left? (7.4) K/U
   (a) increasing the concentration of the reactants of an exothermic reaction
   (b) increasing the temperature of an endothermic reaction
   (c) increasing the concentration of the reactants of an endothermic reaction
   (d) increasing the temperature of an exothermic reaction
8. For the equilibrium reaction represented by the equation

   $$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

   which of the following statements is true at equilibrium? (7.4) K/U
   (a) Decreasing the concentration of $SO_3(g)$ will cause the equilibrium to shift to the left.
   (b) Increasing the concentration of $O_2(g)$ will cause the equilibrium to shift to the right.
   (c) Decreasing the concentration of $SO_2(g)$ will cause the equilibrium to shift to the right.
   (d) Increasing the pressure will cause the equilibrium to shift to the left.
9. Which of the following compounds is a base according to the Brønsted–Lowry theory, but not according to the Arrhenius theory? (8.1) K/U
   (a) $NH_3(aq)$
   (b) $NaOH(aq)$
   (c) $H_2O(l)$
   (d) $HCl(aq)$
10. In the equilibrium reaction equation represented by $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$ the water behaves as a(n):
    (a) Brønsted-Lowry acid
    (b) Brønsted-Lowry base
    (c) Arrhenius acid
    (d) Arrhenius base (8.1) K/U

11. Which of the following characteristics applies to a weak acid? (8.2) K/U
    (a) has a small K_a value
    (b) partially ionizes in solution
    (c) consists of mostly non-ionized molecules in water
    (d) all of the above
12. Which of the following solutions is the most acidic? (8.2) K/U T/I
    (a) pOH = 10
    (b) $[H^+(aq)] = 3.33 \times 10^{-8}$ mol/L
    (c) $[OH^-(aq)] = 4.93 \times 10^{-8}$ mol/L
    (d) pH = 3
13. Which of the following is an example of an organic acid? (8.2) K/U
    (a) $HClO_3(aq)$
    (b) $HNO_2(aq)$
    (c) $HC_2H_3O_2(aq)$
    (d) $H_2CO_3(aq)$
14. What is the value of the ion-product constant for water, K_w, at 25 °C? (8.2) K/U
    (a) 1.00×10^{-14}
    (b) 1.00×10^{-7}
    (c) 0
    (d) 1
15. Which of the following compounds is an example of a polyprotic acid? (8.4) K/U
    (a) HCl(aq)
    (b) HF(aq)
    (c) $H_2SO_3(aq)$
    (d) HClO(aq)
16. The goal of a titration is to determine the exact amount of base required to neutralize a known amount of acid. What term is used to designate this? (8.7) K/U
    (a) endpoint
    (b) transition point
    (c) equivalence point
    (d) all of the above
17. A solution of potassium cyanide, KCN(aq), is likely to be
    (a) acidic
    (b) basic
    (c) neutral
    (d) Insufficient information is provided to make a prediction. (8.8) K/U
18. What components are present in a buffer that enable it to resist pH changes? (8.8) K/U
    (a) a strong acid and a weak base
    (b) a strong acid and a weak acid
    (c) a weak acid and its conjugate base
    (d) a weak acid only

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

19. The double arrow in a chemical equation indicates that the reaction is reversible. (7.1) K/U
20. In a system at equilibrium, both forward and reverse reactions are taking place at the same time. (7.1) K/U
21. Once a reaction reaches equilibrium, the forward and reverse reactions stop. (7.1) K/U
22. Chemical reactions reach equilibrium when the forward reaction and reverse reaction occur at the same rate. (7.1) K/U
23. The coefficients in a balanced chemical equation are used as coefficients in the equilibrium equation. (7.2) K/U
24. The concentrations in the equilibrium equation are the concentrations of the reactants and products before reaction begins. (7.2) K/U
25. When an exothermic reaction system at equilibrium is heated, the equilibrium shifts to the right. (7.4) K/U
26. A change in pressure causes a shift in the equilibrium position in reversible reactions that involve gaseous reactants and/or products. (7.4) K/U
27. A Brønsted–Lowry acid always contains one more hydrogen ion than its conjugate base. (8.1) K/U
28. A Brønsted–Lowry acid will accept protons. (8.1) K/U
29. The conjugate base of $NH_3(aq)$ is $NH_4^+(aq)$. (8.1) K/U
30. In the Arrhenius theory, a base is a substance that dissociates to produce hydroxide ions in aqueous solution. (8.1) K/U
31. $Ca(OH)_2(aq)$ is an Arrhenius acid because it dissociates to produce hydroxide ions in aqueous solution. (8.1) K/U
32. According to the Arrhenius theory, an acid is a proton donor. (8.1) K/U
33. An organic acid is an acid that contains carbon, hydrogen, and oxygen. (8.2) K/U
34. A strong acid is assumed to ionize completely in aqueous solution. (8.2) K/U
35. Using a pH meter is a less accurate way of measuring the pH of a solution than using pH paper. (8.2) K/U
36. Sulfuric acid, $H_2SO_4(aq)$, is an oxyacid. (8.2) K/U
37. A solution of $NH_4NO_3(aq)$ is basic. (8.6) K/U
38. Primary standards are pure and stable chemicals used to accurately determine the concentration of a titrant. (8.7) K/U
39. The solution of unknown concentration being analyzed during a titration is always in the receiving flask. (8.7) K/U
40. Buffers keep the pH of body fluids within the optimal range. (8.8) K/U

UNIT 4 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Which of the following statements correctly describes a chemical reaction that has achieved equilibrium? (7.1) K/U
   (a) The concentrations of the reactants are equal to the concentrations of the products.
   (b) The concentrations of the products are equal to the initial concentrations of the reactants.
   (c) The products and reactants have stopped reacting.
   (d) There are no changes in the concentrations of reactants or products.
2. A gas, A(g), decomposes according to the following equation:

   $A(g) \rightleftharpoons 2\,B(g)$

   A sample of 0.200 mol A(g) is placed in a 1.00 L closed flask and allowed to come to equilibrium. What values should be entered in the second row of **Table 1** to begin solving for the concentrations of A and B at equilibrium? (7.1) K/U

   Table 1 ICE Table for Calculating Equilibrium Concentrations

	$A(g) \rightleftharpoons$	$2\,B(g)$
I	0.200	0.000
C		
E		

   (a) $+x$ and $-x$
   (b) $+x$ and $-2x$
   (c) $-x$ and $+2x$
   (d) $-x$ and $-x$
3. Which of the following factors may affect the value of K for an equilibrium reaction? (7.2) K/U
   (a) reaction temperature
   (b) whether the reaction is endothermic or exothermic
   (c) initial concentration of reactants
   (d) all of the above
4. The value of the equilibrium constant for a reaction allows us to predict
   (a) the speed of the reaction
   (b) the tendency for the reaction to produce products
   (c) the temperature at which the reaction will take place
   (d) the concentrations of the reactants and products (7.2) K/U
5. To which of the following types of reaction do we apply Le Châtelier's principle? (7.4) K/U
   (a) reversible reactions
   (b) all reactions at equilibrium
   (c) precipitation reactions
   (d) all chemical reactions
6. Le Châtelier's principle predicts the effects of certain changes to a chemical reaction system at equilibrium. For a reaction system involving gases, which of the following conditions are addressed by Le Châtelier's principle? (7.4) K/U
   (a) the temperature of the reaction
   (b) the pressure and volume of the reaction
   (c) the concentrations of reactants and products
   (d) all of the above
7. According to Le Châtelier's principle, when a system is in chemical equilibrium
   (a) an increase in concentration of reactants causes the equilibrium to shift to the left
   (b) a decrease in pressure causes the equilibrium to shift to the side that produces a greater amount of gas
   (c) catalysts cause the equilibrium to shift to the left
   (d) an increase in temperature causes the equilibrium to shift in the direction that releases thermal energy (7.4) K/U
8. Adding energy to an exothermic reaction at equilibrium
   (a) causes a decrease in the concentration of the reactants
   (b) causes a decrease in the concentration of the products
   (c) does not affect the system
   (d) causes an increase in the concentration of the products (7.4) K/U
9. Which of the following quantities is calculated to predict in which direction an equilibrium will shift? (7.5) K/U
   (a) $K_{forward}$
   (b) $K_{reverse}$
   (c) Q
   (d) K
10. Which of the following is a base? (8.1) K/U
    (a) NaOH(aq)
    (b) $NH_3(aq)$
    (c) sodium hypochlorite, NaClO(aq)
    (d) all of the above

11. According to the Brønsted–Lowry theory, an acid is a substance that
    (a) can donate one or more hydrogen ions
    (b) can accept one or more hydrogen ions
    (c) produces hydroxide in aqueous solution
    (d) none of the above (8.1) K/U

12. Which of the following statements is true for acids? (8.1, 8.2) K/U
    (a) They taste bitter.
    (b) They feel slippery.
    (c) They turn blue litmus pink.
    (d) all of the above

13. Which of the following terms describes substances that are capable of behaving as either an acid or a base? (8.2) K/U
    (a) diprotic
    (b) electrolytic
    (c) amphiprotic
    (d) conjugate

14. What is the concentration of $H^+(aq)$ in a neutral aqueous solution? (8.2) K/U
    (a) 1.0×10^{-14} mol/L
    (b) 0 mol/L
    (c) equal to $[OH^-(aq)]$
    (d) $1.0 \times 10^{+7}$ mol/L

15. Which of the following compounds is an example of an oxyacid? (8.2) K/U
    (a) $HF(aq)$
    (b) $HCl(aq)$
    (c) $HClO_3(aq)$
    (d) $HCN(aq)$

16. Which of the following statements correctly describes strong bases? (8.2) K/U
    (a) They completely dissociate in water to produce hydrogen ions.
    (b) They completely dissociate in water to produce hydroxide ions.
    (c) They only partially dissociate in water to produce hydroxide ions.
    (d) They only partially dissociate in water to produce hydrogen ions.

17. Which of the following could be true for a solution of a strong acid? (8.4) K/U
    (a) $[H^+(aq)] = 1.0 \times 10^{-1}$ mol/L
    (b) $[OH^-(aq)] = 1.0 \times 10^{-4}$ mol/L
    (c) pH = 7
    (d) pH = 13

18. Which of the following substances would make the best electrolyte? (8.6) K/U
    (a) a strong acid
    (b) a weak acid
    (c) a weak base
    (d) an organic acid

19. A solution of the salt produced by the reaction of a strong acid and a strong base
    (a) is acidic
    (b) is basic
    (c) may be basic or acidic
    (d) is neutral (8.6) K/U

20. The pH at the equivalence point of a strong acid–strong base titration is
    (a) below 7.0
    (b) at 7.0
    (c) above 7.0
    (d) variable depending on the acid (8.7) K/U

21. Which of the following should be combined with sodium acetate to make a buffer? (8.8) K/U
    (a) acetic acid
    (b) hydrochloric acid
    (c) sodium hydroxide
    (d) sodium phosphate

22. Citric acid added to foods can help increase their
    (a) caloric content
    (b) digestibility
    (c) cooking temperature
    (d) safe storage period (8.9) K/U

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

23. In a closed system, reactants and products are separated from each other by a physical boundary. (7.1) K/U
24. Any chemical reaction carried out in a closed vessel will reach equilibrium. (7.1) K/U
25. When a chemical reaction reaches equilibrium, the concentrations of the reactants and products are constantly changing. (7.1) K/U
26. Chemical reactions achieve equilibrium when the forward reaction and reverse reaction occur at the same rate. (7.2) K/U
27. The rate of a chemical reaction is proportional to the volumes of the reacting substances. (7.2) K/U
28. The value of the equilibrium constant, K, remains constant when the temperature of a reaction is changed. (7.2) K/U
29. The equilibrium constant for a reaction provides a measure of the equilibrium position of the reaction. (7.2) K/U
30. Heterogeneous equilibria involve more than one phase of matter. (7.2) K/U
31. Fritz Haber devised a method for the large-scale production of nitrogen gas. (7.3) K/U

32. Catalysts can be used to increase the rate of a chemical reaction. (7.4) K/U

33. A shift toward a new equilibrium will occur whenever forward and reverse reaction rates become balanced. (7.4) K/U

34. Given a balanced chemical equation, a set of instantaneous concentrations for reactants, and a value for *K*, you can calculate whether the system is at equilibrium. (7.5) K/U

35. At equilibrium, the reaction quotient, *Q*, of a reaction has the same value as the equilibrium constant, *K*. (7.5) K/U

36. Conjugate acid–base pairs are two substances that differ only by a single hydrogen ion. (8.1) K/U

37. Hydrogen chloride is classified as an Arrhenius base because it ionizes to produce hydrogen ions in aqueous solution. (8.1) T/I

38. According to the Arrhenius theory, a base is a hydrogen ion acceptor. (8.1) K/U

39. The Brønsted–Lowry theory is an improvement over the Arrhenius theory because it explains the basic nature of substances such as ammonia in aqueous solution. (8.1) T/I

40. The concentration of $H^+(aq)$ in pure water at 25 °C is 1.0×10^{-14} mol/L. (8.2) K/U

41. A solution with a $[H^+(aq)]$ of 1.0×10^{-14} mol/L is neutral. (8.2) K/U

42. The conjugate base of a weak acid is a much weaker base than $H_2O(l)$. (8.2) K/U

43. The base ionization constant, K_b, is the equilibrium constant for the reaction of a base to produce its conjugate acid. (8.2) K/U

44. For any aqueous solution at 25 °C, pH and pOH add up to 14.00. (8.2) K/U

45. The industrial process for manufacturing sulfuric acid uses a catalyst so that the pressure may be kept low. (8.3) K/U

46. A weak acid is one for which the equilibrium lies far to the right. (8.4) K/U

47. When a salt is added to water, the resulting solution may be acidic or basic, but never neutral. (8.6) K/U

48. A strong acid reacts with a weak base to produce a basic salt. (8.6) K/U

49. Acid–base indicators are substances that change colour when they react with acids or bases. (8.2, 8.7) K/U

50. A titration is a laboratory technique used to determine the concentration of a solute in a solution. (8.7) K/U

51. The concentrations of buffer components in a solution should be slightly greater than the concentrations of acid or base added. (8.8) K/U

52. Buffering capacity indicates the ability of a buffer to change its pH. (8.8) K/U

53. The food industry uses acids as additives in foods. (8.9) K/U

Match each term on the left with the most appropriate description on the right.

54. (a) reversible reaction
    (b) chemical equilibrium
    (c) forward reaction
    (d) reverse reaction

    (i) a reaction in which the products can regenerate the original reactants
    (ii) the regeneration of reactants from products
    (iii) the formation of products from reactants
    (iv) the stage at which the forward reaction and the reverse reaction occur at the same rate (7.1) K/U

Write a short answer to each question.

55. What is the significance of the double arrow in a chemical equation? (7.1) K/U

56. What is happening in a reversible reaction at equilibrium? (7.1) K/U

57. Describe the reaction rates in a system in dynamic equilibrium. (7.1) K/U

58. Must the amounts of reactants and products be equal at equilibrium? Explain. (7.1) K/U

59. Write the equilibrium equation for the chemical reaction represented by the equation

    $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

    where *a*, *b*, *c*, and *d* are the coefficients of the chemical substances A, B, C, and D. A, B, C, and D are all in the gas phase. (7.2) K/U

60. Write the equation for the equilibrium constant, *K*, for the gas-phase reaction represented by each of these equations: (7.2) K/U

    (a) $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$
    (b) $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$
    (c) $SiH_4(g) + 2\ Cl_2(g) \rightleftharpoons SiCl_4(g) + 2\ H_2(g)$
    (d) $2\ PBr_3(g) + 3\ Cl_2(g) \rightleftharpoons 2\ PCl_3(g) + 3\ Br_2(g)$

61. Consider the following reaction at room temperature:

$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g) \quad K = 2.0$

Some molecules of water and carbon monoxide are placed in a 1.0 L container as shown in **Figure 1**.

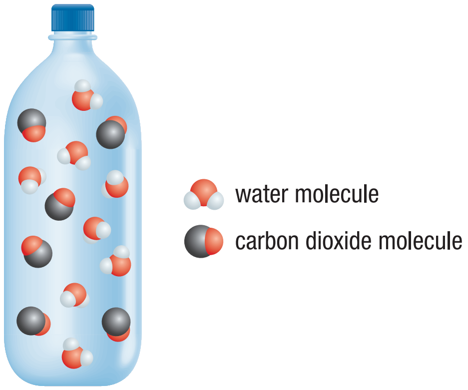


Figure 1 Numbers of reactant molecules in a container

When equilibrium is reached, how many molecules of each reactant and product are present? (Solve this problem by trial and error—that is, if 2 molecules of CO react, is this equilibrium; if 3 molecules of CO react, is this equilibrium; and so on?) (7.2) T/I

62. Sodium hydrogen carbonate (baking soda) decomposes when heated according to the equation

$2\ NaHCO_3(s) + \text{energy} \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g).$

In which direction will equilibrium shift when each of the following changes occurs? (7.4) K/U
   (a) Water vapour is added.
   (b) The temperature is lowered.
   (c) The pressure is decreased.
   (d) A catalyst is added.

63. How are an enzyme and a catalyst similar? (7.4) K/U

64. For the following system, a set of reactant and product concentrations is provided. Determine whether the system has reached equilibrium or not. If not, state in which direction the equilibrium will shift. (7.5) K/U

$CO(g) + 3\ H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

$K = 0.039$ at 927 °C

$[CO(g)] = 0.85$ mol/L; $[H_2(g)] = 2.2$ mol/L;

$[CH_4(g)] = 0.25$ mol/L; $[H_2O(g)] = 0.31$ mol/L

65. In the reaction represented by the equation

$H_2SO_4(aq) + H_2O(aq) \rightleftharpoons HSO_4^-(aq) + H_3O^+(aq),$

identify the
   (a) acid
   (b) base
   (c) conjugate acid
   (d) conjugate base (8.1) K/U

66. Write the equation (omitting water) for the ionization reaction for each of the following acids: (8.1) K/U
   (a) hydrobromic acid, $HBr(aq)$
   (b) ethanoic acid, $HC_2H_3O_2(aq)$
   (c) methanoic acid, $HCHO_2(aq)$

67. Use the Brønsted–Lowry definitions to identify the conjugate acid–base pairs in each of the following acid–base reactions: (8.1) K/U
   (a) $CH_3NH_2(aq) + HClO(aq) \rightleftharpoons ClO^-(aq) + CH_3NH_3^+(aq)$
   (b) $HSO_4^-(aq) + C_2O_4^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HC_2O_4^-(aq)$

68. Aniline, $C_6H_5NH_2(aq)$, is an organic compound that is used in the processing of dyes and pigments. Write the chemical formula for the conjugate acid of aniline. (8.1) K/U C

69. Write the equation to represent the ionization of ammonia in water. (8.2) K/U

70. What is the mathematical relationship between the pH and the pOH of a solution at SATP? (8.2) K/U

71. What is the difference between the hydrogen ion concentrations in two solutions with pH values of 3 and 5? (8.2) K/U

72. Calculate the pH of the following solutions: (8.2) T/I
   (a) $[H^+(aq)] = 2.4 \times 10^{-6}$ mol/L
   (b) $[H^+(aq)] = 1.0 \times 10^{-6}$ mol/L
   (c) $[OH^-(aq)] = 4.33 \times 10^{-8}$ mol/L
   (d) $[H^+(aq)] = 9.1 \times 10^{-9}$ mol/L

73. Determine the hydrogen and hydroxide ion concentrations in the following products: (8.2) T/I
   (a) soap with a pH of 6.10
   (b) borax with a pH of 10.01

74. Use the information given to calculate the unknown $OH^-(aq)$ or $H^+(aq)$ concentration for each solution. State whether each solution is acidic or basic. (8.2) K/U T/I
   (a) 1.0×10^{-7} mol/L $OH^-(aq)$
   (b) 6.6×10^{-9} mol/L $OH^-(aq)$
   (c) 8.5×10^{-12} mol/L $H^+(aq)$

75. Calculate the pH of each of the following solutions at SATP: (8.2) K/U T/I
   (a) $[H^+(aq)] = 5.6 \times 10^{-13}$ mol/L
   (b) $[OH^-(aq)] = 3.9 \times 10^{-14}$ mol/L
   (c) pOH = 10.00

76. What is the $[OH^-(aq)]$ of a solution that has a $[H_3O^+(aq)]$ of 2.0×10^{-3} mol/L at 25 °C? (8.2) K/U T/I

77. What is the pH of a 0.25 mol/L solution of ammonia ($K_b = 1.8 \times 10^{-5}$)? (8.2) T/I

78. (a) What is the $[H^+(aq)]$ of a solution if $[OH^-(aq)] = 4.0 \times 10^{-12}$ mol/L?
   (b) Is the solution an acid or a base? (8.2) T/I

79. What is the concentration of $H^+(aq)$ in pure water at 25 °C? (8.2) K/U

80. Write two equations to represent the stepwise ionization of sulfuric acid. (8.4) K/U

81. Predict whether potassium oxide, $K_2O(s)$, will produce an acidic, basic, or neutral solution when dissolved in water. Write a balanced equation to support your answer. (8.6) K/U

82. Predict whether the following salt solutions are acidic, basic, or neutral: (8.6) K/U
    (a) $NaNO_2(aq)$
    (b) $NaHSO_4(aq)$
    (c) $KCl(aq)$
    (d) $NH_4Cl(aq)$

83. What does it mean when companies that specialize in beauty and hygiene supplies advertise their products as "pH balanced"? (8.2, 8.8) K/U

84. Write a paragraph describing how buffers maintain the pH of a solution. (8.8) K/U

Understanding

85. Construct a Venn diagram comparing and contrasting chemical equilibrium with the dynamic equilibrium that occurs inside a closed half-full bottle of water. (7.1) K/U C

86. Give an example of a system in static equilibrium and another of a system in dynamic equilibrium. Your examples should be from outside the field of chemistry. (7.1) K/U A

87. The decomposition reaction of magnesium carbonate is represented by the following equation: (7.2) K/U C

    $MgCO_3(s) \rightleftharpoons CO_2(g) + MgO(s)$

    (a) What is the equilibrium equation for this reaction?
    (b) Explain why the reactant and one product are not included in your answer to (a).

88. (a) Write the chemical equation for the Haber process.
    (b) Use your answer in (a) to explain why the reaction is carried out at high pressure. (7.3) K/U

89. Explain whether each of the following changes in conditions would affect the value of the equilibrium constant for the system: (7.4) K/U T/I

    $2\ CO_2(g) \rightleftharpoons 2\ CO(g) + O_2(g)$

    (a) increase in temperature
    (b) decrease in pressure
    (c) increase in volume
    (d) addition of neon gas

90. Chromium(VI) forms two different oxyanions: the orange dichromate ion, $Cr_2O_7^{2-}$, and the yellow chromate ion, CrO_4^{2-}. The equilibrium reaction between the two ions is

    $Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2\ CrO_4^{2-}(aq) + 2\ H^+(aq)$

    Explain why orange dichromate solutions turn yellow when sodium hydroxide is added. (7.4) K/U

91. What effect, if any, does a catalyst have on a chemical equilibrium system? Explain your answer. (7.4) K/U

92. Explain why sodium hydroxide, $NaOH(aq)$, is an Arrhenius base. (8.1) K/U

93. (a) Is it possible that an Arrhenius acid is not a Brønsted–Lowry acid? Is it possible that a Brønsted–Lowry acid is not an Arrhenius acid? Explain.
    (b) What advantage does the Brønsted–Lowry theory of a base have over the Arrhenius theory? (8.1) K/U

94. Organic acids, such as ethanoic (acetic) acid, contain hydroxyl groups, which can be represented as –OH. Actually, all oxyacids contain hydroxyl groups. Sulfuric acid, usually written as $H_2SO_4(aq)$, could be represented as $SO_2(OH)_2(aq)$, where S is the central atom. (8.2) K/U
    (a) Name the following acids and write the familiar chemical formula for each one:
        (i) $SO(OH)_2(aq)$
        (ii) $ClO_3(OH)(aq)$
        (iii) $HPO_2(OH)_2(aq)$
    (b) Explain why these compounds behave as acids, while $NaOH(aq)$ and $KOH(aq)$ are bases.

95. Does the ionization of a strong acid in water favour the reactants or the products? Explain. (8.2) K/U

96. Explain why the hydrogen carbonate ion, $HCO_3^-(aq)$, is classified as an amphiprotic ion. Provide two balanced equations to support your explanation. (8.2) K/U

97. Suggest why some economists use the annual production of sulfuric acid as an indicator of the "health" of an economy. (8.3) K/U

98. Use the ammonia, $NH_3(aq)$/ammonium, $NH_4^+(aq)$ buffer to explain how a buffer solution resists changes in pH. (8.8) K/U

99. Explain the factors that determine
    (a) the pH of a buffer solution and
    (b) the capacity of a buffer solution. (8.8)

Analysis and Application

100. Homeostasis is a term used to describe the maintenance of balance among substances and processes in the body. Regulation of body temperature is one type of homeostasis. (7.1) T/I A
    (a) What information can be inferred by examining the parts of the word "homeostasis"?
    (b) What role does the skin play in the maintenance of body temperature?
    (c) In cold conditions, the body releases a hormone called epinephrine. Epinephrine causes an increase in the metabolic rate. How does this assist with the regulation of body temperature?

101. The following chemical equation represents the reaction that takes place during the manufacture of lime:

$$\underset{\text{limestone}}{CaCO_3(s)} \rightleftharpoons \underset{\text{lime}}{CaO(s)} + CO_2(g) \quad \Delta H = +178\ \text{kJ/mol}$$

(7.4) T/I A

(a) Modern manufacturers have replaced older stationary reaction chambers with rotating reaction chambers that constantly feed in limestone and draw off lime. Use Le Châtelier's principle to explain why this increases lime production.

(b) Would you expect this process to be run at high temperatures or at low temperatures? Explain.

102. Your breathing and blood pH participate in your body's biochemical equilibrium. During cellular respiration, your cells produce carbon dioxide, which diffuses into your blood. There it participates in a series of equilibria:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons$$
$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons$$
$$CO_3^{2-}(aq) + 2\,H^+(aq)$$

(7.4) T/I A

(a) Explain how this equilibrium would be affected by someone who is hyperventilating (breathing rapidly to expel more carbon dioxide than normal). Will their blood pH increase, decrease, or remain constant?

(b) Explain why this person might be instructed to breathe into a paper bag.

103. For the following system, determine the equilibrium concentrations of reactants and product if 0.340 mol $H_2(g)$ is combined with 0.220 mol $Br_2(g)$ in a 1.00 L closed container and heated to 430 °C. (7.5) T/I

$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g) \quad K = 56.7 \text{ at } 430\ °C$$

104. Devise a plan for an efficient way to remediate an area of heavy metal contamination. (7.6) T/I A

105. A sample of a solution has a hydrogen ion concentration of 5.9×10^{-3} mol/L at 25 °C. Is this solution human blood or acid rain? (8.2) T/I A

106. Calculate the pH of a solution prepared by dissolving 3.42 g of barium hydroxide, $Ba(OH)_2(s)$, in water to produce 125 mL of solution. (8.2) T/I

107. What is the pH of a 0.25 mol/L HF(aq) solution ($K_a = 6.6 \times 10^{-4}$)? (8.2) T/I

108. Calculate the pH of a 0.050 mol/L solution of hydrofluoric acid, HF(aq) ($K_a = 6.6 \times 10^{-4}$). (8.2) T/I

109. Strontium hydroxide is used in the refining of beet sugar. Only 4.2 g of strontium hydroxide can be dissolved in 1 L of water at 273 K. Given that its solubility is so low, explain how it is possible that strontium hydroxide is considered a strong base. (8.2) A

110. Lactic acid occurs naturally in milk products. It is also a preservative that is added to foods to keep the pH down. Low pH inhibits the growth of bacteria such as *Clostridium botulinum*, the bacteria responsible for botulism. (8.4) T/I A

(a) Lactic acid ($K_a = 7.94 \times 10^{-5}$) is found in yogurt at a concentration of 0.85 mol/L. Determine the pH of the yogurt.

(b) *Clostridium botulinum* will grow in foods with a pH of 4.8 to 7. Is this yogurt safe to eat?

111. Calculate the pH of each of the following strong acid or base solutions: (8.4, 8.5) T/I

(a) 0.004 mol/L hydrochloric acid

(b) 3.5×10^{-8} mol/L potassium hydroxide solution, KOH(aq)

(c) 6.1×10^{-5} mol/L barium hydroxide solution, $Ba(OH)_2(aq)$

(d) 7.3×10^{-6} mol/L nitric acid, $HNO_3(aq)$

(e) 0.25 mol/L hydrobromic acid, HBr(aq)

(f) 0.45 mol/L sodium hydroxide solution, NaOH(aq)

112. Chloroquinine is used in the treatment and prevention of malaria. The K_b for quinine is 1×10^{-6}. Determine the pH of a 0.20 mol/L solution of chloroquinine. (8.5) T/I

113. The hydrangea is an unusual plant: its blooms change colour depending on the pH of the soil. If the pH is above 6, the flowers will be pink; below 5.5 they will be blue.

A landscape gardener planned a garden for a client. The soil in the garden had a pH of 6.5. The gardener planted a hydrangea bush, fertilized it well, and watered it regularly with water collected in a rain barrel. The bush bloomed, but instead of the expected pink colour, the flowers were blue. (8.6) K/U T/I A

(a) Suggest an explanation for this unexpected observation.

(b) What type of salt could the gardener safely add to the soil to make the blooms blue? Give at least two examples of suitable salts.

114. Construct a graphic organizer that includes three examples for each type of solution (acidic, basic, and neutral) that will form when salts dissolve in water. (8.6) K/U C

115. Calculate the pH of a solution made by dissolving 1.00 g sodium ethanoate, $NaC_2H_3O_2(s)$, in water to make a final volume of 1.00 L. (See Appendix B5, Table 1.) (8.6) T/I

116. **Figure 2** shows two titration curves on a single graph for two different acids titrated with sodium hydroxide. (8.7) K/U T/I

(a) Interpret the shapes of the curves and predict the difference between the two acids.

(b) Would it be reasonable to use methyl red as an indicator for both titrations if its colour change occurs between pH 6.8 and 8.4? Explain.

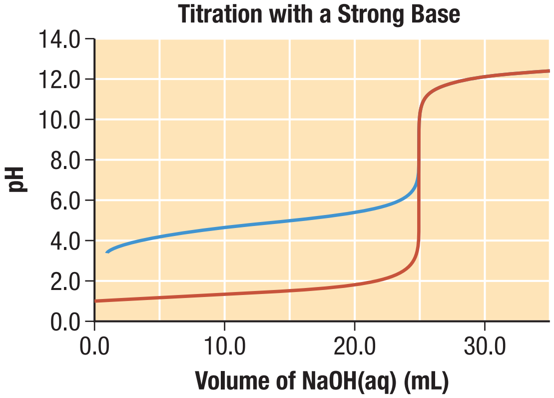


Figure 2

117. Four indicator solutions (as shown in **Table 2**) were dripped separately into a Petri dish containing a 1.0 mol/L solution of a weak acid, HA(aq). The observations are recorded in the last column of the table. (8.7) K/U T/I

(a) What is the approximate pH of the solution containing HA(aq)? (Use Figure 10 in Section 8.7.)

(b) Calculate the approximate value of K_a for HA(aq).

Table 2 Addition of Indicators to 1.0 mol/L HA(aq)

Indicator	Colour of HIn(aq)	Colour of In^-(aq)	p*Ka* of HIn	Colour of indicator
bromophenol blue	yellow	blue	4.0	blue
bromocresol purple	yellow	purple	6.0	yellow
bromocresol green	yellow	blue	4.8	green
alizarin	yellow	red	6.5	yellow

118. A buffer contains 1.0 mol/L ethanoic acid, $HC_2H_3O_2(aq)$, and 1.0 mol/L sodium ethanoate, $NaC_2H_3O_2(aq)$. Calculate the pH of this solution. (8.8) T/I

119. Tris(hydroxymethyl)aminomethane, commonly called TRIS or Trizma, is often used as a buffer in biochemical studies. Its buffering range is pH 7 to 9, and K_b is 1.19×10^{-6} for the aqueous reaction

$$\underset{\text{TRIS}}{(HOCH_2)_3CNH_2(aq)} + H_2O(l) \rightleftharpoons \underset{\text{TRIS}^+}{(HOCH_2)_3CNH_3{}^+(aq)} + OH^-(aq) \quad (8.8)$$ T/I A

(a) What pH do TRIS buffers maintain?

(b) Calculate the [TRIS]/[$TRISH^+$] ratio at pH 7.00 and at pH 9.00.

(c) A buffer is prepared by diluting 50.0 g TRIS base and 65.0 g TRIS hydrochloride (written as TRISHCl) to a total volume of 2.00 L. What is the pH of this buffer? What is the pH after 0.500 mL of 12 mol/L HCl is added to a 200.0 mL portion of the buffer?

120. A student makes a buffer by combining 0.100 mol ammonia, 0.100 mol ammonium chloride, and water to make a final volume of 1.00 L. K_b for ammonia is 1.8×10^{-5}. (8.8) T/I

(a) Calculate the pH of the buffer.

(b) Calculate the buffer pH if 0.010 mol hydrochloric acid is added. (Assume no change in volume.)

(c) What change in pH would occur if the same amount of hydrochloric acid had been added to 1.00 L of water instead of to the buffer?

Evaluation

121. Compare the following *K* values for various equilibrium systems at various temperatures. Assume that all are at equilibrium at the temperature indicated for that system. Which of these systems will produce the highest percentage of products? Which will produce the lowest percentage of products? Explain. (7.2) T/I

(a) $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$
$K = 4.1 \times 10^{-4}$ at 2000 °C

(b) $Br_2(g) + Cl_2(g) \rightleftharpoons 2\,BrCl(g)$ $K = 7.0$ at 130 °C

(c) $Br_2(g) \rightleftharpoons 2\,Br(g)$ $K = 1.04 \times 10^{-3}$ at 1285 °C

(d) $2\,IBr(g) \rightleftharpoons I_2(g) + Br_2(g)$
$K = 3.57 \times 10^{-3}$ at 150 °C

122. Is the Brønsted–Lowry theory of acids and bases an improvement over the Arrhenius theory? Explain. (8.1) T/I

123. Suppose you have two unlabelled samples of ethanoic acid at two different concentrations: 0.1 mol/L and 0.5 mol/L. Your teacher directs you to use phenolphthalein solution to determine which is which. Is this possible? Explain, providing an alternative suggestion if necessary. (8.7) T/I

124. **Figure 3** shows a titration curve for an acid titrated with a base. A student wants to use bromocresol green as the indicator for future titrations of this acid. Evaluate whether the student should go ahead with this titration plan. (8.7) T/I

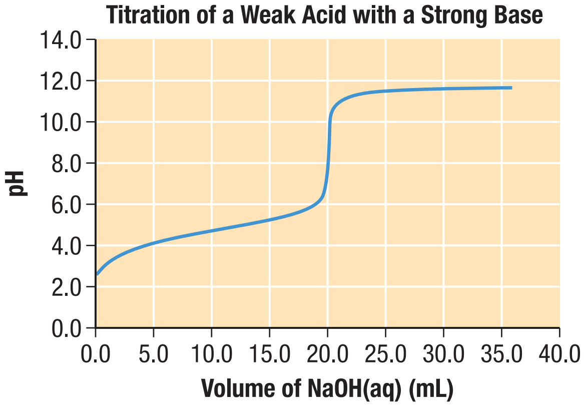


Figure 3

125. You are presented with two solutions: one has 0.1 mol KOH(aq) in 1.00 L of solution; the other has 0.1 mol $Ba(OH)_2$ in 1.00 L of solution. (8.5, 8.7, 8.8) T/I
    (a) You are planning a titration procedure to determine the concentration of a weak acid. Which solution would be the better choice to use as the titrant? Explain your answer.
    (b) Your classmate predicts that the solution in the flask after the titration will be a buffer. Do you think this prediction is valid? Explain.

126. A student performing a biology experiment places some living frog muscle cells in a buffer. The pH of the system stays constant for an hour, but then starts to decline. What was most likely the problem with the buffer solution? How could the student increase the length of time that the buffer maintains a constant pH in her system? Explain your reasoning. (8.8) T/I A

Reflect on Your Learning

127. Construct a flow chart or concept map using the key terms in Chapter 7 with chemical equilibrium as the central concept. T/I C

128. Choose four specific examples of acid–base reactions. Create a graphic organizer relating these four examples to the concept of equilibrium. Include the complete chemical equation for each reaction as well as its social and economic implications. T/I C A

Research

WEB LINK

129. Thousands of biochemical processes taking place in your body right now are being catalyzed by proteins called enzymes. Inhibitors are molecules that bind to enzymes and decrease their activity. Research the role of enzymes and inhibitors in living things. Include applications of manufactured compounds that function as enzymes or inhibitors. Share your findings with other high-school science students in an appropriate format. C A

130. Research the effects of increasing atmospheric carbon dioxide levels on the acidity of the oceans. Prepare an illustrated poster that explains the shifts in equilibrium and the effects on organisms living in the oceans. C A

131. Heavy metals such as copper, lead, and zinc can cause serious illness if consumed in even small quantities. What treatments are used to remove these metals from the body to prevent permanent organ damage from occurring? A

132. Research the structure of salicylic acid, used in the manufacture of acetylsalicylic acid (commonly known as ASA or Aspirin). Evaluate the hydrogen atoms in the salicylic acid molecule based on your knowledge about ionizable hydrogen in the acetic acid molecule, CH_3COOH. Predict which of salicylic acid's hydrogen atoms is likely to be ionizable. Summarize your findings as a poster, digital illustration, or animation. C A

133. The ingredients in a topical treatment for insect bites include 3.5 % ammonia. T/I A
    (a) Write the formula for the reaction of ammonia with the stinging compound produced by ants when they bite. Identify the acids and bases.
    (b) Suggest why the topical treatment reduces the sting of an ant bite.

134. Research how oven cleaners work. Design a hang tag that could be attached to a container of oven cleaner. Your tag should communicate your findings, along with the necessary safety precautions, to the user of the product. C A

135. Many cleaning products contain basic or acidic substances. Research this topic and create a table listing at least four acids or bases that are used in cleaning products and what they are used for. C A

136. Use Internet resources to prepare a paper outlining factors that are responsible for acid precipitation and how it affects a body of water. C A

137. Create an illustration showing how the substances dissolved in human blood help maintain a blood pH level between 7.2 and 7.4. T/I C A

UNIT 5 Electrochemistry

OVERALL EXPECTATIONS

- analyze technologies and processes relating to electrochemistry, and their implications for society, health and safety, and the environment
- investigate oxidation–reduction reactions using a galvanic cell, and analyze electrochemical reactions in qualitative and quantitative terms
- demonstrate an understanding of the principles of oxidation–reduction reactions and the many practical applications of electrochemistry

BIG IDEAS

- Oxidation and reduction are paired chemical reactions in which electrons are transferred from one substance to another in a predictable way.
- The control and applications of oxidation and reduction reactions have significant implications for industry, health and safety, and the environment.

UNIT TASK **PREVIEW**

In this Unit Task, you will use materials readily available at home or at school to construct a battery that can activate a small device. You will then describe how your battery works and how its design features compare to commercial batteries. Finally, you will evaluate its effectiveness as a source of electrical energy and suggest steps to make your battery more functional. The Unit Task is described in detail on page 684. As you work through the unit, look for Unit Task Bookmarks to see how information in the section relates to the Unit Task.

WHAT COMES AFTER GASOLINE?

Many car manufacturers are currently producing fully electric vehicles. These electric vehicles, such as the Tesla Roadster, rely on lithium-based batteries as their energy source. These vehicles convert the chemical energy in a rechargeable lithium battery into the electrical energy that makes the car move. Lithium batteries can store more energy than other types of batteries, so lithium battery–powered vehicles can accelerate faster and travel longer distances than electric vehicles that use other types of batteries.

Since electric vehicles do not burn hydrocarbon fuel, they do not emit pollutants, such as the greenhouse gas carbon dioxide. Electric vehicles are also much more efficient than gasoline-powered vehicles. An internal combustion engine converts only about 20–22 % of gasoline's available chemical energy into the mechanical energy that moves the vehicle. The rest is lost as thermal energy, both in the hot exhaust gases and through the cooling system. By using electric current and magnets instead of exothermic chemical reactions, electric motors produce far less thermal energy. As a result, electric motors convert from 75–96 % of the battery's stored energy into useful mechanical energy. The Tesla Roadster, for example, converts 88 % of its battery's stored energy into mechanical energy. Additionally, electric motors are quieter and are generally more reliable since they have far fewer moving parts compared to an internal combustion engine.

Electric vehicles have always been burdened by heavy batteries and frequent and inconveniently long recharging times. However, new electric vehicles have higher-efficiency batteries that boast a range of nearly 400 km with a recharging time of about 6 hours. With improved infrastructure for recharging, these vehicles may become viable alternatives in the future.

How environmentally friendly an electric vehicle is depends on how the electrical energy used to charge the battery is generated. Electrical energy is generated through either renewable or non-renewable sources. Running water (hydroelectric), wind, and solar are renewable and non-polluting energy sources. Non-renewable sources, such as coal, oil, gas, and nuclear power, are less environmentally friendly. Coal-fired electrical generators, for example, release significant amounts of greenhouse gases and other pollutants. An increased demand for electrical energy by more electric vehicles may increase our reliance on less environmentally friendly electrical generation options.

Clearly, many factors will affect the future of electric vehicles in Ontario. They may have a major impact on the auto industry as technology advances and fossil-fuel use changes in the next five to ten years.

Questions

1. How does a lithium battery provide energy to power an electric vehicle?
2. How can temperature affect the performance of an electric vehicle?
3. Why may electric vehicles be less “green” than they may first appear?
4. Using an appropriate graphic organizer, compare the advantages and disadvantages of gasoline-powered vehicles to those of electric vehicles.
5. Imagine that five years from now you will be purchasing a new vehicle. What criteria do you think will be most important for you when selecting a vehicle?

UNIT 5 ARE YOU READY?

CONCEPTS

- differences between atoms and ions
- how ions are formed
- the difference between ionic and covalent compounds
- characteristics of a chemical system at equilibrium
- types of chemical reactions
- potential energy difference

SKILLS

- represent chemical reactions with balanced chemical equations
- write net ionic equations
- select and communicate appropriate vocabulary describing chemical reactions
- carry out an investigation regarding chemical reactions
- follow proper laboratory protocols for handling chemicals and operating electrical equipment

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Concepts Review

1. Is each of the following entities an atom or an ion? K/U
   (a) oxygen with 6 valence electrons
   (b) chlorine with 8 valence electrons
   (c) sodium with 0 valence electrons
   (d) magnesium with 2 valence electrons
   (e) helium with 2 valence electrons
2. What needs to occur to form each of the following ions from their atoms? K/U
   (a) Li^+
   (b) F^-
   (c) O^{2-}
   (d) Ca^{2+}
3. Distinguish between a cation and an anion. K/U
4. (a) Describe what happens when a metal atom forms an ion and then state the sign of the charge of the ion that forms. K/U
   (b) Describe what happens when a non-metal atom forms an ion and then state the sign of the charge of the non-metal ion that forms. K/U
5. (a) Complete the following chemical reactions using Lewis symbols or structures for the products.
      (i) $\mathrm{Na}^{\bullet} + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\!: \longrightarrow$
      (ii) $\cdot\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{S}}}\!: + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\!: \longrightarrow$
      (iii) $\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\!: + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\!: \longrightarrow$
   (b) Compare the types of bonding occurring in the products of these reactions.
   (c) According to bonding theory, what determines whether electrons are shared or transferred during chemical bond formation? K/U T/I
6. A scientist combines two aqueous solutions. One solution had an initial pH of 10.0 and the final pH of the combined solutions is 6.5. K/U T/I
   (a) What do you know about the properties of the second solution?
   (b) What type of reaction occurred?
7. Identify the type of chemical reaction represented by each of the following equations: K/U
   (a) $HBr(aq) + NaOH(aq) \rightarrow NaBr(aq) + H_2O(l)$
   (b) $Mg(s) + 2\,H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)$
   (c) $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$
   (d) $Pb(NO_3)_2(aq) + 2\,KI(aq) \rightarrow PbI_2(s) + 2\,KNO_3(aq)$
8. In the battery of a car, chemical energy is converted to electrical energy by a chemical reaction (**Figure 1**). K/U T/I

Figure 1 A jump-start pushes electrons through the wire.

   (a) What factors can affect the rate of the reaction in the battery?
   (b) In a dead battery, the chemical reaction has reached equilibrium. What factors could affect the equilibrium conditions of the battery?
   (c) Most car batteries are 12 V, and a volt is the SI unit of electrical potential difference. Define electrical potential difference.
   (d) Compare the amount of work that can be done by a 12 V battery and a 6 V battery. (*Hint*: 1 V = 1 J/C.)

9. Complete and balance the following unbalanced chemical equations. T/I
   (a) $K(s) + O_2(g) \rightarrow$
   (b) $Al(s) + HCl(aq) \rightarrow$
   (c) $C_2H_4(g) + O_2(g) \rightarrow$
   (d) $Fe(NO_3)_3(aq) + K_2CO_3(aq) \rightarrow$

Skills Review

10. (a) Describe the reactants and products in the neutralization of an aqueous solution of an acid with an aqueous solution of a base.
    (b) Write and balance an equation to represent the reaction of sulfuric acid with potassium hydroxide solution.
    (c) If 2 mol of sulfuric acid reacts with excess potassium hydroxide solution, what amount of water will be produced? T/I
11. In a single displacement reaction, zinc metal reacts with hydrochloric acid to produce a solution of zinc chloride and hydrogen gas. K/U T/I
    (a) Write the balanced chemical equation for this reaction.
    (b) Suggest two observations that would indicate that a chemical reaction had occurred in the above reaction.
    (c) Write the net ionic equation for this reaction.
12. The reaction of solutions of lead(II) nitrate, $Pb(NO_3)_2$, and potassium iodide produce solid lead(II) iodide and a solution of potassium nitrate (**Figure 2**): T/I

$$Pb(NO_3)_2(aq) + 2\,KI(aq) \rightarrow PbI_2(s) + 2\,KNO_3(aq)$$

Figure 2 Products of the reaction of lead(II) nitrate and potassium iodide

    (a) What evidence would you observe that a chemical reaction has occurred?
    (b) Write the net ionic equation for this reaction.

13. You have a solution that is either 1.0 mol/L lithium nitrate, $LiNO_3(aq)$, or 1.0 mol/L silver nitrate, $AgNO_3(aq)$. When you add potassium carbonate, $K_2CO_3(aq)$, to the solution, a white precipitate forms. T/I
    (a) What is most likely the starting solution?
    (b) Write the balanced chemical equation for this reaction.
    (c) Write the net ionic equation for this reaction.
14. Suppose you will be performing an investigation that requires mixing aqueous solutions and using electrical equipment. List at least three safety precautions that you would need to follow during your investigation. T/I
15. When designing an experiment, list two advantages of
    (a) reducing the quantity of the reactants used
    (b) decreasing the concentration of the reactants A
16. The test tube in **Figure 3** contains a solution of hydrogen peroxide and black manganese(IV) oxide, MnO_2. Manganese(IV) oxide catalyzes the decomposition of hydrogen peroxide. One of the products of this reaction is water. A glowing wooden splint inserted into the test tube bursts into flames, providing evidence of the other reaction product. T/I

Figure 3 The reaction of a solution of hydrogen peroxide and black manganese(IV) oxide, MnO_2, produces two products.

    (a) Write a balanced chemical equation for this reaction.
    (b) Describe an experiment that could be done to support the theory that manganese(IV) oxide is not changed during this reaction.

CAREER PATHWAYS **PREVIEW**

Throughout this unit you will see Career Links. Go to the Nelson Science website to find information about careers related to Electrochemistry. On the Chapter Summary page at the end of each chapter you will find a Career Pathways feature that shows you the educational requirements of the careers. There are also some career-related questions for you to research.

CHAPTER

9

Oxidation–Reduction Reactions

KEY CONCEPTS

After completing this chapter you will be able to

- understand the terms "reduction" and "oxidation"
- determine the oxidation number of an atom in a compound or ion
- identify and manipulate reduction and oxidation reactions
- identify reducing and oxidizing agents
- balance redox equations using oxidation numbers and half-reaction equations
- predict spontaneity of redox reactions using tables of oxidizing and reducing agents
- analyze the health and safety issues of processes that involve redox reactions

What Is the Role of Electron Transfer in Chemical Reactions?

The European Space Agency uses the Ariane 5 rocket to deliver satellites into space. Ariane 5 is fuelled by the highly exothermic reaction of a solid mixture of aluminum, Al(s), and ammonium perchlorate, $NH_4ClO_4(s)$. The energy released causes the rapid expansion of gases produced in the reaction. The force exerted by these expanding gases pushes the rocket into the sky. The white "smoke" beneath the rocket is another reaction product: aluminum oxide, $Al_2O_3(s)$.

Aluminum also undergoes an exothermic reaction with chlorine gas, $Cl_2(g)$, creating a white powder: aluminum chloride, $AlCl_3(s)$. Aluminum chloride was the active ingredient in the first antiperspirants developed in the early twentieth century. Modern antiperspirants now contain a related aluminum compound that is less irritating to the skin.

In both reactions discussed above, aluminum undergoes an exothermic reaction to produce a white, powdery solid. These reactions also have similarities at the atomic level. During most reactions, the aluminum atom tends to lose the 3 electrons in its third energy level. The result is the aluminum ion, Al^{3+}. A chlorine atom typically gains 1 electron to fill its third energy level to form the chloride ion, Cl^-. During the aluminum chloride reaction, the electrons lost by aluminum atoms are transferred to the chlorine atoms. A similar electron transfer occurs when aluminum reacts with ammonium perchlorate during a rocket launch.

After the discovery of the electron in the late nineteenth century, chemists soon realized that electron transfer is a characteristic of many important reactions. These reactions, no matter how complex, all share three characteristics:

- One entity loses electrons.
- One entity gains electrons.
- The total numbers of electrons gained and lost are equal.

STARTING **POINTS**

Answer the following questions using your current knowledge. You will have a chance to revisit these questions later, applying concepts and skills from the chapter.

1. The surface of a freshly cleaned sheet of aluminum metal reacts almost instantly with oxygen to form a hard coating of aluminum oxide, $Al_2O_3(s)$. This oxide coating adheres tightly to the underlying metal.
   (a) Which element loses electrons in the reaction? Which element gains electrons?
   (b) Make a general prediction about the movement of electrons when a non-metal and a metal react.
   (c) How might this property affect the use of aluminum as a building material?
2. Steel, which is a mixture of iron, carbon, and other metals, also forms an oxide layer or "rust" when exposed to air and moisture. This oxide layer is porous and does not adhere well to the underlying metal.
   (a) How might this property affect the use of steel as a building material?
   (b) Identify two rust-prevention strategies with which you may be familiar. How do they work?
3. Cars of the future may perhaps be fuelled by hydrogen gas. Hydrogen undergoes an exothermic reaction with oxygen to produce water.
   (a) Compare the bonding in the water molecule with the bonding in aluminum oxide.
   (b) Use the concept of polar covalent bonding to explain why the formation of the water molecule involves the partial transfer of electrons.
   (c) Why do you think using a gas such as hydrogen as a fuel might be less convenient than using a liquid such as gasoline?

Mini Investigation

Copper Cleanup

Skills: Performing, Observing, Analyzing

SKILLS HANDBOOK **A1, A2.2**

Copper(II) ions are toxic, so must always be removed from solutions before they are disposed of. In this investigation, you will test the ability of three different metals to remove copper ions from solution.

Equipment and Materials: chemical safety goggles; lab apron; 24-well plate; small pieces of aluminum, magnesium, and zinc; dropper bottle containing copper(II) sulfate solution, $CuSO_4(aq)$ (0.1 mol/L)

Copper(II) sulfate is toxic and an irritant. Avoid skin and eye contact. In the case of contact, wash the affected area with lots of cool water and inform your teacher.

1. Predict, using your knowledge of the activity series of metals (Appendix B8), what you will observe when each of the three metals is placed in copper(II) sulfate solution.
2. Put on your safety goggles and apron.
3. Place the three pieces of metal into three separate wells of the plate.
4. Half-fill each well with copper(II) sulfate solution.
5. After about 5 min, compare each well to each other. Record your observations.
6. Dispose of the contents of the wells according to your teacher's instructions.

A. In which well(s) does a solid form? What could this solid be? Explain. T/I

B. What evidence suggests that the copper(II) ion is a reactant? T/I

C. Compare your prediction with your observations. Try to explain any discrepancies. T/I

D. Which metal would be the best choice for removing toxic copper(II) ions from solution on an industrial scale? Justify your selection. A

E. Are there any drawbacks to using this method for removing toxic ions from solution? Explain. T/I A

9.1

Electron Transfer Reactions

Copper wire is shiny and slightly pinkish. **Figure 1(a)** shows a piece of copper wire when it is first placed in a solution of silver nitrate, $AgNO_3(aq)$. Over time, a fuzz of silver metal, Ag(s), forms on the copper wire (**Figure 1(b)**). The solution turns blue as copper(II) ions are released.

$$Cu(s) + 2\ AgNO_3(aq) \rightarrow 2\ Ag(s) + Cu(NO_3)_2(aq)$$

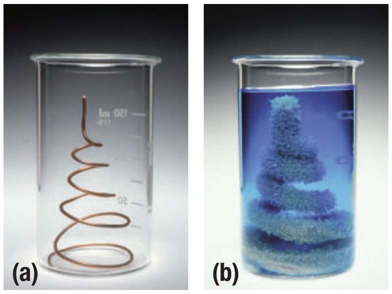


Figure 1 Copper wire placed in a solution of silver nitrate. Over time, copper atoms in the wire are displaced by silver ions in solution. The blue tint of the solution is due to copper ions, and the fuzzy coating on the wire is silver metal.

Remember that the copper(II) nitrate produced is completely dissociated into ions in the solution: $Cu^{2+}(aq)$ and $NO_3^{-}(aq)$. The equation above may also be written with its ionic compounds dissociated:

$$Cu(s) + 2\ Ag^{+}(aq) + 2\ NO_3^{-}(aq) \rightarrow 2\ Ag(s) + Cu^{2+}(aq) + 2\ NO_3^{-}(aq)$$

This form of the equation is sometimes called the total ionic equation. Notice that nitrate ions appear on both sides of the equation. This means that they remain unchanged. Ions that do not participate in a chemical reaction are called spectator ions. These ions can be eliminated from the total ionic equation to give the net ionic equation: WEB LINK

$$Cu(s) + 2\ Ag^{+}(aq) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$$

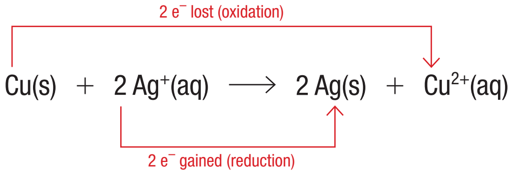
During this reaction, copper atoms, Cu(s), each lose 2 electrons to form $Cu^{2+}(aq)$ ions. Each $Ag^{+}(aq)$ ion gains 1 of these electrons to become a neutral silver atom, Ag(s). Since there are 2 silver ions in the equation, a total of 2 electrons are transferred for each atom of copper that reacts.

In chemistry, the loss of electrons is called **oxidation**, and the gain of electrons is called **reduction**. Thus, a reaction in which electrons are transferred from one entity to another is called an **oxidation–reduction reaction**, or **redox** reaction. We can summarize the oxidation and reduction occurring in the copper–silver reaction as follows:

oxidation the process in which one or more electrons is lost by a chemical entity

reduction the process in which one or more electrons is gained by a chemical entity

oxidation–reduction (redox) reaction the reaction in which one or more electrons are transferred between chemical entities



Half-Reaction Equations

You have seen that a redox reaction involves the transfer of electrons. One element in the reaction gains electrons and another element loses electrons. Not all reactions are redox reactions. To clarify the behaviour of the electrons, we can break the chemical equation for this reaction into two separate parts called half-reaction equations. A **half-reaction equation** is a chemical equation that represents one of the two parts of a redox reaction. For the reaction in Figure 1, copper atoms lose 2 electrons to form $Cu^{2+}(aq)$ ions. The half-reaction equation for this oxidation is

half-reaction equation the part of an oxidation–reduction reaction equation representing either the oxidation reaction or the reduction reaction

$$Cu^{0}(s) \rightarrow Cu^{2+}(aq) + 2\ e^{-}$$

The oxidation of copper supplies the electrons needed for the reduction of silver ions. The half-reaction equation for this reduction is

$$Ag^{+}(aq) + e^{-} \rightarrow Ag^{0}(s)$$

Note that when the silver ion, with a charge of +1, gains an electron, the atom of silver metal that forms has a charge of 0. Since the silver ion gains electrons, it becomes reduced in the chemical reaction. It may seem odd to say that the silver is reduced, when in fact it gained an electron. However, its charge is reduced by going from +1 to 0. WEB LINK

LEARNING **TIP**

A Redox Mnemonic

Use the mnemonic "LEO says GER" to help remember the difference between reduction and oxidation.

LEO: Losing Electrons is Oxidation

GER: Gaining Electrons is Reduction

If we compare the number of electrons in the two half-reaction equations, we see that the number of electrons is not the same. In a redox reaction, the number of electrons lost by oxidation must always be equal to the number of electrons gained by reduction. To make the number of electrons equal in our example, we must multiply all of the entities in the reduction half-reaction equation by 2 (**Figure 2**).

$2\ Ag^{+}(aq) + 2\ e^{-} \rightarrow 2\ Ag(s)$

The overall balanced redox reaction equation can be shown as

$Cu(s) + 2\ Ag^{+}(aq) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$

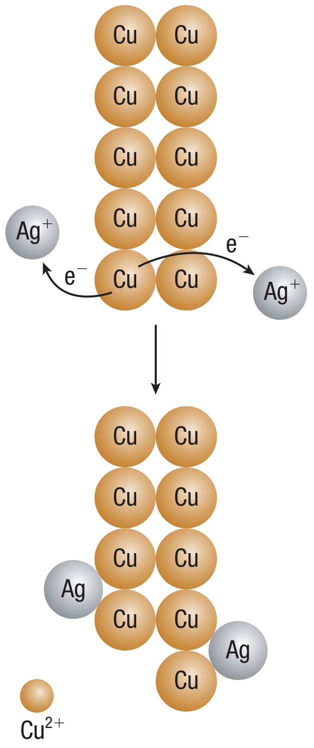


Figure 2 In the reaction of copper metal with silver ions, the copper atom transfers 2 electrons to 2 silver ions. The added electrons reduce the silver ions to uncharged silver atoms, while the electron loss oxidizes the uncharged copper atom to a copper ion.

Tutorial 1 Writing Half-Reaction Equations for Redox Reactions

In this tutorial, you will write the oxidation and reduction half-reaction equations from the net ionic equation of a redox reaction.

Sample Problem 1: Writing a Half-Reaction Equation

Write the oxidation and reduction half-reaction equations for the reaction of aluminum metal in an aqueous solution containing silver ions:

$$Al(s) + 3\ Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3\ Ag(s)$$

Solution

Step 1. Separate the equation into two half-reactions one for each element.

$Al(s) \rightarrow Al^{3+}(aq)$

$3\ Ag^{+}(aq) \rightarrow 3\ Ag(s)$

Step 2. If necessary, divide each equation by a whole number so that the coefficients in the equation are in the simplest whole-number ratio.

In this case, simplify the silver half-reaction by dividing both sides by 3:

$Al(s) \rightarrow Al^{3+}(aq)$

$Ag^{+}(aq) \rightarrow Ag(s)$

Step 3. Add electrons to both equations so that the net charge on both sides of each equation is equal. If you add electrons on one side of the arrow in one half-reaction equation, then you will add electrons on the opposite side of the arrow in the other half-reaction equation. Note, though, that the *number* of electrons added may not be the same in both half-reaction equations.

$Al(s) \rightarrow Al^{3+}(aq) + 3\ e^{-}$

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$

Step 4. Determine whether each half-reaction equation represents an oxidation or a reduction.

The first equation represents an oxidation half-reaction since the aluminum atom loses electrons. The second equation represents a reduction half-reaction since the silver ion gains an electron.

Oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3\ e^{-}$

Reduction: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$

Practice

1. Write the oxidation and reduction half-reaction equations for the following redox reactions: T/I
   (a) $Sn^{2+}(aq) + Co(s) \rightarrow Sn(s) + Co^{2+}(aq)$
   (b) $2\ Ag^{+}(aq) + Pb(s) \rightarrow 2\ Ag(s) + Pb^{2+}(aq)$
   (c) $2\ Fe^{2+}(aq) + I_2(s) \rightarrow 2\ I^{-}(aq) + 2\ Fe^{3+}(aq)$

2. Identify the reactant oxidized and the reactant reduced in Question 1. T/I
3. Write the oxidation and reduction half-reaction equations for each of the following redox reactions. Identify the spectator ion(s) in each reaction. T/I
   (a) $Ni(s) + CuCl_2(aq) \rightarrow NiCl_2(aq) + Cu(s)$
   (b) A solution of tin(II) nitrate reacts with a solution of chromium(II) nitrate to produce tin metal and a solution of chromium(III) nitrate.
4. Chlorine gas reacts with potassium iodide solution to produce solid iodine in a solution of potassium chloride. T/I
   (a) Write the balanced chemical equation for this reaction.
   (b) Write the net ionic equation for the reaction.
   (c) Write the oxidation and reduction half-reaction equations for the reaction.
   (d) Identify the reactant oxidized and the reactant reduced.

Oxidation Numbers

oxidation number a number used to keep track of electrons in oxidation–reduction reactions according to certain rules; also known as oxidation state

Chemists use a type of "electron bookkeeping" to keep track of which atoms are losing electrons and which atoms are gaining electrons in a redox reaction. In this system, an atom's **oxidation number**, also known as its oxidation state, is defined as the apparent net electric charge that the atom would have if electron pairs in covalent bonds belonged entirely to the more electronegative atom. The oxidation number system is a useful way to keep track of electrons, but it does not usually represent an actual charge on an atom. An oxidation number can be a positive or a negative number.

Consider the oxidation numbers for atoms in a covalently bonded molecule. Recall that atoms share electrons in covalent bonds. You can determine the oxidation numbers of atoms in covalent compounds by assigning the shared electrons to particular atoms. In covalent bonds between two identical atoms, the electrons are shared equally between the two atoms. However, in cases where a covalent bond exists between two different atoms, the atoms share the electrons unequally. For the purposes of assigning oxidation numbers, the shared electrons go to the atom that has the stronger attraction for electrons (the more electronegative atom).

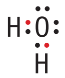


Figure 3 In a molecule of water, oxygen and hydrogen atoms share electrons. The oxygen atom is more electronegative, so it has a greater attraction for the electrons than the hydrogen atoms do.

For example, in a molecule of water, oxygen is more electronegative than hydrogen (**Figure 3**). When you assign oxidation numbers to oxygen and hydrogen in water, you assume that the oxygen atom actually possesses all of the electrons, even the electrons it shares with hydrogen. Recall that a hydrogen atom has 1 electron. Therefore, in water, you assume that the oxygen atom has "taken" the electrons from the 2 hydrogen atoms. This gives the oxygen atom an excess of 2 electrons. Thus, the oxidation number of oxygen is -2. Each hydrogen atom has no electrons and is given an oxidation number of $+1$.

Therefore, we define the oxidation numbers of the atoms in a covalent compound as the imaginary charges the atoms would have if (a) the shared electrons were divided equally between identical atoms bonded to each other, and (b) the shared electrons were assigned to the atom that has the greater attraction for electrons if the atoms are different. CAREER LINK

Table 1 (next page) provides a set of rules for assigning oxidation numbers to atoms. Applying these rules allows you to assign oxidation numbers to the atoms or ions of most compounds.

There are two additional rules for assigning oxidation numbers:

1. The sum of the oxidation numbers of all atoms in an electrically neutral compound must equal zero. This rule is often referred to as the zero-sum rule.
2. The sum of the oxidation numbers of all atoms in ions containing 2 or more atoms must equal the overall charge of the ion.

Table 1 Rules for Assigning Oxidation Numbers

The oxidation number of . . .	Summary	Examples
an atom in an element is 0.	element: 0	Na(s), O_2(g), O_3(g), Hg(l)
a monatomic ion is the same as its charge.	monatomic ion: charge of ion	Na^+, Cl^-
fluorine is −1 in its compounds.	fluorine: −1	HF, PF_3
oxygen is usually −2 in its compounds. (Exception: peroxides, containing O_2^{2-}, in which oxygen is −1)	oxygen: −2	H_2O, CO_2 (Exception: H_2O_2)
hydrogen is +1 in its covalent compounds. (Exception: metal hydrides, in which hydrogen is −1)	hydrogen: +1	H_2O, HCl, NH_3 (Exception: CaH_2)

The convention is to write actual charges on ions as $^{n+}$ or $^{n-}$, placing the number before the plus or minus sign as a superscript. However, you write oxidation numbers (not actual charges) as $+n$ or $-n$, placing the number after the plus or minus sign. Thus, you would write a magnesium ion as Mg^{2+}, but the oxidation number of the magnesium ion as +2.

Tutorial 2 Assigning Oxidation Numbers

In this tutorial, you will learn how to correctly assign an oxidation number to an element within a compound or an ion. The following steps are a useful guide:

1. Assign oxidation numbers to elements as listed in Table 1.
2. Identify any elements not mentioned in Table 1, and use the zero-sum rule or ion-charge rule to assign their oxidation numbers.
3. Check that the sum of the oxidation numbers is equal to zero (for a neutral compound) or the charge (for a polyatomic ion).

Sample Problem 1: Assigning Oxidation Numbers for a Molecular Compound

Assign the oxidation numbers to all atoms in a molecule of carbon dioxide.

Solution

Step 1. Assign oxidation numbers to elements as listed in Table 1.

The oxidation number of oxygen is usually –2.

Step 2. Identify any elements not mentioned in Table 1, and use the zero-sum rule to assign their oxidation numbers.

There is no specific oxidation number for carbon atoms. Since CO_2 is an electrically neutral compound, the sum of the oxidation numbers of oxygen and carbon must be zero. Since each oxygen atom has an oxidation number of −2, and there are 2 oxygen atoms in carbon dioxide, the carbon atom in a molecule of carbon dioxide must have an oxidation number of +4 to balance the −4 of the oxygen atoms.

$$\overset{+4}{\mathrm{C}}\overset{-2}{\mathrm{O}}_2 \quad \text{for each atom}$$

Step 3. Check that the sum of the oxidation numbers is equal to zero. Make sure that you account for the number of each atom in the carbon dioxide molecule.

$$\underset{\substack{\uparrow \\ \text{number of C} \\ \text{atoms}}}{1}(+\,4) + \underset{\substack{\uparrow \\ \text{number of O} \\ \text{atoms}}}{2}(-\,2) = 0$$

In a CO_2 molecule, the oxidation number of the carbon atom is +4 and the oxidation number of each oxygen atom is −2.

Sample Problem 2: Assigning Oxidation Numbers for a Polyatomic Ion

Assign oxidation numbers to all atoms in the nitrate ion, NO_3^-.

Solution

Step 1. Assign oxidation numbers to elements as listed in Table 1.

The oxidation number of oxygen is −2.

Step 2. Identify any elements not mentioned in Table 1, and use the ion-charge rule to assign their oxidation numbers.

Nitrogen is not mentioned in Table 1. The nitrate ion has a net charge of −1. Therefore, the sum of the oxidation numbers of all the atoms in the nitrate ion must equal −1. Each nitrate ion contains 3 oxygen atoms, each of which has an oxidation number of −2. Therefore, the total charge due to oxygen is −6. Since the net charge of the ion is −1, the oxidation number of the nitrogen atom must be +5.

$$\overset{+5}{\mathrm{N}}\overset{-2\ \text{for each atom}}{\mathrm{O}_3^{-}}$$

Step 3. Check that the sum of the oxidation numbers is equal to the charge on the polyatomic ion.

$$\underset{\substack{\uparrow\\ \text{number of N}\\ \text{atoms}}}{1(+5)} + \underset{\substack{\uparrow\\ \text{number of O}\\ \text{atoms}}}{3(-2)} = -1$$

In the nitrate ion, NO_3^-, the oxidation number of the nitrogen atom is +5 and the oxidation number of each oxygen atom is –2.

Sample Problem 3: Assigning Oxidation Numbers for an Ionic Compound

Assign the oxidation numbers to all atoms or ions in sodium thiosulfate, $Na_2S_2O_3$.

Solution

Step 1. Assign oxidation numbers to elements as listed in Table 1.

The oxidation number of the sodium ion, a monatomic ion, is +1. The oxidation number of oxygen is –2.

Step 2. Identify any elements not mentioned in Table 1, and use the zero-sum rule to assign their oxidation numbers.

The sum of the oxidation numbers of the atoms in a compound must equal zero. Since each sodium ion has an oxidation number of +1 and there are 2 sodium ions, the total contribution of sodium is +2. The polyatomic thiosulfate ion must therefore have an overall charge of −2.

Since each oxygen atom has an oxidation number of −2, and there are 3 oxygen atoms, the total contribution from oxygen is −6. Since the total charge of the ion is −2, the total contribution from the 2 sulfur atoms is +4. Therefore, the oxidation number for each sulfur atom is +2.

$$\overset{+1}{\mathrm{Na}_2}\overset{+2}{\mathrm{S}_2}\overset{-2\ \text{for each atom}}{\mathrm{O}_3}$$

Step 3. Check that the sum of the oxidation numbers is equal to zero.

$$\underset{\substack{\uparrow\\ \text{number of Na}\\ \text{atoms}}}{2(+1)} + \underset{\substack{\uparrow\\ \text{number of S}\\ \text{atoms}}}{2(+2)} + \underset{\substack{\uparrow\\ \text{number of O}\\ \text{atoms}}}{3(-2)} = 0$$

In sodium thiosulfate, $Na_2S_2O_3$, the oxidation number of each sodium ion is +1; the oxidation number of each sulfur atom is +2; and the oxidation number of each oxygen atom is −2.

Practice

1. Determine the oxidation number of nitrogen in each of the following substances: T/I
   - (a) N_2
   - (b) NO_2
   - (c) N_2O
   - (d) $NaNO_3$
   - (e) NH_3
2. Determine the oxidation number of carbon in each of the following compounds: T/I
   - (a) CO
   - (b) CH_4
   - (c) Na_2CO_3
   - (d) $C_6H_{12}O_6$
3. Determine the oxidation number of sulfur in each of the following substances: T/I
   - (a) SO_2
   - (b) SO_3^{2-}
   - (c) SO_4^{2-}
   - (d) $S_2O_8^{2-}$
4. Assign the oxidation number to each element in each of the following compounds: T/I
   - (a) Na_2CO_3
   - (b) $K_2Cr_2O_7$
   - (c) $HClO_4$
   - (d) $Cu_3(PO_4)_2$

Oxidation Numbers in Redox Reactions

We can use oxidation numbers to identify the reactant that is oxidized and the reactant that is reduced in a redox reaction. The reaction of nickel(II) oxide with carbon is a useful example. The mining industry uses this reaction during the extraction of nickel from its ore. CAREER LINK

Assigning oxidation numbers to each atom/ion in the chemical equation gives

$$\overset{+2-2}{\mathrm{NiO}}(s) + \overset{0}{\mathrm{C}}(s) \longrightarrow \overset{0}{\mathrm{Ni}}(s) + \overset{+2\ -2}{\mathrm{CO}}(g)$$

Note that the oxidation number of carbon changes from 0 to +2. This means that the carbon atom loses 2 electrons and becomes oxidized. The oxidation number of nickel changes from +2 to 0. This means that the Ni^{2+} ion in NiO gains 2 electrons and is reduced to nickel metal, Ni (**Figure 4**).

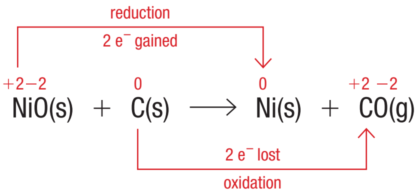


Figure 4 Note how the oxidation numbers change during the reaction of nickel oxide with carbon.

The reaction of nickel(II) oxide with carbon involves the direct transfer of electrons from one reactant to another. However, many redox reactions involve the partial transfer of electrons from one reactant to another. This occurs in the redox reactions involving molecular substances. Consider the synthesis of water from its elements:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$$

Using the rules from Table 1, we can assign the following oxidation numbers:

$$2\ \overset{0}{H_2}(g) + \overset{0}{O_2}(g) \longrightarrow 2\ \overset{+1\ -2}{H_2O}(g)$$

Note that the oxidation number of each atom in H_2 and O_2 is 0 because both hydrogen and oxygen are in their elemental form. Also, the oxidation number of hydrogen changes from 0 in H_2 to +1 in H_2O. This change indicates that each hydrogen atom effectively loses 1 electron in the reaction. However, the oxidation number of each oxygen atom changes from 0 in O_2 to −2 in H_2O. This means that each oxygen atom effectively gains 2 electrons. Since water is a molecular compound rather than an ionic compound, we know that the electrons are not completely transferred from the hydrogen atoms to the oxygen atom. Instead, the electrons in the covalent bond between oxygen and hydrogen shift toward the more electronegative element: oxygen. Hence, only a partial transfer of electrons occurs during the synthesis of water.

Oxidizing Agents and Reducing Agents

Oxidation–reduction reactions involve the transfer of electrons (**Figure 5**). The substance that gains electrons is referred to as an **oxidizing agent**. The oxidizing agent is reduced in a redox reaction. In the previous example, the oxidizing agent is oxygen gas, since it gained electrons from hydrogen. The corresponding substance that loses electrons is called the **reducing agent**. The reducing agent in the example above is hydrogen, since it lost electrons to oxygen. The reducing agent is oxidized in a redox reaction. In all oxidation–reduction reactions, electrons transfer from the reducing agent to the oxidizing agent (**Table 2**).

oxidizing agent the reactant that is reduced (gains electrons from another substance) during an oxidation–reduction reaction

reducing agent the reactant that is oxidized (loses electrons to another substance) during an oxidation–reduction reaction

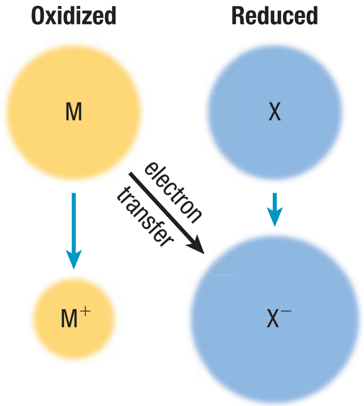


Figure 5 A summary of the oxidation–reduction process in which M is oxidized and X is reduced.

Table 2 Characteristics of Oxidizing and Reducing Agents

Oxidizing agent	Reducing agent
causes oxidation	causes reduction
gains electrons	loses electrons
is reduced	is oxidized

As an example, consider the synthesis of water:

$$2\ \overset{0}{H_2}(g) + \overset{0}{O_2}(g) \longrightarrow 2\ \overset{+1\ -2}{H_2O}(g)$$

For this reaction, we can say the following:

- Hydrogen is oxidized because its oxidation number increases. Each hydrogen atom has partially lost its electron.
- Oxygen is reduced because its oxidation number decreases. The oxygen atom has partially gained electrons.
- H_2 is the reducing agent.
- O_2 is the oxidizing agent.

Note that when you name the reducing or oxidizing agent, you specify the whole substance and not just the element that undergoes the change in oxidation number. This becomes more relevant when we consider redox reactions involving compounds: the compound is the oxidizing (or reducing) agent.

Investigation **9.1.1**

Single Displacement Reactions (page 624)

In this investigation, you will design and perform tests on metals and metal ions, and then rank the strength of the ions as oxidizing agents.

Tutorial 3 Analyzing Redox Reactions

In this tutorial, you will identify atoms that become oxidized and reduced during an oxidation–reduction reaction. It will also help you identify the oxidizing and reducing agents in a redox reaction. Note that you always start by assigning an oxidation number to each element, just as you did in Tutorial 2.

Sample Problem 1: Analyzing a Redox Reaction

Metallurgy, the process of producing a metal from its ore, always involves oxidation–reduction reactions. The valuable component of lead ore is the compound lead(II) sulfide, PbS(s), also called galena. The first step in extracting lead from its ore is the conversion of lead(II) sulfide to its oxide by a process called roasting:

(a) $2\,PbS(s) + 3\,O_2(g) \rightarrow 2\,PbO(s) + 2\,SO_2(g)$

The oxide then reacts with carbon monoxide to produce the metallic element:

(b) $PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$

For each reaction, identify the entities that are oxidized and reduced, and specify the oxidizing and reducing agents.

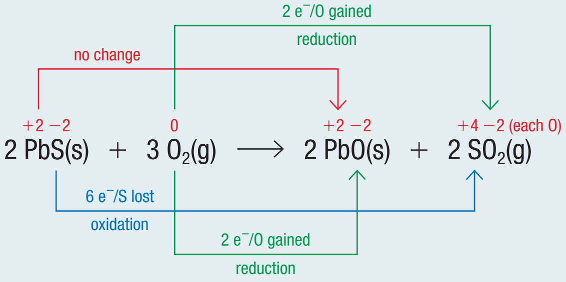
Solution (a)

Step 1. Assign oxidation numbers to elements as listed in Table 1.

Lead(II) sulfide and lead(II) oxide are simple ionic compounds, so the oxidation numbers of their elements are the same as the charges on those elements.

$$2\,\overset{+2\;-2}{PbS}(s) + 3\,\overset{0}{O_2}(g) \rightarrow 2\,\overset{+2\;-2}{PbO}(s) + 2\,\overset{+4\;-2\text{ (each O)}}{SO_2}(g)$$

Step 2. Determine how the oxidation number on each element changes, and identify these changes as either oxidation or reduction.



The oxidation number for sulfur increases from −2 to +4. Sulfur is oxidized (**Figure 6**). The oxidation number for oxygen decreases from 0 to −2 (in both products). Oxygen is reduced. The oxidation number for lead does not change. The oxidizing agent (the substance that gains electrons) is O_2. The reducing agent (the substance that loses electrons) is PbS.

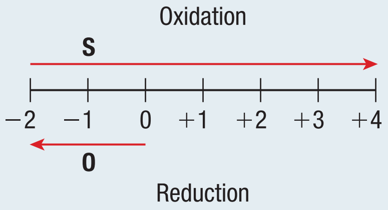


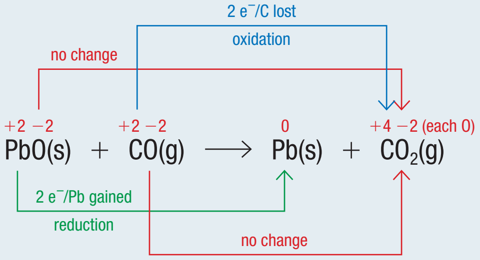
Figure 6 This number line shows the changes in oxidation number of sulfur and oxygen.

Solution (b)

Step 1. Assign oxidation numbers to elements as listed in Table 1.

$$\overset{+2\;-2}{PbO}(s) + \overset{+2\;-2}{CO}(g) \rightarrow \overset{0}{Pb}(s) + \overset{+4\;-2\text{ (each O)}}{CO_2}(g)$$

Step 2. Determine how the oxidation number on each element changes, and identify these changes as either oxidation or reduction.



The oxidation number for lead decreases from +2 to 0. Lead is reduced. The oxidation number for carbon increases from +2 to +4. Carbon is oxidized. The oxidation number for oxygen does not change (in both products). The oxidizing agent (the substance that gains electrons) is PbO. The reducing agent (the substance that loses electrons) is CO.

Practice

1. Identify the entities that are oxidized and reduced in the following reactions: T/I
   (a) $Cu(s) + 2\,Ag^+(aq) \rightarrow 2\,Ag(s) + Cu^{2+}(aq)$ (b) $4\,Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$
2. Identify the oxidizing agent and the reducing agent in the following reactions: T/I
   (a) $Zn(s) + 2\,HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$ (b) $SnO_2(s) + C(s) \rightarrow Sn(s) + CO_2(g)$
3. For the following reactions, assign the oxidation numbers to each atom, then indicate the oxidizing and reducing agents: T/I
   (a) $2\,H_2S(g) + 3\,O_2(g) \rightarrow SO_2(g) + H_2O(g)$ (b) $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$

9.1 Review

Summary

- Many reactions involve the transfer of electrons.
- Oxidation–reduction reactions, or redox reactions, are reactions in which electrons transfer from one entity to another. Neither oxidation nor reduction can occur without the other.
- Chemists assign oxidation numbers to atoms or ions to keep track of the electrons in an oxidation–reduction reaction.
- The rules in Table 1 (page 603) allow oxidation numbers to be assigned for common entities. Oxidation numbers can then be assigned to remaining atoms or ions.
- In an oxidation–reduction reaction, one element is oxidized (loses electrons). Another element is reduced (gains electrons).
- An oxidizing agent causes oxidation to occur (and is reduced in the process). A reducing agent causes reduction to occur (and is oxidized in the process).

UNIT TASK **BOOKMARK**

You can apply what you learned about redox reactions to the Unit Task described on page 684.

Questions

1. Explain, in your own words, the process that occurs in a redox reaction. K/U
2. Write the oxidation and reduction half-reaction equations for the reactions represented by each of the following equations: T/I
   (a) $Mg(s) + 2\,H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
   (b) $2\,Al(s) + Fe_2O_3(s) \rightarrow 2\,Fe(l) + Al_2O_3(s)$
3. Identify the oxidation number of the specified element in each of the following entities: T/I
   (a) S in S_8
   (b) Cr in $Cr_2O_7^{\,2-}$
   (c) N in N_2H_4
   (d) I in MgI_2
   (e) C in CO
   (f) N in NH_3
   (g) P in P_4O_6
   (h) Mn in $MnO_4^{\,-}$
   (i) C in C_2H_5OH
   (j) S in $Al_2(SO_3)_3$
4. Identify the entity that is oxidized and the entity that is reduced in the chemical reactions represented by the following equations: T/I
   (a) $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3\,H_2(g)$
   (b) $8\,H^+(aq) + MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq) + 4\,H_2O(l)$
   (c) a single displacement reaction in which copper metal reacts with silver nitrate
5. (a) Describe the change in the oxidation number of an entity when it becomes oxidized.
   (b) Describe the change in the oxidation number of an entity when it is reduced.
   (c) Why do oxidation and reduction half-reactions both have to occur in the same reaction? K/U
6. Use oxidation numbers to determine which of the following chemical equations represent a redox reaction. For all that ARE redox reactions, indicate the oxidizing agent, the reducing agent, the element being oxidized, and the element being reduced. T/I
   (a) $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
   (b) $SiCl_4(l) + 2\,Mg(s) \rightarrow 2\,MgCl_2(s) + Si(s)$
   (c) $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$
7. Assign oxidation numbers to each element in the following equations: T/I
   (a) $4\,PH_3(g) + 8\,O_2(g) \rightarrow P_4O_{10}(s) + 6\,H_2O(l)$
   (b) $2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g)$
   (c) $Pb(s) + PbO_2(s) + 2\,H_2SO_4(aq) \rightarrow 2\,PbSO_4(s) + 2\,H_2O(g)$
8. Describe each of the reactions in Question 7 using the terms "oxidation," "reduction," "oxidizing agent," and "reducing agent." K/U
9. In the process of photosynthesis, carbon dioxide and water form glucose and oxygen: T/I A
   $6\,CO_2(g) + 6\,H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6\,O_2(g)$
   (a) What is the oxidation number of carbon in CO_2 and $C_6H_{12}O_6$?
   (b) Describe the process of photosynthesis using the terms "oxidation," "reduction," "oxidizing agent," and "reducing agent."
10. Carbon dioxide can be progressively reduced to methane through a series of reactions. What is the oxidation number of carbon in each of the following compounds? T/I
    $CO_2 \rightarrow CH_2O_2 \rightarrow CH_2O \rightarrow CH_4O \rightarrow CH_4$

9.1

Electron Transfer Reactions

Copper wire is shiny and slightly pinkish. **Figure 1(a)** shows a piece of copper wire when it is first placed in a solution of silver nitrate, $AgNO_3(aq)$. Over time, a fuzz of silver metal, $Ag(s)$, forms on the copper wire (**Figure 1(b)**). The solution turns blue as copper(II) ions are released.

$$Cu(s) + 2\ AgNO_3(aq) \rightarrow 2\ Ag(s) + Cu(NO_3)_2(aq)$$

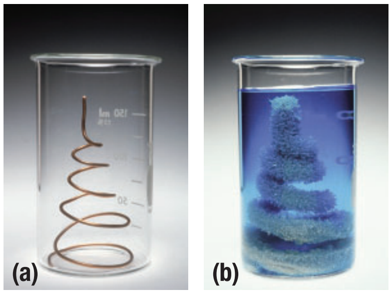


Figure 1 Copper wire placed in a solution of silver nitrate. Over time, copper atoms in the wire are displaced by silver ions in solution. The blue tint of the solution is due to copper ions, and the fuzzy coating on the wire is silver metal.

Remember that the copper(II) nitrate produced is completely dissociated into ions in the solution: $Cu^{2+}(aq)$ and $NO_3^-(aq)$. The equation above may also be written with its ionic compounds dissociated:

$$Cu(s) + 2\ Ag^+(aq) + 2\ NO_3^-(aq) \rightarrow 2\ Ag(s) + Cu^{2+}(aq) + 2\ NO_3^-(aq)$$

This form of the equation is sometimes called the total ionic equation. Notice that nitrate ions appear on both sides of the equation. This means that they remain unchanged. Ions that do not participate in a chemical reaction are called spectator ions. These ions can be eliminated from the total ionic equation to give the net ionic equation: WEB LINK

$$Cu(s) + 2\ Ag^+(aq) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$$

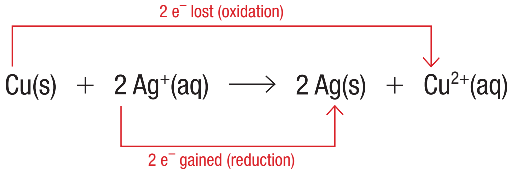
During this reaction, copper atoms, $Cu(s)$, each lose 2 electrons to form $Cu^{2+}(aq)$ ions. Each $Ag^+(aq)$ ion gains 1 of these electrons to become a neutral silver atom, $Ag(s)$. Since there are 2 silver ions in the equation, a total of 2 electrons are transferred for each atom of copper that reacts.

In chemistry, the loss of electrons is called **oxidation**, and the gain of electrons is called **reduction**. Thus, a reaction in which electrons are transferred from one entity to another is called an **oxidation–reduction reaction**, or **redox** reaction. We can summarize the oxidation and reduction occurring in the copper–silver reaction as follows:

oxidation the process in which one or more electrons is lost by a chemical entity

reduction the process in which one or more electrons is gained by a chemical entity

oxidation–reduction (redox) reaction the reaction in which one or more electrons are transferred between chemical entities



Half-Reaction Equations

You have seen that a redox reaction involves the transfer of electrons. One element in the reaction gains electrons and another element loses electrons. Not all reactions are redox reactions. To clarify the behaviour of the electrons, we can break the chemical equation for this reaction into two separate parts called half-reaction equations. A **half-reaction equation** is a chemical equation that represents one of the two parts of a redox reaction. For the reaction in Figure 1, copper atoms lose 2 electrons to form $Cu^{2+}(aq)$ ions. The half-reaction equation for this oxidation is

half-reaction equation the part of an oxidation–reduction reaction equation representing either the oxidation reaction or the reduction reaction

$$Cu^0(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$$

The oxidation of copper supplies the electrons needed for the reduction of silver ions. The half-reaction equation for this reduction is

$$Ag^+(aq) + e^- \rightarrow Ag^0(s)$$

Note that when the silver ion, with a charge of +1, gains an electron, the atom of silver metal that forms has a charge of 0. Since the silver ion gains electrons, it becomes reduced in the chemical reaction. It may seem odd to say that the silver is reduced, when in fact it gained an electron. However, its charge is reduced by going from +1 to 0. WEB LINK

LEARNING **TIP**

A Redox Mnemonic

Use the mnemonic "LEO says GER" to help remember the difference between reduction and oxidation.

LEO: Losing Electrons is Oxidation

GER: Gaining Electrons is Reduction

If we compare the number of electrons in the two half-reaction equations, we see that the number of electrons is not the same. In a redox reaction, the number of electrons lost by oxidation must always be equal to the number of electrons gained by reduction. To make the number of electrons equal in our example, we must multiply all of the entities in the reduction half-reaction equation by 2 (**Figure 2**).

$$2\ Ag^{+}(aq) + 2\ e^{-} \rightarrow 2\ Ag(s)$$

The overall balanced redox reaction equation can be shown as

$$Cu(s) + 2\ Ag^{+}(aq) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$$

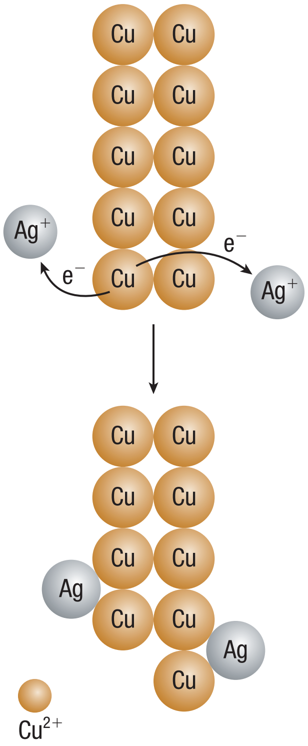


Figure 2 In the reaction of copper metal with silver ions, the copper atom transfers 2 electrons to 2 silver ions. The added electrons reduce the silver ions to uncharged silver atoms, while the electron loss oxidizes the uncharged copper atom to a copper ion.

Tutorial 1 Writing Half-Reaction Equations for Redox Reactions

In this tutorial, you will write the oxidation and reduction half-reaction equations from the net ionic equation of a redox reaction.

Sample Problem 1: Writing a Half-Reaction Equation

Write the oxidation and reduction half-reaction equations for the reaction of aluminum metal in an aqueous solution containing silver ions:

$$Al(s) + 3\ Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3\ Ag(s)$$

Solution

Step 1. Separate the equation into two half-reactions one for each element.

$Al(s) \rightarrow Al^{3+}(aq)$

$3\ Ag^{+}(aq) \rightarrow 3\ Ag(s)$

Step 2. If necessary, divide each equation by a whole number so that the coefficients in the equation are in the simplest whole-number ratio.

In this case, simplify the silver half-reaction by dividing both sides by 3:

$Al(s) \rightarrow Al^{3+}(aq)$

$Ag^{+}(aq) \rightarrow Ag(s)$

Step 3. Add electrons to both equations so that the net charge on both sides of each equation is equal. If you add electrons on one side of the arrow in one half-reaction equation, then you will add electrons on the opposite side of the arrow in the other half-reaction equation. Note, though, that the *number* of electrons added may not be the same in both half-reaction equations.

$Al(s) \rightarrow Al^{3+}(aq) + 3\ e^{-}$

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$

Step 4. Determine whether each half-reaction equation represents an oxidation or a reduction.

The first equation represents an oxidation half-reaction since the aluminum atom loses electrons. The second equation represents a reduction half-reaction since the silver ion gains an electron.

Oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3\ e^{-}$

Reduction: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$

Practice

1. Write the oxidation and reduction half-reaction equations for the following redox reactions: T/I
   (a) $Sn^{2+}(aq) + Co(s) \rightarrow Sn(s) + Co^{2+}(aq)$
   (b) $2\ Ag^{+}(aq) + Pb(s) \rightarrow 2\ Ag(s) + Pb^{2+}(aq)$
   (c) $2\ Fe^{2+}(aq) + I_2(s) \rightarrow 2\ I^{-}(aq) + 2\ Fe^{3+}(aq)$

2. Identify the reactant oxidized and the reactant reduced in Question 1. T/I
3. Write the oxidation and reduction half-reaction equations for each of the following redox reactions. Identify the spectator ion(s) in each reaction. T/I
   (a) $Ni(s) + CuCl_2(aq) \rightarrow NiCl_2(aq) + Cu(s)$
   (b) A solution of tin(II) nitrate reacts with a solution of chromium(II) nitrate to produce tin metal and a solution of chromium(III) nitrate.
4. Chlorine gas reacts with potassium iodide solution to produce solid iodine in a solution of potassium chloride. T/I
   (a) Write the balanced chemical equation for this reaction.
   (b) Write the net ionic equation for the reaction.
   (c) Write the oxidation and reduction half-reaction equations for the reaction.
   (d) Identify the reactant oxidized and the reactant reduced.

Oxidation Numbers

Chemists use a type of "electron bookkeeping" to keep track of which atoms are losing electrons and which atoms are gaining electrons in a redox reaction. In this system, an atom's **oxidation number**, also known as its oxidation state, is defined as the apparent net electric charge that the atom would have if electron pairs in covalent bonds belonged entirely to the more electronegative atom. The oxidation number system is a useful way to keep track of electrons, but it does not usually represent an actual charge on an atom. An oxidation number can be a positive or a negative number.

oxidation number a number used to keep track of electrons in oxidation–reduction reactions according to certain rules; also known as oxidation state

Consider the oxidation numbers for atoms in a covalently bonded molecule. Recall that atoms share electrons in covalent bonds. You can determine the oxidation numbers of atoms in covalent compounds by assigning the shared electrons to particular atoms. In covalent bonds between two identical atoms, the electrons are shared equally between the two atoms. However, in cases where a covalent bond exists between two different atoms, the atoms share the electrons unequally. For the purposes of assigning oxidation numbers, the shared electrons go to the atom that has the stronger attraction for electrons (the more electronegative atom).

For example, in a molecule of water, oxygen is more electronegative than hydrogen (**Figure 3**). When you assign oxidation numbers to oxygen and hydrogen in water, you assume that the oxygen atom actually possesses all of the electrons, even the electrons it shares with hydrogen. Recall that a hydrogen atom has 1 electron. Therefore, in water, you assume that the oxygen atom has "taken" the electrons from the 2 hydrogen atoms. This gives the oxygen atom an excess of 2 electrons. Thus, the oxidation number of oxygen is −2. Each hydrogen atom has no electrons and is given an oxidation number of +1.

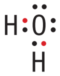


Figure 3 In a molecule of water, oxygen and hydrogen atoms share electrons. The oxygen atom is more electronegative, so it has a greater attraction for the electrons than the hydrogen atoms do.

Therefore, we define the oxidation numbers of the atoms in a covalent compound as the imaginary charges the atoms would have if (a) the shared electrons were divided equally between identical atoms bonded to each other, and (b) the shared electrons were assigned to the atom that has the greater attraction for electrons if the atoms are different. CAREER LINK

Table 1 (next page) provides a set of rules for assigning oxidation numbers to atoms. Applying these rules allows you to assign oxidation numbers to the atoms or ions of most compounds.

There are two additional rules for assigning oxidation numbers:

1. The sum of the oxidation numbers of all atoms in an electrically neutral compound must equal zero. This rule is often referred to as the zero-sum rule.
2. The sum of the oxidation numbers of all atoms in ions containing 2 or more atoms must equal the overall charge of the ion.

Table 1 Rules for Assigning Oxidation Numbers

The oxidation number of . . .	Summary	Examples
an atom in an element is 0.	element: 0	Na(s), O_2(g), O_3(g), Hg(l)
a monatomic ion is the same as its charge.	monatomic ion: charge of ion	Na^+, Cl^-
fluorine is −1 in its compounds.	fluorine: −1	HF, PF_3
oxygen is usually −2 in its compounds. (Exception: peroxides, containing O_2^{2-}, in which oxygen is −1)	oxygen: −2	H_2O, CO_2 (Exception: H_2O_2)
hydrogen is +1 in its covalent compounds. (Exception: metal hydrides, in which hydrogen is −1)	hydrogen: +1	H_2O, HCl, NH_3 (Exception: CaH_2)

The convention is to write actual charges on ions as $^{n+}$ or $^{n-}$, placing the number before the plus or minus sign as a superscript. However, you write oxidation numbers (not actual charges) as $+n$ or $-n$, placing the number after the plus or minus sign. Thus, you would write a magnesium ion as Mg^{2+}, but the oxidation number of the magnesium ion as +2.

Tutorial 2 Assigning Oxidation Numbers

In this tutorial, you will learn how to correctly assign an oxidation number to an element within a compound or an ion. The following steps are a useful guide:

1. Assign oxidation numbers to elements as listed in Table 1.
2. Identify any elements not mentioned in Table 1, and use the zero-sum rule or ion-charge rule to assign their oxidation numbers.
3. Check that the sum of the oxidation numbers is equal to zero (for a neutral compound) or the charge (for a polyatomic ion).

Sample Problem 1: Assigning Oxidation Numbers for a Molecular Compound

Assign the oxidation numbers to all atoms in a molecule of carbon dioxide.

Solution

Step 1. Assign oxidation numbers to elements as listed in Table 1.

The oxidation number of oxygen is usually –2.

Step 2. Identify any elements not mentioned in Table 1, and use the zero-sum rule to assign their oxidation numbers.

There is no specific oxidation number for carbon atoms. Since CO_2 is an electrically neutral compound, the sum of the oxidation numbers of oxygen and carbon must be zero. Since each oxygen atom has an oxidation number of −2, and there are 2 oxygen atoms in carbon dioxide, the carbon atom in a molecule of carbon dioxide must have an oxidation number of +4 to balance the −4 of the oxygen atoms.

$$\overset{+4}{C}\overset{-2}{O}_2 \quad \text{for each atom}$$

Step 3. Check that the sum of the oxidation numbers is equal to zero. Make sure that you account for the number of each atom in the carbon dioxide molecule.

$$\underset{\substack{\uparrow \\ \text{number of C} \\ \text{atoms}}}{1}(+\,4) + \underset{\substack{\uparrow \\ \text{number of O} \\ \text{atoms}}}{2}(-\,2) = 0$$

In a CO_2 molecule, the oxidation number of the carbon atom is +4 and the oxidation number of each oxygen atom is −2.

Sample Problem 2: Assigning Oxidation Numbers for a Polyatomic Ion

Assign oxidation numbers to all atoms in the nitrate ion, NO_3^-.

Solution

Step 1. Assign oxidation numbers to elements as listed in Table 1.

The oxidation number of oxygen is −2.

Step 2. Identify any elements not mentioned in Table 1, and use the ion-charge rule to assign their oxidation numbers.

Nitrogen is not mentioned in Table 1. The nitrate ion has a net charge of −1. Therefore, the sum of the oxidation numbers of all the atoms in the nitrate ion must equal −1. Each nitrate ion contains 3 oxygen atoms, each of which has an oxidation number of −2. Therefore, the total charge due to oxygen is −6.

Since the net charge of the ion is −1, the oxidation number of the nitrogen atom must be +5.

$$\overset{+5}{N}\overset{-2}{O}_3^- \quad \text{for each atom}$$

Step 3. Check that the sum of the oxidation numbers is equal to the charge on the polyatomic ion.

$$\underset{\substack{\uparrow\\\text{number of N}\\\text{atoms}}}{1}(+5) \quad + \quad \underset{\substack{\uparrow\\\text{number of O}\\\text{atoms}}}{3}(-2) = -1$$

In the nitrate ion, NO_3^-, the oxidation number of the nitrogen atom is +5 and the oxidation number of each oxygen atom is –2.

Sample Problem 3: Assigning Oxidation Numbers for an Ionic Compound

Assign the oxidation numbers to all atoms or ions in sodium thiosulfate, $Na_2S_2O_3$.

Solution

Step 1. Assign oxidation numbers to elements as listed in Table 1.

The oxidation number of the sodium ion, a monatomic ion, is +1. The oxidation number of oxygen is –2.

Step 2. Identify any elements not mentioned in Table 1, and use the zero-sum rule to assign their oxidation numbers.

The sum of the oxidation numbers of the atoms in a compound must equal zero. Since each sodium ion has an oxidation number of +1 and there are 2 sodium ions, the total contribution of sodium is +2. The polyatomic thiosulfate ion must therefore have an overall charge of −2.

Since each oxygen atom has an oxidation number of −2, and there are 3 oxygen atoms, the total contribution from oxygen is −6. Since the total charge of the ion is −2, the total contribution from the 2 sulfur atoms is +4. Therefore, the oxidation number for each sulfur atom is +2.

$$\overset{+1}{Na}_2\overset{+2}{S}_2\overset{-2}{O}_3 \quad \text{for each atom}$$

Step 3. Check that the sum of the oxidation numbers is equal to zero.

$$\underset{\substack{\uparrow\\\text{number of Na}\\\text{atoms}}}{2}(+1) \quad + \quad \underset{\substack{\uparrow\\\text{number of S}\\\text{atoms}}}{2}(+2) \quad + \quad \underset{\substack{\uparrow\\\text{number of O}\\\text{atoms}}}{3}(-2) = 0$$

In sodium thiosulfate, $Na_2S_2O_3$, the oxidation number of each sodium ion is +1; the oxidation number of each sulfur atom is +2; and the oxidation number of each oxygen atom is −2.

Practice

1. Determine the oxidation number of nitrogen in each of the following substances: T/I
   (a) N_2
   (b) NO_2
   (c) N_2O
   (d) $NaNO_3$
   (e) NH_3
2. Determine the oxidation number of carbon in each of the following compounds: T/I
   (a) CO
   (b) CH_4
   (c) Na_2CO_3
   (d) $C_6H_{12}O_6$
3. Determine the oxidation number of sulfur in each of the following substances: T/I
   (a) SO_2
   (b) SO_3^{2-}
   (c) SO_4^{2-}
   (d) $S_2O_8^{2-}$
4. Assign the oxidation number to each element in each of the following compounds: T/I
   (a) Na_2CO_3
   (b) $K_2Cr_2O_7$
   (c) $HClO_4$
   (d) $Cu_3(PO_4)_2$

Oxidation Numbers in Redox Reactions

We can use oxidation numbers to identify the reactant that is oxidized and the reactant that is reduced in a redox reaction. The reaction of nickel(II) oxide with carbon is a useful example. The mining industry uses this reaction during the extraction of nickel from its ore. CAREER LINK

Assigning oxidation numbers to each atom/ion in the chemical equation gives

$$\overset{+2-2}{NiO}(s) + \overset{0}{C}(s) \longrightarrow \overset{0}{Ni}(s) + \overset{+2\ -2}{CO}(g)$$

Note that the oxidation number of carbon changes from 0 to +2. This means that the carbon atom loses 2 electrons and becomes oxidized. The oxidation number of nickel changes from +2 to 0. This means that the Ni^{2+} ion in NiO gains 2 electrons and is reduced to nickel metal, Ni (**Figure 4**).

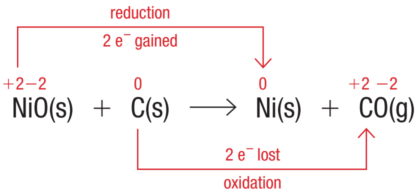


Figure 4 Note how the oxidation numbers change during the reaction of nickel oxide with carbon.

The reaction of nickel(II) oxide with carbon involves the direct transfer of electrons from one reactant to another. However, many redox reactions involve the partial transfer of electrons from one reactant to another. This occurs in the redox reactions involving molecular substances. Consider the synthesis of water from its elements:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$$

Using the rules from Table 1, we can assign the following oxidation numbers:

$$2\ \overset{0}{H_2}(g) + \overset{0}{O_2}(g) \longrightarrow 2\ \overset{+1\ -2}{H_2O}(g)$$

Note that the oxidation number of each atom in H_2 and O_2 is 0 because both hydrogen and oxygen are in their elemental form. Also, the oxidation number of hydrogen changes from 0 in H_2 to +1 in H_2O. This change indicates that each hydrogen atom effectively loses 1 electron in the reaction. However, the oxidation number of each oxygen atom changes from 0 in O_2 to −2 in H_2O. This means that each oxygen atom effectively gains 2 electrons. Since water is a molecular compound rather than an ionic compound, we know that the electrons are not completely transferred from the hydrogen atoms to the oxygen atom. Instead, the electrons in the covalent bond between oxygen and hydrogen shift toward the more electronegative element: oxygen. Hence, only a partial transfer of electrons occurs during the synthesis of water.

Oxidizing Agents and Reducing Agents

Oxidation–reduction reactions involve the transfer of electrons (**Figure 5**). The substance that gains electrons is referred to as an **oxidizing agent**. The oxidizing agent is reduced in a redox reaction. In the previous example, the oxidizing agent is oxygen gas, since it gained electrons from hydrogen. The corresponding substance that loses electrons is called the **reducing agent**. The reducing agent in the example above is hydrogen, since it lost electrons to oxygen. The reducing agent is oxidized in a redox reaction. In all oxidation–reduction reactions, electrons transfer from the reducing agent to the oxidizing agent (**Table 2**).

oxidizing agent the reactant that is reduced (gains electrons from another substance) during an oxidation–reduction reaction

reducing agent the reactant that is oxidized (loses electrons to another substance) during an oxidation–reduction reaction

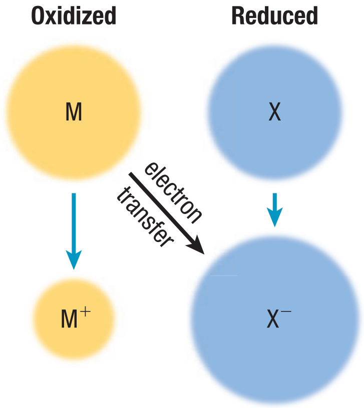


Figure 5 A summary of the oxidation–reduction process in which M is oxidized and X is reduced.

Table 2 Characteristics of Oxidizing and Reducing Agents

Oxidizing agent	Reducing agent
causes oxidation	causes reduction
gains electrons	loses electrons
is reduced	is oxidized

As an example, consider the synthesis of water:

$$2\ \overset{0}{H_2}(g) + \overset{0}{O_2}(g) \longrightarrow 2\ \overset{+1\ -2}{H_2O}(g)$$

For this reaction, we can say the following:

- Hydrogen is oxidized because its oxidation number increases. Each hydrogen atom has partially lost its electron.
- Oxygen is reduced because its oxidation number decreases. The oxygen atom has partially gained electrons.
- H_2 is the reducing agent.
- O_2 is the oxidizing agent.

Note that when you name the reducing or oxidizing agent, you specify the whole substance and not just the element that undergoes the change in oxidation number. This becomes more relevant when we consider redox reactions involving compounds: the compound is the oxidizing (or reducing) agent.

Investigation **9.1.1**

Single Displacement Reactions (page 624)
In this investigation, you will design and perform tests on metals and metal ions, and then rank the strength of the ions as oxidizing agents.

Tutorial 3 Analyzing Redox Reactions

In this tutorial, you will identify atoms that become oxidized and reduced during an oxidation–reduction reaction. It will also help you identify the oxidizing and reducing agents in a redox reaction. Note that you always start by assigning an oxidation number to each element, just as you did in Tutorial 2.

Sample Problem 1: Analyzing a Redox Reaction

Metallurgy, the process of producing a metal from its ore, always involves oxidation–reduction reactions. The valuable component of lead ore is the compound lead(II) sulfide, PbS(s), also called galena. The first step in extracting lead from its ore is the conversion of lead(II) sulfide to its oxide by a process called roasting:

(a) $2\ \mathrm{PbS(s)} + 3\ \mathrm{O_2(g)} \rightarrow 2\ \mathrm{PbO(s)} + 2\ \mathrm{SO_2(g)}$

The oxide then reacts with carbon monoxide to produce the metallic element:

(b) $\mathrm{PbO(s)} + \mathrm{CO(g)} \rightarrow \mathrm{Pb(s)} + \mathrm{CO_2(g)}$

For each reaction, identify the entities that are oxidized and reduced, and specify the oxidizing and reducing agents.

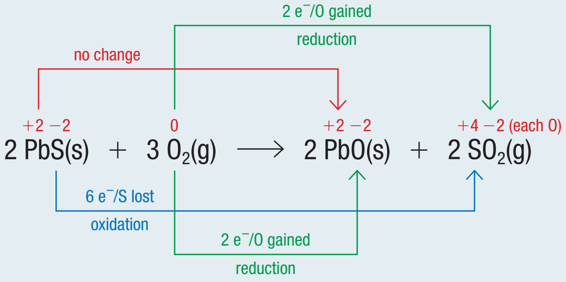
Solution (a)

Step 1. Assign oxidation numbers to elements as listed in Table 1.

Lead(II) sulfide and lead(II) oxide are simple ionic compounds, so the oxidation numbers of their elements are the same as the charges on those elements.

$$2\ \overset{+2\ -2}{\mathrm{PbS}}\mathrm{(s)} + 3\ \overset{0}{\mathrm{O_2}}\mathrm{(g)} \rightarrow 2\ \overset{+2\ -2}{\mathrm{PbO}}\mathrm{(s)} + 2\ \overset{+4\ -2\ \text{(each O)}}{\mathrm{SO_2}}\mathrm{(g)}$$

Step 2. Determine how the oxidation number on each element changes, and identify these changes as either oxidation or reduction.



The oxidation number for sulfur increases from −2 to +4. Sulfur is oxidized (**Figure 6**). The oxidation number for oxygen decreases from 0 to −2 (in both products). Oxygen is reduced. The oxidation number for lead does not change. The oxidizing agent (the substance that gains electrons) is $\mathrm{O_2}$. The reducing agent (the substance that loses electrons) is PbS.

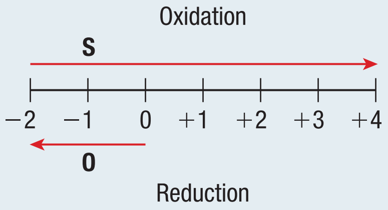


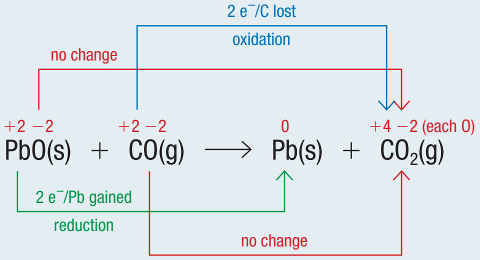
Figure 6 This number line shows the changes in oxidation number of sulfur and oxygen.

Solution (b)

Step 1. Assign oxidation numbers to elements as listed in Table 1.

$$\overset{+2\ -2}{\mathrm{PbO}}\mathrm{(s)} + \overset{+2\ -2}{\mathrm{CO}}\mathrm{(g)} \rightarrow \overset{0}{\mathrm{Pb}}\mathrm{(s)} + \overset{+4\ -2\ \text{(each O)}}{\mathrm{CO_2}}\mathrm{(g)}$$

Step 2. Determine how the oxidation number on each element changes, and identify these changes as either oxidation or reduction.



The oxidation number for lead decreases from +2 to 0. Lead is reduced. The oxidation number for carbon increases from +2 to +4. Carbon is oxidized. The oxidation number for oxygen does not change (in both products). The oxidizing agent (the substance that gains electrons) is PbO. The reducing agent (the substance that loses electrons) is CO.

Practice

1. Identify the entities that are oxidized and reduced in the following reactions: T/I
   (a) $\mathrm{Cu(s)} + 2\ \mathrm{Ag^+(aq)} \rightarrow 2\ \mathrm{Ag(s)} + \mathrm{Cu^{2+}(aq)}$ (b) $4\ \mathrm{Fe(s)} + 3\ \mathrm{O_2(g)} \rightarrow 2\ \mathrm{Fe_2O_3(s)}$
2. Identify the oxidizing agent and the reducing agent in the following reactions: T/I
   (a) $\mathrm{Zn(s)} + 2\ \mathrm{HCl(aq)} \rightarrow \mathrm{ZnCl_2(aq)} + \mathrm{H_2(g)}$ (b) $\mathrm{SnO_2(s)} + \mathrm{C(s)} \rightarrow \mathrm{Sn(s)} + \mathrm{CO_2(g)}$
3. For the following reactions, assign the oxidation numbers to each atom, then indicate the oxidizing and reducing agents: T/I
   (a) $2\ \mathrm{H_2S(g)} + 3\ \mathrm{O_2(g)} \rightarrow \mathrm{SO_2(g)} + \mathrm{H_2O(g)}$ (b) $\mathrm{CH_4(g)} + 2\ \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} + 2\ \mathrm{H_2O(g)}$

9.1 Review

Summary

- Many reactions involve the transfer of electrons.
- Oxidation–reduction reactions, or redox reactions, are reactions in which electrons transfer from one entity to another. Neither oxidation nor reduction can occur without the other.
- Chemists assign oxidation numbers to atoms or ions to keep track of the electrons in an oxidation–reduction reaction.
- The rules in Table 1 (page 603) allow oxidation numbers to be assigned for common entities. Oxidation numbers can then be assigned to remaining atoms or ions.
- In an oxidation–reduction reaction, one element is oxidized (loses electrons). Another element is reduced (gains electrons).
- An oxidizing agent causes oxidation to occur (and is reduced in the process). A reducing agent causes reduction to occur (and is oxidized in the process).

UNIT TASK BOOKMARK

You can apply what you learned about redox reactions to the Unit Task described on page 684.

Questions

1. Explain, in your own words, the process that occurs in a redox reaction. K/U
2. Write the oxidation and reduction half-reaction equations for the reactions represented by each of the following equations: T/I
   (a) $Mg(s) + 2\,H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
   (b) $2\,Al(s) + Fe_2O_3(s) \rightarrow 2\,Fe(l) + Al_2O_3(s)$
3. Identify the oxidation number of the specified element in each of the following entities: T/I
   (a) S in S_8
   (b) Cr in $Cr_2O_7^{2-}$
   (c) N in N_2H_4
   (d) I in MgI_2
   (e) C in CO
   (f) N in NH_3
   (g) P in P_4O_6
   (h) Mn in MnO_4^-
   (i) C in C_2H_5OH
   (j) S in $Al_2(SO_3)_3$
4. Identify the entity that is oxidized and the entity that is reduced in the chemical reactions represented by the following equations: T/I
   (a) $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3\,H_2(g)$
   (b) $8\,H^+(aq) + MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq) + 4\,H_2O(l)$
   (c) a single displacement reaction in which copper metal reacts with silver nitrate
5. (a) Describe the change in the oxidation number of an entity when it becomes oxidized.
   (b) Describe the change in the oxidation number of an entity when it is reduced.
   (c) Why do oxidation and reduction half-reactions both have to occur in the same reaction? K/U
6. Use oxidation numbers to determine which of the following chemical equations represent a redox reaction. For all that ARE redox reactions, indicate the oxidizing agent, the reducing agent, the element being oxidized, and the element being reduced. T/I
   (a) $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
   (b) $SiCl_4(l) + 2\,Mg(s) \rightarrow 2\,MgCl_2(s) + Si(s)$
   (c) $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$
7. Assign oxidation numbers to each element in the following equations: T/I
   (a) $4\,PH_3(g) + 8\,O_2(g) \rightarrow P_4O_{10}(s) + 6\,H_2O(l)$
   (b) $2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g)$
   (c) $Pb(s) + PbO_2(s) + 2\,H_2SO_4(aq) \rightarrow 2\,PbSO_4(s) + 2\,H_2O(g)$
8. Describe each of the reactions in Question 7 using the terms "oxidation," "reduction," "oxidizing agent," and "reducing agent." K/U
9. In the process of photosynthesis, carbon dioxide and water form glucose and oxygen: T/I A
   $6\,CO_2(g) + 6\,H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6\,O_2(g)$
   (a) What is the oxidation number of carbon in CO_2 and $C_6H_{12}O_6$?
   (b) Describe the process of photosynthesis using the terms "oxidation," "reduction," "oxidizing agent," and "reducing agent."
10. Carbon dioxide can be progressively reduced to methane through a series of reactions. What is the oxidation number of carbon in each of the following compounds? T/I
    $CO_2 \rightarrow CH_2O_2 \rightarrow CH_2O \rightarrow CH_4O \rightarrow CH_4$

9.2 Balancing Redox Reaction Equations

Figure 1 Potassium permanganate is widely used to analyze chemicals that undergo redox reactions, including determining the concentration of iron(II) ions in a sample. When all the iron(II) ions are used up, the solution in the flask turns purple.

Geologists sometimes use potassium permanganate, $KMnO_4(aq)$, to analyze the iron content in a mineral ore sample. It is a common oxidizing agent used in quantitative analysis. A typical analysis involves titrating a prepared ore sample with a potassium permanganate solution of known concentration until an endpoint is reached (**Figure 1**). The analyst must know the balanced chemical equation for the titration reaction before analyzing the titration data. Most simple redox reactions can be balanced by inspection. For more complex reactions, we can use either of two strategies: the oxidation numbers method or the half-reactions method. CAREER LINK

The Oxidation Numbers Method

As shown in Section 9.1, the oxidation numbers of atoms or ions change during a redox reaction. One way to determine if a reaction is a redox reaction is to assign oxidation numbers to each element in the reaction and then see if oxidation numbers have changed between the reactant side and product side of the equation. A change in the oxidation number of an element indicates that electron transfer and, therefore, a redox reaction has occurred.

Redox reactions often take place in aqueous solutions. In these cases, water molecules, $H_2O(l)$, may participate in the redox reaction. An aqueous solution may be acidic, basic, or neutral. If a redox reaction occurs in an acidic solution, hydrogen ions, $H^+(aq)$, may be participants in the reaction. If a redox reaction occurs in a basic solution, hydroxide ions, $OH^-(aq)$, may be participants. In these cases, the redox reactions are balanced in the same way as other redox reactions. However, when you balance redox reactions that occur in acidic or basic solutions, you will need to include $H_2O(l)$, $H^+(aq)$, and/or $OH^-(aq)$ during the balancing procedure. CAREER LINK

Tutorial 1 Balancing Equations Using Oxidation Numbers

In this tutorial, you will balance redox reaction equations using the oxidation numbers method. For Sample Problem 1, you will use the oxidation numbers method to balance a straightforward equation for a single displacement reaction. In Sample Problems 2 and 3, this procedure is adjusted to balance equations for reactions that occur in acidic and basic solutions.

The following steps are an effective problem-solving approach:

1. Write the unbalanced chemical equation from the given information. Determine the oxidation numbers for each element in the equation and identify the elements for which the oxidation numbers change.
2. Adjust the values of the coefficients to balance the electrons transferred.
3. Balance the rest of the equation by inspection. If necessary, balance oxygen by adding water.
4. If necessary, balance hydrogen by adding $H^+(aq)$ and/or $OH^-(aq)$.
5. Check your answer.
6. Write the balanced equation.

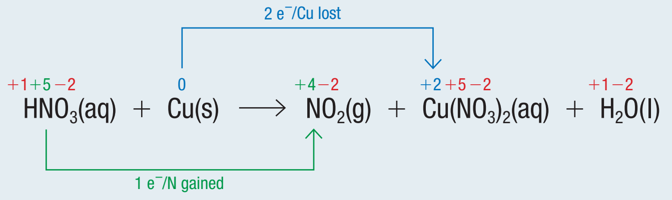
Sample Problem 1: A Redox Reaction Involving Compounds

Concentrated nitric acid, $HNO_3(aq)$, is very reactive: it oxidizes copper metal to produce toxic nitrogen dioxide gas, dissolved copper(II) nitrate, and water (**Figure 2**). Use the oxidation numbers method to write a balanced chemical equation for this reaction.

Figure 2 Nitrogen dioxide is a toxic reddish-brown gas produced when concentrated nitric acid oxidizes copper metal.

Solution

Step 1. Write the unbalanced chemical equation. Determine the oxidation numbers for each element in the equation and identify the elements for which the oxidation numbers change.



$$\overset{+1+5-2}{HNO_3}(aq) + \overset{0}{Cu}(s) \longrightarrow \overset{+4-2}{NO_2}(g) + \overset{+2+5-2}{Cu(NO_3)_2}(aq) + \overset{+1-2}{H_2O}(l)$$

The oxidation number of Cu increases from 0 to +2. Cu is oxidized by losing 2 electrons (**Figure 3**). The oxidation number of N decreases from +5 to +4. N is reduced by gaining 1 electron. Note that the oxidation number of nitrogen in $Cu(NO_3)_2$(aq) is unchanged.

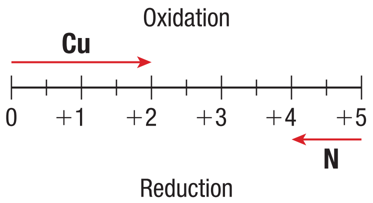
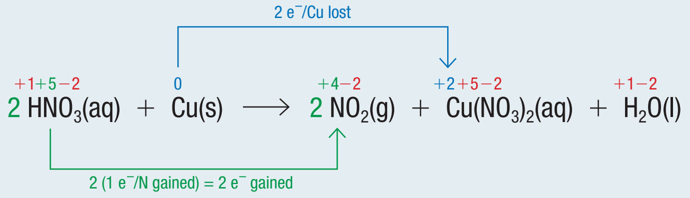


Figure 3 A redox number line shows the oxidation number of the copper atom increasing and the oxidation number of the nitrogen atom decreasing.

Step 2. Adjust the values of the coefficients to balance the electrons transferred.

During a redox reaction, electrons are transferred from one element to another. Therefore, the total number of electrons transferred must be equal. To balance the electrons, determine the simplest whole numbers that will equalize the electrons gained or lost in the reaction. Then, use those numbers as coefficients.



$$2\,\overset{+1+5-2}{HNO_3}(aq) + \overset{0}{Cu}(s) \longrightarrow 2\,\overset{+4-2}{NO_2}(g) + \overset{+2+5-2}{Cu(NO_3)_2}(aq) + \overset{+1-2}{H_2O}(l)$$

Since you multiplied the number of electrons gained by 2, the coefficients for HNO_3(aq) and NO_2(g) must be 2. The coefficient of copper remains unchanged.

Step 3. Balance the rest of the equation by inspection, assigning coefficients for the reactants and products as necessary.

Since there are 2 nitrate ions in $Cu(NO_3)_2$(aq), we need 2 more nitrate ions on the left side of the equation. Therefore, the coefficient of HNO_3(aq) changes to 4.

$$4\,HNO_3(aq) + Cu(s) \rightarrow 2\,NO_2(g) + Cu(NO_3)_2(aq) + 2\,H_2O(l)$$

Step 4. Since hydrogen is balanced, proceed to Step 5.

Step 5. Check your answer. Check the number of atoms (**Table 1**).

The equation is balanced if

(a) the total number of atoms of each element is equal on each side of the equation, and

(b) the sums of the charges on each side of the equation are equal.

Table 1 Number of Atoms of All Elements

$4\,HNO_3(aq) + Cu(s) \rightarrow 2\,NO_2(g) + Cu(NO_3)_2(aq) + 2\,H_2O(l)$		
Element	**Number of atoms in reactants**	**Number of atoms in products**
N	4 from 4 HNO_3	2 from 2 NO_2 + 2 from $Cu(NO_3)_2$ = 4
H	4 from 4 HNO_3	4 from 2 H_2O
O	12 from 4 HNO_3	4 from 2 NO_2 + 6 from $Cu(NO_3)_2$ + 2 from 2 H_2O = 12
Cu	1 from 1 Cu	1 from 1 $Cu(NO_3)_2$

The numbers of entities of each element are equal on both sides of the equation.

The reactants and products consist of only molecules. Since any molecule has a charge of 0, the sum of the charges of the reactants and products equals 0. This confirms that the number of electrons lost equals the number of electrons gained.

Step 6. Write the balanced equation:

$$4\ HNO_3(aq) + Cu(s) \rightarrow 2\ NO_2(g) + Cu(NO_3)_2(aq) + 2\ H_2O(l)$$

Sample Problem 2: A Redox Reaction in an Acidic Solution

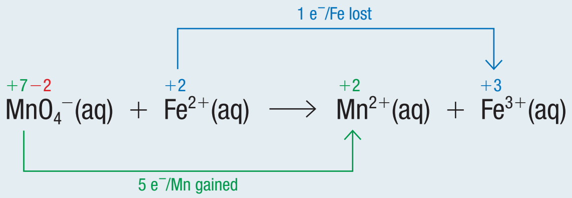
To determine the iron content of an ore sample, you can perform a titration using an acidified solution of potassium permanganate, $KMnO_4(aq)$. Before the titration begins, all of the iron in the sample is converted to $Fe^{2+}(aq)$ ions. The net ionic equation that occurs during the titration is

$$MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$$ WEB LINK

Balance the equation for this reaction.

Solution

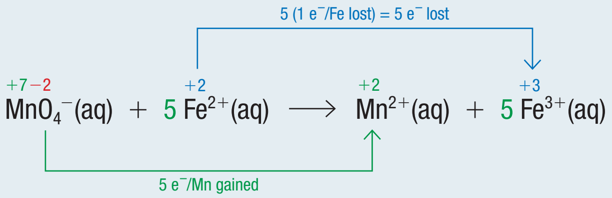
Step 1. Write the unbalanced chemical equation. Determine the oxidation numbers for each element in the equation and identify the elements for which the oxidation numbers change.



The oxidation number of Fe increases from +2 to +3. Fe is oxidized by losing 1 electron. The oxidation number of Mn decreases from +7 to +2. Mn is reduced by gaining 5 electrons.

Step 2. Adjust the values of the coefficients to balance the electrons transferred.

To do this, determine the simplest whole numbers that will equalize the electrons gained or lost in the reaction. Then, use those numbers as coefficients in the equation.



Since you multiplied the number of electrons lost by 5, the coefficient of $Fe^{2+}(aq)$ is 5. The coefficient of $MnO_4^-(aq)$ remains unchanged. The equation now becomes

$$1\ MnO_4^-(aq) + 5\ Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq)$$

There are 5 Fe^{2+} ions on the left and 5 Fe^{3+} ions on the right. Therefore, the elements involved in the electron transfer are balanced. Note that this equation represents only the elements for which oxidation numbers change during the chemical reaction. However, since the reaction occurs in acidic solution, $H_2O(l)$ and $H^+(aq)$ also participate in the redox reaction.

Step 3. Balance the rest of the equation by inspection. If necessary, balance oxygen by adding water.

Although manganese and iron are now balanced, oxygen is not: there are 4 oxygen atoms on the left and none on the right. Since this reaction occurs in an aqueous solution, we may add 4 oxygen atoms (from 4 $H_2O(l)$) to equal the 4 oxygen atoms on the product side.

$$1\ MnO_4^-(aq) + 5\ Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$$

Step 4. If necessary, balance hydrogen by adding $H^+(aq)$.

Since this reaction occurred in an acidic solution, we may add $H^+(aq)$ to balance the hydrogen atoms in the 4 water molecules. The water molecules in this example are products, so add 8 $H^+(aq)$ ions to the reactant side of the equation to balance the 8 hydrogen atoms on the product side:

$$1\ MnO_4^-(aq) + 5\ Fe^{2+}(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$$

Step 5. Check your answer.

(a) Check the number of entities of each element in the balanced equation (**Table 2**).

Table 2 Number of Entities of All Elements

<table>
<tr><td colspan="3">$MnO_4^-(aq) + 5\ Fe^{2+}(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$</td></tr>
<tr><th>Element</th><th>Number in reactants</th><th>Number in products</th></tr>
<tr><td>Mn</td><td>1 from MnO_4^-</td><td>1 from Mn^{2+}</td></tr>
<tr><td>Fe</td><td>5 from 5 Fe^{2+}</td><td>5 from 5 Fe^{3+}</td></tr>
<tr><td>O</td><td>4 from MnO_4^-</td><td>4 from 4 H_2O</td></tr>
<tr><td>H</td><td>8 from 8 H^+</td><td>8 from 4 H_2O</td></tr>
</table>

Therefore, all elements are balanced.

(b) To confirm that all the electrons involved in the reaction are accounted for, check that the sums of the charges on both sides of the equation are equal.

$$\underbrace{\underset{1\times 1^-}{MnO_4^-(aq)} + \underset{5\times 2^+}{5\ Fe^{2+}(aq)} + \underset{8\times 1^+}{8\ H^+(aq)}}_{17+} \longrightarrow \underbrace{\underset{1\times 2^+}{Mn^{2+}(aq)} + \underset{5\times 3^+}{5\ Fe^{3+}(aq)} + \underset{4\times 0}{4\ H_2O(l)}}_{17+}$$

The blue numbers are the charges for each side of the equation and not oxidation numbers. Since the sums of the charges on both sides are the same, the electrons transferred during the reaction are accounted for. Therefore, the equation is balanced.

Step 6. Write the balanced equation.

$$MnO_4^-(aq) + 5\ Fe^{2+}(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$$

Sample Problem 3: A Redox Reaction in a Basic Solution

The process for balancing equations in basic solutions is similar to balancing equations in acidic solutions. The only difference is that you add hydroxide ions at the end to account for the reaction taking place in a basic solution. For example, iodate ions, $IO_3^-(aq)$, react with oxalate ions, $C_2O_4^{2-}(aq)$, in a basic solution to produce carbon dioxide gas and aqueous iodide ions.

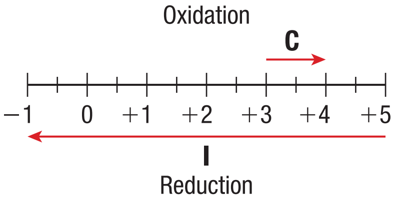
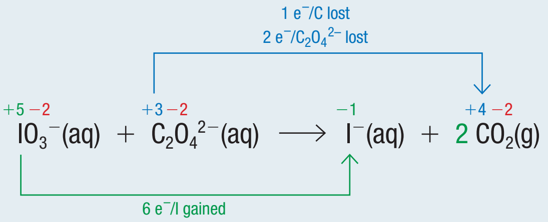


Figure 4 A redox number line shows the change in oxidation numbers of iodine and carbon.

Solution

Step 1. Write the unbalanced chemical equation. Identify the elements for which the oxidation numbers change.

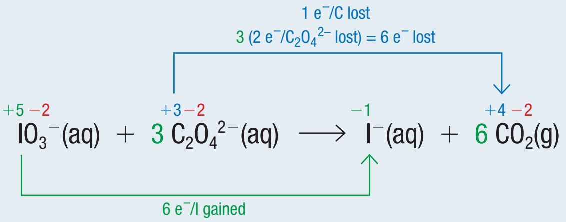


$$\overset{+5\;-2}{IO_3^-}(aq) + \overset{+3\;-2}{C_2O_4^{2-}}(aq) \longrightarrow \overset{-1}{I^-}(aq) + 2\,\overset{+4\;-2}{CO_2}(g)$$

The oxidation number of iodine decreases from +5 to −1 (**Figure 4**). Iodine is reduced by gaining 6 electrons. The oxidation number of C increases from +3 to +4. C is oxidized by losing 1 electron. However, there are 2 carbon atoms in $C_2O_4^{2-}$. Therefore, 2 electrons in total are lost. Note that a coefficient 2 is included on the right side to account for the second carbon atom.

Step 2. Adjust the values of the coefficients to balance the electrons transferred.

Determine the simplest whole numbers that will equalize the electrons gained or lost in the reaction. Then, use those numbers as coefficients in the equation.



$$\overset{+5\;-2}{IO_3^-}(aq) + 3\,\overset{+3\;-2}{C_2O_4^{2-}}(aq) \longrightarrow \overset{-1}{I^-}(aq) + 6\,\overset{+4\;-2}{CO_2}(g)$$

Since you multiplied the number of electrons lost by 3, the coefficient of $C_2O_4^{2-}(aq)$ is 3. As a result, the coefficient of CO_2 increases from 2 to 6. The coefficient of $IO_3^-(aq)$ remains unchanged. The equation now becomes

$$IO_3^-(aq) + 3\,C_2O_4^{2-}(aq) \rightarrow I^-(aq) + 6\,CO_2(g)$$

The entities involved in the electron transfer are now balanced. Note that this equation represents only the entities for which oxidation numbers change during the chemical reaction. However, since the reaction occurs in a basic solution, $H_2O(l)$ and $OH^-(aq)$ may also participate in the redox reaction.

Step 3. Balance the rest of the equation by inspection. If necessary, balance oxygen by adding water.

Notice that oxygen is not balanced: there are 15 oxygen atoms on the left and 12 on the right. Since this reaction occurs in an aqueous solution, we may add H_2O molecules on the product side to balance the oxygen atoms on the reactant side. The product side now requires 3 oxygen atoms (from 3 $H_2O(l)$) to balance.

$$IO_3^-(aq) + 3\,C_2O_4^{2-}(aq) \rightarrow I^-(aq) + 6\,CO_2(g) + 3\,H_2O(l)$$

Step 4. If necessary, balance hydrogen by adding $H^+(aq)$ and $OH^-(aq)$.

Although the reaction occurs in a basic solution, it is simpler to add $H^+(aq)$ to balance the hydrogen atoms rather than adding hydroxide. We will correct for this $H^+(aq)$ in the next step. Since the water molecules in this example are products, add 6 $H^+(aq)$ ions to the reactant side of the equation:

$$IO_3^-(aq) + 3\,C_2O_4^{2-}(aq) + 6\,H^+(aq) \rightarrow I^-(aq) + 6\,CO_2(g) + 3\,H_2O(l)$$

Since the reaction occurred in basic solution, the solution contains $OH^-(aq)$ ions. Therefore, it is not likely that $H^+(aq)$ ions took part in the reaction. You can eliminate $H^+(aq)$ ions by adding $OH^-(aq)$ ions to both sides of the equation. By adding $OH^-(aq)$ ions to both sides, you are not changing the equation.

$$IO_3^-(aq) + 3\,C_2O_4^{2-}(aq) + 6\,H^+(aq) + 6\,OH^-(aq) \rightarrow I^-(aq) + 6\,CO_2(g) + 3\,H_2O(l) + 6\,OH^-(aq)$$

Since $6\,H^+(aq) + 6\,OH^-(aq) \rightarrow 6\,H_2O(l)$, the H^+ and OH^- ions on the reactant side are equivalent to 6 water molecules. Subtracting 3 water molecules from each side eliminates the redundant water molecules from the equation:

$$IO_3^-(aq) + 3\,C_2O_4^{2-}(aq) + \cancel{6}\,3\,H_2O(l) \rightarrow I^-(aq) + 6\,CO_2(g) + \cancel{3\,H_2O(l)} + 6\,OH^-(aq)$$

Step 5. Check your answer.

(a) Check the number of entities of each element in the balanced equation (**Table 3**).

Table 3 Number of Entities of All Elements

$IO_3^-(aq) + 3\,C_2O_4^{2-}(aq) + 3\,H_2O(l) \rightarrow I^-(aq) + 6\,CO_2(g) + 6\,OH^-(aq)$		
Element	**Number in reactants**	**Number in products**
I	1 from IO_3^-	1 from I^-
C	6 from 3 $C_2O_4^{2-}$	6 from 6 CO_2
O	3 from IO_3^- + 12 from $C_2O_4^{2-}$ + 3 from 3 H_2O = 18	12 from 6 CO_2 + 6 from 6 OH^- = 18
H	6 from 3 H_2O	6 from 6 OH^-

Therefore, all elements are balanced.

(b) Check that the sums of the charges on both sides of the equation are equal.

$$\underbrace{\underset{1\times1^-}{IO_3^-(aq)} \underset{+}{+} \underset{3\times2^-}{3\,C_2O_4^{2-}(aq)} \underset{+}{+} \underset{3\times0}{3\,H_2O(l)}}_{7-} \longrightarrow \underbrace{\underset{1\times1^-}{I^-(aq)} \underset{+}{+} \underset{6\times0}{6\,CO_2(g)} \underset{+}{+} \underset{6\times1^-}{6\,OH^-(aq)}}_{7-}$$

Since the sums of the charges on both sides are the same, the electrons transferred during the reaction are accounted for. Therefore, the equation is balanced.

Step 6. Write the balanced equation.

$$IO_3^-(aq) + 3\,C_2O_4^{2-}(aq) + 3\,H_2O(l) \rightarrow I^-(aq) + 6\,CO_2(g) + 6\,OH^-(aq)$$

Practice

1. Use the oxidation numbers method to write a balanced chemical equation for the reaction between lead(II) oxide, $PbO_2(s)$, and ammonia, $NH_3(g)$, to produce nitrogen gas, liquid water, and solid lead. T/I
2. Hydrogen sulfide, $H_2S(g)$, is a poisonous gas with an odour like rotten eggs. Natural gas in well water can be removed by reacting it with pressurized oxygen. The unbalanced equation for this reaction is

   $H_2S(g) + O_2(g) \rightarrow S(s) + H_2O(l)$

   Write a balanced chemical equation for this reaction using the oxidation numbers method. T/I
3. Balance the following chemical equations representing reactions that take place in acidic solutions: T/I

   (a) $MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$

   (b) $I_2(s) + OCl^-(aq) \rightarrow IO_3^-(aq) + Cl^-(aq)$

4. Balance the following chemical equations representing reactions that take place in basic solutions: T/I
   (a) $MnO_4^-(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + MnO_2(s)$
   (b) $S^{2-}(aq) + I_2(s) \rightarrow SO_4^{2-}(aq) + I^-(aq)$
5. Iodate ions react in solution with hydrogen sulfite ions to produce sulfate ions and a precipitate of solid iodine. The unbalanced equation for this reaction is $IO_3^-(aq) + HSO_3^-(aq) \rightarrow SO_4^{2-}(aq) + I_2(s)$. T/I
   (a) Determine the entities that change oxidation number, and indicate the numbers of electrons that are lost or gained.
   (b) Balance the equation, assuming that the reaction takes place in an acidic solution.
6. Chromium hydroxide is a solid compound that reacts in a basic solution with chlorate ions. The products are aqueous chromate ions and chloride ions. The unbalanced chemical equation for this reaction is
   $Cr(OH)_3(s) + ClO_3^-(aq) \rightarrow CrO_4^{2-}(aq) + Cl^-(aq)$. T/I
   (a) Determine the entities that change oxidation number and indicate the numbers of electrons that are lost or gained.
   (b) Balance the equation. Assume that the reaction takes place in a basic solution.

The Half-Reactions Method

The second strategy to balance redox equations is to separate the reaction into two half-reaction equations: one involving oxidation and the other involving reduction. These equations are balanced separately, then added together to give the balanced chemical equation for the complete redox reaction. Although the half-reactions method differs from the oxidation numbers method in approach, the result is the same: a balanced redox reaction.

Tutorial 2 Balancing Equations Using Half-Reactions

To balance the equation of a redox reaction by this method, you will first identify and write the half-reaction equations for redox reactions. Then, you will balance the equations for the half-reactions separately. Finally, you will add the half-reaction equations to arrive at the balanced redox reaction equation. The following steps are an effective problem-solving approach:

1. Write the unbalanced equation and assign oxidation numbers to all entities.
2. Write unbalanced equations for the oxidation and reduction half-reactions.
3. Balance each half-reaction equation.
4. Use electrons to balance the charge in each half-reaction equation.
5. Equalize the electron transfer in the two half-reaction equations.
6. Add the half-reaction equations.
7. Check your answer.
8. Write the balanced equation.

Sample Problem 1: A Redox Reaction in an Acidic Solution

Consider again the permanganate reaction from Tutorial 1, Sample Problem 2. The net ionic equation for the reaction is

$$MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$$

Using the half-reactions method, balance the equation for this reaction in an acidic solution. (Note that this will be a different way of solving the same problem as in Tutorial 1, Sample Problem 2.)

Solution

Step 1. Write the unbalanced equation and assign oxidation numbers to all entities.

$$\overset{+7}{Mn}\overset{-2}{O}{}_4^-(aq) + \overset{+2}{Fe}{}^{2+}(aq) \rightarrow \overset{+2}{Mn}{}^{2+}(aq) + \overset{+3}{Fe}{}^{3+}(aq)$$

Step 2. Write unbalanced equations for the oxidation and reduction half-reactions.

Look at the change in oxidation number of the manganese atom in the permanganate ion during the redox reaction. Since the oxidation number of Mn decreases, we know that Mn is reduced. The equation for the half-reaction involving the permanganate ion is

$$\overset{+7}{Mn}\overset{-2}{O}{}_4^-(aq) \rightarrow \overset{+2}{Mn}{}^{2+}(aq) \qquad \text{(reduction)}$$

The other half-reaction involves the oxidation of iron(II) to iron(III):

$$\overset{+2}{Fe}{}^{2+}(aq) \rightarrow \overset{+3}{Fe}{}^{3+}(aq) \qquad \text{(oxidation)}$$

Step 3. Balance each half-reaction equation. As you did in the oxidation numbers method, use $H_2O(l)$ to balance oxygen and $H^+(aq)$ ions to balance hydrogen.

Consider the reduction half-reaction:

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$

Balancing the oxygen and hydrogen gives

$$8\,H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Iron in the oxidation half-reaction is already balanced:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$

Step 4. Use electrons to balance the charge in each half-reaction equation.

All the elements have been balanced, but you now need to balance the charge using electrons. At this point we have the following overall charges for reactions and products in the reduction half-reaction:

$$\underbrace{\underset{8+}{8\,H^+(aq)} \;\underset{+}{+}\; \underset{1-}{MnO_4^-(aq)}}_{7+} \longrightarrow \underbrace{\underset{2+}{Mn^{2+}(aq)} \;\underset{+}{+}\; \underset{0}{4\,H_2O(l)}}_{2+}$$

You may now equalize the charges by adding 5 electrons to the left side of the equation. Remember that electrons have a negative charge, so you are effectively adding a negative number to the total charge.

$$\underbrace{5e^- + 8\,H^+(aq) + MnO_4^-(aq)}_{2+} \longrightarrow \underbrace{Mn^{2+}(aq) + 4\,H_2O(l)}_{2+}$$

Now, both the elements and charges for the reduction half-reaction are balanced. The fact that 5 electrons appear on the reactant side of the equation makes sense when you consider the change in oxidation numbers that occurs. Manganese has an oxidation number of +7 in MnO_4^- and +2 in Mn^{2+}. Five electrons must be added in order for this change to occur.

In the oxidation half-reaction equation, the overall charges for the reactants and products are

$$\underbrace{Fe^{2+}(aq)}_{2+} \longrightarrow \underbrace{Fe^{3+}(aq)}_{3+}$$

You must add 1 electron to the right side of the equation to give a net charge of 2+ on both sides of the equation.

$$\underbrace{Fe^{2+}(aq)}_{2+} \longrightarrow \underbrace{Fe^{3+}(aq) + e^-}_{2+}$$

Step 5. Equalize the electron transfer in the two half-reaction equations.

The elements and charges for the oxidation half-reaction are now balanced. However, at this point, the reduction half-reaction involves a transfer of 5 electrons and the oxidation half-reaction involves a transfer of only 1 electron. To equalize the number of electrons transferred, multiply the oxidation half-reaction by 5:

$$5\,Fe^{2+}(aq) \rightarrow 5\,Fe^{3+}(aq) + 5\,e^-$$

Step 6. Add the half-reaction equations.

$$5\,e^- + 5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \rightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l) + 5\,e^-$$

Any identical entities on both sides of the arrow cancel out. Here, you can cross out the electrons on both sides, giving the final balanced redox equation:

$$5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \rightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

Step 7. Check your answer.

(a) Check the number of atoms (**Table 4**).

Table 4 Number of Entities of All Elements

$5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \rightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$		
Element	**Number in reactants**	**Number in products**
Fe	5 from 5 Fe^{2+}	5 from 5 Fe^{3+}
Mn	1 from MnO_4^-	1 from Mn^{2+}
O	4 from MnO_4^-	4 from 4 H_2O
H	8 from 8 H^+	8 from 4 H_2O

Therefore, all elements are balanced.

(b) To confirm that all the electrons involved in the reaction are accounted for, check that the sums of the charges on both sides of the equation are equal.

$$\underbrace{\underset{1-}{MnO_4^-(aq)} + \underset{10+}{5\,Fe^{2+}(aq)} + \underset{8+}{8\,H^+(aq)}}_{17+} \longrightarrow \underbrace{\underset{2+}{Mn^{2+}(aq)} + \underset{15+}{5\,Fe^{3+}(aq)} + \underset{0}{4\,H_2O(l)}}_{17+}$$

Since the sums of the charges on both sides are the same, the electrons transferred during the reaction are accounted for.

Step 8. Write the balanced equation.

$$MnO_4^-(aq) + 5\,Fe^{2+}(aq) + 8\,H^+(aq) \rightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4\,H_2O(l)$$

Practice

1. Using the half-reaction method, balance the following equations: T/I
   (a) $Zn(s) + H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
   (b) $HNO_3(aq) + Cu(s) \rightarrow NO_2(g) + Cu^{2+}(aq)$ in acid
2. Methanol reacts with permanganate in a basic solution:
   $CH_3OH(aq) + MnO_4^-(aq) \rightarrow CO_3^{2-}(aq) + MnO_4^{2-}(aq)$ T/I
   (a) Write the balanced half-reaction equations for this reaction.
   (b) Write the overall balanced equation for the reaction.

9.2 Review

Summary

- In a balanced redox equation, the total numbers of each type of atom or ion on either side of the equation are equal and the numbers of electrons transferred are equal.
- Redox equations may be balanced by using the oxidation numbers method or the half-reactions method.
- Oxidation–reduction reactions can occur in acidic or basic solutions. In these cases, it may be necessary to add water molecules, hydrogen ions, and/or hydroxide ions to balance the equation.

Questions

1. When magnesium metal is added to a beaker that contains hydrochloric acid, HCl(aq), a gas forms. T/I
   (a) If the magnesium is oxidized and the hydrogen is reduced, write the balanced half-reaction equations for the reaction.
   (b) Write the balanced equation for the reaction.
   (c) How many electrons transfer in the balanced equation?
2. Write balanced half-reactions for the following equations: T/I
   (a) $2\ AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2\ Ag(s)$
   (b) $Cr^{3+}(aq) + Cl_2(g) \rightarrow Cr_2O_7^{\ 2-}(aq) + Cl^-(aq)$
   (c) $H_2SO_4(aq) + Ca(s) \rightarrow CaSO_4(aq) + H_2(g)$
3. Balance the following equations for reactions occurring in acidic conditions: T/I
   (a) $ClO_3^{\ -}(aq) + I_2(aq) \rightarrow Cl^-(aq) + IO_3^{\ -}(aq)$
   (b) $Cr_2O_7^{\ 2-}(aq) + Cl^-(aq) \rightarrow Cr^{3+}(aq) + Cl_2(aq)$
4. Balance the following equations for reactions occurring in basic conditions: T/I
   (a) $Pb(OH)_4^{\ 2-}(aq) + ClO^-(aq) \rightarrow PbO_2(s) + Cl^-(aq)$
   (b) $NO_2^{\ -}(aq) + Al(s) \rightarrow NH_3(aq) + Al(OH)_4^{\ -}(aq)$
5. Permanganate ions, $MnO_4^{\ -}(aq)$, and oxalate ions, $C_2O_4^{\ 2-}(aq)$, react as follows: T/I
   $MnO_4^{\ -}(aq) + C_2O_4^{\ 2-}(aq) \rightarrow Mn^{2+}(aq) + CO_2(aq)$
   (a) How many electrons are transferred for each $MnO_4^{\ -}(aq)$ ion?
   (b) How many electrons are transferred for each $C_2O_4^{\ 2-}(aq)$ ion?
   (c) Write the balanced chemical equation using the oxidation numbers method.
6. Silver metal can be found in nature as large nuggets. Usually, it is mixed with other metals and ores. An aqueous solution of toxic cyanide ions can be used to extract the silver using the following reaction that occurs in basic solution: T/I A
   $Ag(s) + CN^-(aq) + O_2(g) \rightarrow Ag(CN)_2^{\ -}(aq)$
   (a) Balance the above equation using the half-reactions method.
   (b) If the cyanide ions are used up during the reaction, why is there still an environmental concern about the use of cyanide in this process? CAREER LINK
7. Potassium dichromate, $K_2Cr_2O_7(aq)$, is a bright orange compound that can be reduced to a blue-violet solution of $Cr^{3+}(aq)$ ions. Under certain conditions, $K_2Cr_2O_7(aq)$ reacts with ethanol, $C_2H_5OH(aq)$, as follows: T/I A
   $Cr_2O_7^{\ 2-}(aq) + C_2H_5OH(aq) \rightarrow Cr^{3+}(aq) + CO_2(g)$
   (a) Balance the above equation in acidic conditions using either the oxidation numbers method or the half-reactions method.
   (b) Which method do you prefer to use? Explain.
8. Potassium permanganate is used to determine the amount of hydrogen peroxide in a sample:
   $MnO_4^{\ -}(aq) + H_2O_2(aq) \rightarrow Mn^{2+}(aq) + O_2(g)$ T/I
   (a) Write the balanced half-reaction equations for this reaction.
   (b) Balance the equation for the redox reaction involving these substances in acidic solution.
9. Write a balanced chemical equation for the oxidation of a sulfite solution by a nitrate solution. Assume the reaction products include dissolved sulfate and nitrogen dioxide gas. T/I
10. Chlorine bubbled into a basic solution produces the chloride and chlorate ions:
   $Cl_2(g) \rightarrow Cl^-(aq) + ClO_3^{\ -}(aq)$ K/U T/I
   (a) Balance this equation using the half-reactions method.
   (b) Assign oxidation numbers to each element in this reaction.
   (c) What is unusual about the role of the element chlorine in this reaction?

9.3

Predicting Redox Reactions

Figure 1 The presence of hydrogen sulfide gas gives water an unpleasant odour. The dissolved gas evaporates quickly so tests should be carried out "on site."

Hydrogen sulfide is a toxic, colourless gas with a distinctive "rotten eggs" smell. Hydrogen sulfide is produced by naturally occurring bacteria that digest dissolved sulfate ions in the water. Redox reactions within these bacteria reduce sulfate into sulfur-containing compounds such as sulfites and hydrogen sulfide. These ions and compounds also dissolve in water. Many Canadian homes rely on groundwater as their source of drinking water. Normally, the concentrations of hydrogen sulfide in groundwater are too low to pose a health hazard. However, low levels of hydrogen sulfide are a nuisance because they give drinking water a foul odour and taste (**Figure 1**). CAREER LINK

One way to remove hydrogen sulfide from drinking water is to oxidize it into a less offensive substance. How do you choose the appropriate oxidizing agent? Conducting trial-and-error chemical tests is one option. The hydrogen ions in acids are known to oxidize certain metals. Yet, tests show that hydrogen ions do not oxidize hydrogen sulfide. Chlorine bleach, on the other hand, does react. Chlorine bleach is a solution of sodium hypochlorite, $NaClO(aq)$. Bubbling hydrogen sulfide gas through chlorine bleach produces solid sulfur and chloride ions. Using this information and the skills you learned in Section 9.2, we can write the following half-reaction equations:

$$\text{Reduction:}\quad 2\,H^+(aq) + ClO^-(aq) + 2\,e^- \rightarrow Cl^-(aq) + H_2O(l)$$
$$\text{Oxidation:}\quad H_2S(g) \rightarrow S(s) + 2\,H^+(aq) + 2\,e^-$$

Combining these equations gives the net ionic equation for the reaction:

$$H_2S(g) + ClO^-(aq) \rightarrow Cl^-(aq) + S(s) + H_2O(l)$$

The success of hypochlorite at oxidizing hydrogen sulfide indicates that the hypochlorite ion is a stronger oxidizing agent than hydrochloric acid. Could we have predicted the results without actually mixing the reactants? Can we predict if a redox reaction will occur and what products will arise? The answer is yes. Patterns in experimental data from many different redox reactions allow us to make generalizations that can be used to make such predictions.

Relative Strengths of Oxidizing and Reducing Agents

Suppose we place samples of silver, lead, nickel, and magnesium metal in solutions of silver, lead(II), nickel(II), and magnesium ions. Some of the metal–ion combinations react immediately, but others do not react at all. All the reactions that occur are redox reactions in which the metal ion oxidizes the metal. The general pattern for these reactions is

$$\underset{\text{(oxidizing agent)}}{A^{2+}(aq)} + \underset{\text{(reducing agent)}}{M(s)} \rightarrow M^{2+}(aq) + A(s)$$

Table 1 ranks the results of these combinations according to the reactivity of each metal with each aqueous metal ion tested. This ranking may look familiar: it reflects the reactivity series of metals that you learned about in earlier Chemistry courses.

Table 1 Reactivity of Metals with Aqueous Metal Ions

Metal	Mg(s)	Ni(s)	Pb(s)	Ag(s)
Reacted with	$Ag^+(aq)$, $Ni^{2+}(aq)$, $Pb^{2+}(aq)$	$Ag^+(aq)$, $Pb^{2+}(aq)$	$Ag^+(aq)$	none
Reactivity order	most reactive metal	→	→	least reactive metal

Magnesium metal reacts with all the other metal ions. This evidence suggests that magnesium has the greatest tendency to lose electrons, which implies that its nucleus has the weakest hold on its electrons. Recall that a reducing agent is a substance that loses electrons in a redox reaction. Therefore, magnesium metal is the strongest reducing agent—the element that is most readily oxidized—in this set of metals.

Silver metal does not react with any of the metal ions, so it has the least tendency to lose electrons. Silver metal is the weakest reducing agent in this set. If we write the half-reaction equations for these metals in order from strongest to weakest reducing agents, we get the following list:

Strongest reducing agent (SRA): $Mg(s) \rightarrow Mg^{2+}(aq) + 2\,e^-$

↓ $Ni(s) \rightarrow Ni^{2+}(aq) + 2\,e^-$

$Pb(s) \rightarrow Pb^{2+}(aq) + 2\,e^-$

Weakest reducing agent: $Ag(s) \rightarrow Ag^{+}(aq) + e^-$

In Table 1, we observed the reaction from the perspective of the reducing agent (the metal). We can also view the reaction from the perspective of the oxidizing agent (the ion). In **Table 2**, we use the results from our set of reactions to rank the reactivities of the aqueous metal ions with the different metals.

Table 2 Reactivity of Aqueous Metal Ions with Different Metals

Ion in solution	**$Ag^{+}(aq)$**	**$Pb^{2+}(aq)$**	**$Ni^{2+}(aq)$**	**$Mg^{2+}(aq)$**
Reacted with	Mg(s), Ni(s), Pb(s)	Mg(s), Ni(s)	Mg(s)	none
Reactivity order	most reactive	→	→	least reactive

Recall that the oxidizing agent in a redox reaction gains electrons. According to the evidence in Table 2, silver ions had the greatest tendency to gain electrons in this set of reactions. Therefore, the silver ion is the strongest oxidizing agent in this group. Since the magnesium ion did not react with any metal in this set, it is the weakest oxidizing agent. If we now write the half-reaction equations for the metal ions in order from strongest to weakest oxidizing agent, we get

Strongest oxidizing agent (SOA): $Ag^{+}(aq) + e^- \rightarrow Ag(s)$

↓ $Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)$

$Ni^{2+}(aq) + 2\,e^- \rightarrow Ni(s)$

Weakest oxidizing agent: $Mg^{2+}(aq) + 2\,e^- \rightarrow Mg(s)$

Since our two sets of reactions are opposites of each other, we can combine them to produce **Table 3**. The double arrows in these equations indicate that these equations can be read from left to right (as reductions) or from right to left (as oxidations). By convention, tables of half-reactions are written from left to right as reductions, with the electrons on the left. The strongest oxidizing agent (SOA) is found on the top left side of Table 3 and the strongest reducing agent (SRA) appears on the bottom right side.

Table 3 Relative Strength of Oxidizing and Reducing Agents

Decreasing strength of oxidizing agents	**SOA** ↓	$Ag^{+}(aq) + e^- \rightleftharpoons Ag(s)$	↑	Decreasing strength of reducing agents
		$Pb^{2+}(aq) + 2\,e^- \rightleftharpoons Pb(s)$		
		$Ni^{2+}(aq) + 2\,e^- \rightleftharpoons Ni(s)$		
		$Mg^{2+}(aq) + 2\,e^- \rightleftharpoons Mg(s)$	**SRA**	

Based on a great deal of empirical evidence (observations) of redox reactions, scientists have organized the metals into an ordered list. You have encountered this list as the reactivity series of metals. When the reduction half-reactions are included, the arrangement is called a redox (or standard reduction potentials) table. Reactions

LEARNING **TIP**

Metals and Metal Ions

Elemental metals always lose electrons in redox reactions to form cations (positively charged ions). As a result, metals are reducing agents. Conversely, metal cations usually gain electrons to form metal atoms. Hence, metal ions are usually oxidizing agents. There are some exceptions. For example, the iron(II) ion can be both oxidized and reduced:

Oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

Reduction: $Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$

UNIT TASK BOOKMARK

How could you use information about predicting the spontaneity of a redox reaction as you work on the Unit Task on page 684?

occur spontaneously only when the oxidizing agent is combined with a reducing agent that is below it on the redox table (**Figure 2**). For example, for the half-reactions shown in Table 3, silver ions were observed to react spontaneously with magnesium metal. Notice how a line from the oxidizing agent, $Ag^+(aq)$, to the reducing agent, Mg(s), forms a downward diagonal (left to right) on the redox table in Figure 2. Any combination of an oxidizing agent with a reducing agent that is above it in Table 3 does not react spontaneously. For example, when $Mg^{2+}(aq)$ is the oxidizing agent and Ag(s) is the reducing agent, the line joining them would form an upward diagonal (left to right) on the redox table. We can therefore predict that no reaction occurs.

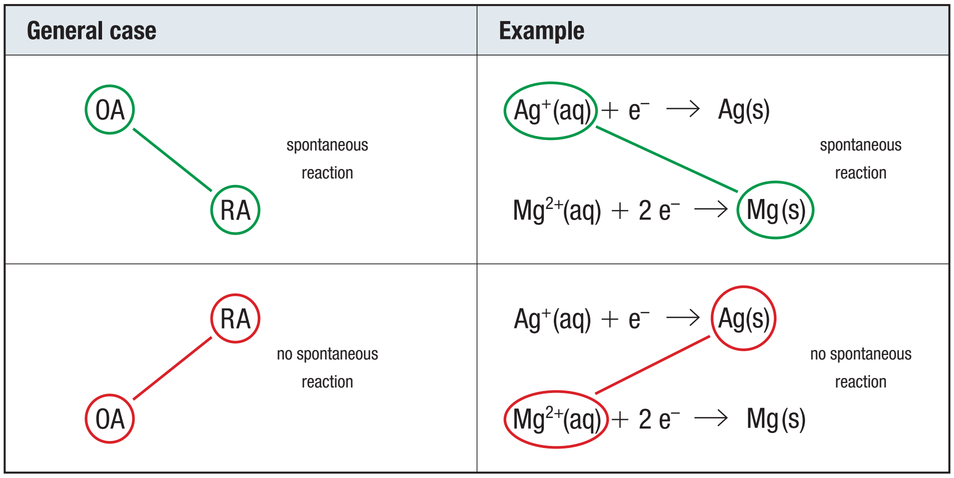


Figure 2 When an oxidizing agent (OA) is above the reducing agent (RA) on the redox table, a spontaneous reaction occurs. But when an oxidizing agent is below the reducing agent, no spontaneous reaction occurs. As an example, when $Ag^+(aq)$ is the oxidizing agent and Mg(s) is the reducing agent, a reaction occurs.

An Expanded Table of Oxidizing and Reducing Agents

redox table a table listing standard reduction potentials of common oxidizing agents and reducing agents in order from strongest to weakest; standard reduction potentials table

The collection of empirical evidence on various combinations of oxidizing and reducing agents has led to the development of an expanded redox table (Table 1 in Appendix B7). This **redox table**, also called a standard reduction potentials table, lists some of the most common oxidizing and reducing agents. In all the redox tables in this book, the oxidizing agents are listed on the left-hand side of the table with the strongest oxidizing agent at the top. Consequently, the reducing agents are on the right side with the strongest reducing agent at the bottom.

We can use a redox table to predict whether a reaction will occur spontaneously between an oxidizing agent and a reducing agent, using the method illustrated in Figure 2. However, such predictions do not guarantee that a reaction will occur. Other factors, such as the nature of the reactants, temperature, or the presence of a catalyst, also affect whether a reaction will occur. Tutorial 1 outlines how to use a redox table to predict which combinations of oxidizing and reducing agents react spontaneously.

Tutorial 1 Predicting Redox Reactions Using a Redox Table

In this tutorial, you will use Table 1 in Appendix B7 to predict redox reactions and write chemical equations for those that are likely to occur. Since many redox reactions occur in solution, hydrogen ions, hydroxide ions, and water may also participate in the reaction.

The following steps outline a general problem-solving approach:

1. List all of the entities present.
2. Use Table 1 to identify the strongest oxidizing agent in the reaction mixture. Oxidizing agents (OA) are located on the left side of the table.

3. Use Table 1 to identify the strongest reducing agent in the reaction mixture. Reducing agents are located on the right side and the strongest reducing agents are toward the bottom of the table.
4. Predict whether the reaction will occur spontaneously.
5. Write the half-reaction equations.
6. Balance the electrons in each equation, if necessary.
7. Combine the half-reaction equations to give the overall reaction equation.

Sample Problem 1 Predicting the Occurrence of a Redox Reaction

Does a redox reaction occur when copper metal is placed into a solution of nitric acid? If it does, write a balanced equation for the reaction.

Solution

Step 1. List all of the entities present.

Since nitric acid is a strong acid, it completely ionizes. You must therefore list hydrogen ions and nitrate ions instead of $HNO_3(aq)$. Therefore, the reaction mixture contains

$H^+(aq)$, $NO_3^-(aq)$, $H_2O(l)$, and $Cu(s)$.

Step 2. Use Table 1 to identify the strongest oxidizing agent in the reaction mixture.

The only equations relating to chemicals in the reaction mixture as oxidizing agents are

$NO_3^-(aq) + 2\,H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)\quad E°_r = +0.80\ V$

$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)\quad E°_r = 0.00\ V$

$2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)\quad E°_r = -0.83\ V$

Since $NO_3^-(aq)$ occurs highest on the table, $NO_3^-(aq)$ is the strongest oxidizing agent.

Step 3. Use Table 1 to identify the strongest reducing agent in the reaction mixture.

The only equations relating to chemicals in the reaction mixture as reducing agents are

$O_2(g) + 2\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)\ E°_r = +0.70\ V$

$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)\quad E°_r = +0.34\ V$

Since copper occurs lower on the table, copper is the stronger reducing agent.

Step 4. Predict whether the reaction will occur spontaneously.

The relative positions of NO_3^- and Cu do form a downward diagonal to the right on Table 1. Therefore, you can predict that the reaction will occur spontaneously.

Step 5. Write the half-reaction equations.

Remember to reverse the direction of the oxidation reaction.

Reduction: $NO_3^-(aq) + 2\,H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$

Step 6. Balance the electrons.

The number of electrons gained and lost must be equal. You can accomplish this by multiplying one or both equations by an integer. In this case, you must multiply the reduction half-reaction by 2.

Reduction: $NO_3^-(aq) + 2\,H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$

$2\,NO_3^-(aq) + 4\,H^+(aq) + 2\,e^- \rightarrow 2\,NO_2(g) + 2\,H_2O(l)$

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$

LEARNING **TIP**

Half-Reactions Involving Water

There are several half-reaction equations that include water listed in Table 1 in Appendix B7.

For example,

$SO_4^{2-}(aq) + H_2O(l) + 2\,e^- \rightarrow SO_3^{2-}(aq) + 2\,OH^-(aq)\quad E°_r = -0.93\ V$

The only equation in which only water is reduced is

$2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)\quad E°_r = -0.83\ V$

The only equation in which only water is oxidized is

$O_2(g) + 2\,H^+(aq) + 4e^- \rightarrow 2\,H_2O(l)\quad E°_r = +0.70\ V$

Investigation **9.3.1**

Spontaneity of Redox Reactions (page 625)

In this investigation, you will determine experimentally whether a redox table accurately predicts the spontaneity of a redox reaction.

Step 7. Combine the half-reaction equations to give the overall reaction equation.

Reduction: $2\ NO_3^-(aq) + 4\ H^+(aq) + 2\ e^- \rightarrow 2\ NO_2(g) + 2\ H_2O(l)$

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$

$$Cu(s) + 2\ NO_3^-(aq) + 4\ H^+(aq) + \cancel{2\ e^-} \rightarrow$$
$$Cu^{2+}(aq) + \cancel{2\ e^-} + 2\ NO_2(g) + 2\ H_2O(l)$$

The reaction is spontaneous and the balanced equation is

$$Cu(s) + 2\ NO_3^-(aq) + 4\ H^+(aq) \rightarrow Cu^{2+}(aq) + 2\ NO_2(g) + 2\ H_2O(l)$$

Practice

1. Identify the half-reactions in each of the following equations, and use them to determine if the reaction is spontaneous: T/I
   (a) $Co(s) + Cu(NO_3)_2(aq) \rightarrow Cu(s) + Co(NO_3)_2(aq)$
   (b) $Br_2(l) + 2\ KI(aq) \rightarrow I_2(s) + 2\ KBr(aq)$
   (c) $Ni(s) + Zn(NO_3)_2(aq) \rightarrow Zn(s) + Ni(NO_3)_2(aq)$
2. Determine whether copper pipe would react spontaneously with hydrochloric acid. If it would, determine the balanced equation for the reaction. T/I A
3. Does a redox reaction occur when solid calcium is placed into water? If it does, write the half-reaction equations, state whether the calcium is oxidized or reduced, and write a balanced chemical equation for the reaction. T/I
4. Does a redox reaction occur when a solution of potassium permanganate, $KMnO_4(aq)$, is poured into a solution of chromium(II) sulfate, $CrSO_4(aq)$, under acidic conditions? If it does, write the half-reaction equations and a balanced equation for the reaction. T/I

Research This

Which Bleach Is Best?

Skills: Questioning, Researching, Evaluating, Communicating, Identifying Alternatives, Defending a Decision SKILLS HANDBOOK A5

Chlorine bleach (a solution of sodium hypochlorite, NaClO(aq)) has many applications as an oxidizing agent (**Figure 3**). As you saw in the opening of this section, chlorine is used to remove hydrogen sulfide from groundwater. It also removes stains by oxidizing coloured substances to substances without colour. However, because of its reactivity with acids and bases, many workplaces have banned the use of chlorine bleach. CAREER LINK

1. Research the hazards of accidentally mixing chlorine bleach with acids or bases.
2. Research at least five uses of chlorine bleach.
3. Many workplaces now have replaced chlorine bleach with hydrogen peroxide as their primary bleach. Research the use of hydrogen peroxide as a replacement for chlorine bleach.

A. Create a table to compare the pros and cons of chlorine bleach and hydrogen peroxide bleach. C

B. What else should also be considered, besides safety, when approving a product for use in the workplace? K/U A

C. For which uses is chlorine bleach the better choice and for which is hydrogen peroxide better? Give reasons. K/U A

Figure 3 Containers of chlorine bleach that are sold to consumers have HHPS on their labels, which warn of the danger of mixing the contents with other chemicals.

WEB LINK

9.3 Review

Summary

- A relative ranking of the strength of oxidizing and reducing agents has been developed from empirical evidence.
- Redox tables list the strongest oxidizing agent in the top left corner of the table and the strongest reducing agent in the bottom right corner of the table.
- Redox tables can be used to predict whether a redox reaction occurs spontaneously.

Questions

1. Rank the strength of the following as oxidizing agents, going from strongest to weakest:
   $Hg^{2+}(aq)$, $Au^{3+}(aq)$, $Cu^{2+}(aq)$, $Sn^{2+}(aq)$ K/U
2. Identify a substance that would react spontaneously with chromium ions, $Cr^{2+}(aq)$, to form solid chromium metal. T/I
3. Identify which of the following equations represent(s) spontaneous reactions: T/I
   (a) $Cu(s) + Br_2(l) \rightarrow Cu^{2+}(aq) + 2\ Br^-(aq)$
   (b) $2\ Al(s) + 3\ Pb^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Pb(s)$
   (c) $Na^+(aq) + Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + Na(s)$
4. A student places a piece of solid iron into a solution containing copper(II) ions. T/I
   (a) Write the chemical equation for the reaction that produces iron(II) ions and solid copper.
   (b) Predict whether the reaction is spontaneous.
5. A geology lab technician mixes a solution of potassium permanganate with a solution of iron(II) sulfate, under acidic conditions. T/I
   (a) List all the possible oxidizing agents in the mixture and identify which is the strongest.
   (b) List all the possible reducing agents in the mixture and identify which is the strongest.
6. A chemist's pure gold ring accidentally falls into a solution of nitric acid, $HNO_3(aq)$. T/I
   (a) Write the two half-reaction equations for the reaction of nitric acid and gold forming a solution of $Au^{3+}(aq)$.
   (b) Use the data in a redox table to predict whether nitric acid will damage the ring.
7. Use Table 1 in Appendix B7 to answer the following questions: T/I
   (a) Predict which combinations of the following metals and metal ions react spontaneously:
   Metals: $Cu(s)$, $Au(s)$, $Zn(s)$, $Co(s)$
   Metal ions: $Cu^+(aq)$, $Au^{3+}(aq)$, $Zn^{2+}(aq)$, $Co^{2+}(aq)$
   (b) Identify the strongest reducing agent and oxidizing agent in (a). Justify your answer.
8. Based on an investigation of four metals and solutions of four metal ions, a student summarized the observations in **Table 4**. T/I

Table 4 Observations

Ion solution	$Ba^{2+}(aq)$	$Fe^{2+}(aq)$	$Pb^{2+}(aq)$	$Cu^{2+}(aq)$
Reacts with the following metals:	none	Ba(s)	Ba(s), Fe(s)	Ba(s), Fe(s), Pb(s)

   (a) List the metal ions from strongest to weakest oxidizing agent.
   (b) Write the balanced equation for the redox reaction of copper(II) ions with solid lead.
   (c) From these observations, what can you determine about the strongest reducing agent?
   (d) Gold is a weaker reducing agent than copper. Predict how gold metal would react with each of the ion solutions in Table 4.
9. **Figure 4** shows what happens when copper is added to different concentrations of hydrochloric acid and nitric acid. T/I A

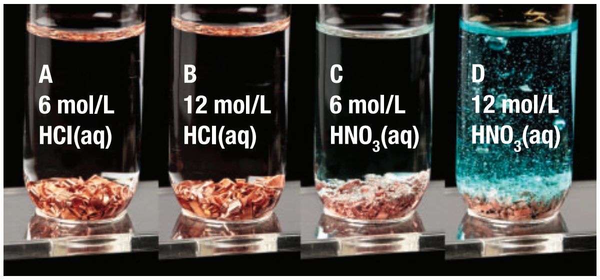


Figure 4 Identical pieces of copper metal are placed in hydrochloric acid and nitric acid. A reaction is only observed in test tube D. After a few minutes the solution in this test tube turns blue, the characteristic colour of the copper(II) ion.

   (a) Use the Table 1 in Appendix B7 to justify the difference between the reactivity of copper in hydrochloric acid and its reactivity in nitric acid.
   (b) Suggest an explanation for the difference in reactivity in the two nitric acid solutions.

CHAPTER 9 Investigations

Investigation 9.1.1 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Single Displacement Reactions

In this investigation, you will study and observe some single displacement reactions that are redox reactions. Remember that in a single displacement reaction, one element is replaced by another in a compound. You will test several combinations of metals and metal ions. From each combination, you will collect evidence that indicates whether or not a reaction occurred. You will use this evidence to rank the metal ions according to their strength as an oxidizing agent. The metal ion that reacts with the most metals will be the strongest oxidizing agent.

In this investigation, staples are used as a source of iron. Staples are made of steel, which is an alloy of mostly iron and carbon. Iron can be oxidized to form two ions: iron(II) and iron(III). For this investigation, assume that only iron(II) forms.

Purpose

To rank the strength of four oxidizing agents ($Cu^{2+}(aq)$, $Fe^{3+}(aq)$, $Zn^{2+}(aq)$, and $Mg^{2+}(aq)$) by observing their behaviour in a single displacement reaction with a metal

Equipment and Materials

- chemical safety goggles
- lab apron
- 24-well plate
- sandpaper
- dropper bottles containing solutions of
  - copper(II) nitrate, $Cu(NO_3)_2(aq)$ (0.1 mol/L)
  - iron(III) nitrate, $Fe(NO_3)_3(aq)$ (0.1 mol/L)
  - zinc nitrate, $Zn(NO_3)_2(aq)$ (0.1 mol/L)
  - magnesium nitrate, $Mg(NO_3)_2(aq)$ (0.1 mol/L)
- 2 copper strips, Cu(s)
- 2 staples, Fe(s)
- 2 zinc strips or pieces of zinc shot, Zn(s)
- 2 short pieces of magnesium ribbon, Mg(s)

All of the solutions are irritants. Copper(II) nitrate is also toxic. Avoid skin and eye contact. If you spill these chemicals on your skin, wash the affected area with plenty of cool water and inform your teacher.

Procedure

SKILLS HANDBOOK A1, A2.3

1. Plan a procedure as a series of numbered steps. Make sure that you clearly identify the quantities and equipment that you will use.
2. Ask your teacher to approve your procedure before continuing.
3. Perform your procedure, recording your observations in an appropriate table.

Analyze and Evaluate

(a) Write a net ionic equation for each reaction observed in this investigation. T/I

(b) Rank the metal ions in order from strongest to weakest oxidizing agent. T/I

(c) How might your results be affected if you did not clean the metal with sandpaper prior to use? T/I

(d) A student placed the four metals in a solution of lead(II) nitrate and found that only zinc and magnesium reacted. Predict where $Pb^{2+}(aq)$ would fit in your ranking in (b). T/I

(e) Evaluate the design of your investigation. Are there any flaws in your procedure? What effect would this flaw have on your results? T/I

Apply and Extend

(f) A student performed a similar experiment using halogens and halide ions instead of metals and metal ions. **Table 1** shows the observations.

Table 1 Observations of Halogen Reactivity in Halide Solutions

	Halogen		
Halide ion	**$Br_2(aq)$**	**$Cl_2(aq)$**	**$I_2(aq)$**
$I^-(aq)$	yellow-brown precipitate	yellow-brown precipitate	no reaction occurs
$Cl^-(aq)$	no reaction occurs	no reaction occurs	no reaction occurs
$Br^-(aq)$	no reaction occurs	yellow-brown precipitate	no reaction occurs

Create a table similar to the one you created with your observed results in order from strongest to weakest oxidizing agent. T/I C

Investigation 9.3.1 CONTROLLED EXPERIMENT

Spontaneity of Redox Reactions

In this investigation, you will use a redox table to predict whether a number of redox reactions will occur spontaneously. You will then test your predictions.

Testable Question

Can a redox table be used to successfully predict the spontaneity of redox reactions?

Prediction

Predict the combinations of reactants that will spontaneously react. Then, write the balanced chemical equations for the reactions.

Variables

Identify all variables that will be measured and/or controlled in the experiment, specifying the independent and dependent variables.

Experimental Design

Conduct an investigation to determine the spontaneity of five redox reactions. In each case, you will mix an oxidizing agent and a reducing agent, and predict whether the reaction will proceed spontaneously. Then, you will perform the reaction to test your prediction.

Equipment and Materials

- chemical safety goggles
- lab apron
- 5 test tubes
- test-tube rack
- dropper bottles containing solutions of
  - 3 % hydrogen peroxide, $H_2O_2(aq)$
  - iron(II) sulfate, $FeSO_4(aq)$ (0.1 mol/L)
  - distilled water
  - copper(II) sulfate, $CuSO_4(aq)$ (0.1 mol/L)
  - potassium iodide, KI(aq) (0.1 mol/L)
  - acidified potassium permanganate, $KMnO_4(aq)$ (0.1 mol/L)
- calcium pellets, Ca(s)
- aluminum foil, Al(s)
- copper strip, Cu(s)

Copper(II) sulfate is both toxic and an irritant. Iron(II) sulfate and potassium permanganate are irritants. Avoid skin and eye contact. If you spill these chemicals on your skin, wash the affected area with plenty of cool water and inform your teacher.

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Procedure

SKILLS HANDBOOK A1, A2.2

1. Put on your safety goggles and lab apron.
2. Fill each test tube to a depth of 1 cm (~20 drops) with Reactant A for each reaction listed in **Table 1**.

Table 1 Combinations of Reactants

Reaction	Reactant A	Reactant B
1	$H_2O_2(aq)$	KI(aq)
2	$FeSO_4(aq)$	$KMnO_4(aq)$, $H^+(aq)$
3	$H_2O(l)$	Ca(s)
4	$CuSO_4(aq)$	Al(s)
5	$H_2O_2(aq)$	$KMnO_4(aq)$, $H^+(aq)$

3. Add Reactant B dropwise (or add about 0.25 g of the solid reactants) until you observe evidence of a reaction or until 10 drops are added. Record your observations.

Analyze and Evaluate

(a) Identify the manipulated variables, the responding variables, and the controlled variables. T/I

(b) Answer the testable question. K/U

(c) Identify the entities that acted as oxidizing agents and those that acted as reducing agents. T/I

(d) Identify any entities that acted as both oxidizing and reducing agents. T/I

(e) Did your observations support your predictions in each case? Attempt to account for any observations that differed from your predictions. T/I

(f) In your opinion, is a redox table a reliable tool to predict the spontaneity of a reaction? Explain. T/I

Apply and Extend

(g) Design a procedure to test the identity of the products in each of the reactions you have performed. Include safety precautions. With your teacher's approval, conduct the tests. Compare your observations to the expected results. T/I

CHAPTER 9 SUMMARY

Summary Questions

1. Create a concept map for this chapter based on the Key Concepts on page 598. For each main concept, create three or four sub-concepts that provide further information, relevant examples, explanatory diagrams, or general equations.
2. Look back at the Starting Points questions on page 598. Answer these questions using what you have learned in this chapter. Compare your latest answers with those that you wrote at the beginning of the chapter. Note how your answers have changed.
3. Some students find the terms “oxidation,” “reduction,” “oxidizing agent,” and “reducing agent” confusing. Develop a poem or mnemonic to help remember the meaning of each term.
4. Devise a game involving cards representing a wide variety of elements and compounds listed in a redox table. A player picks two cards, refers to the redox table to determine whether or not a reaction will occur, and moves a marker around a game board accordingly.

Vocabulary

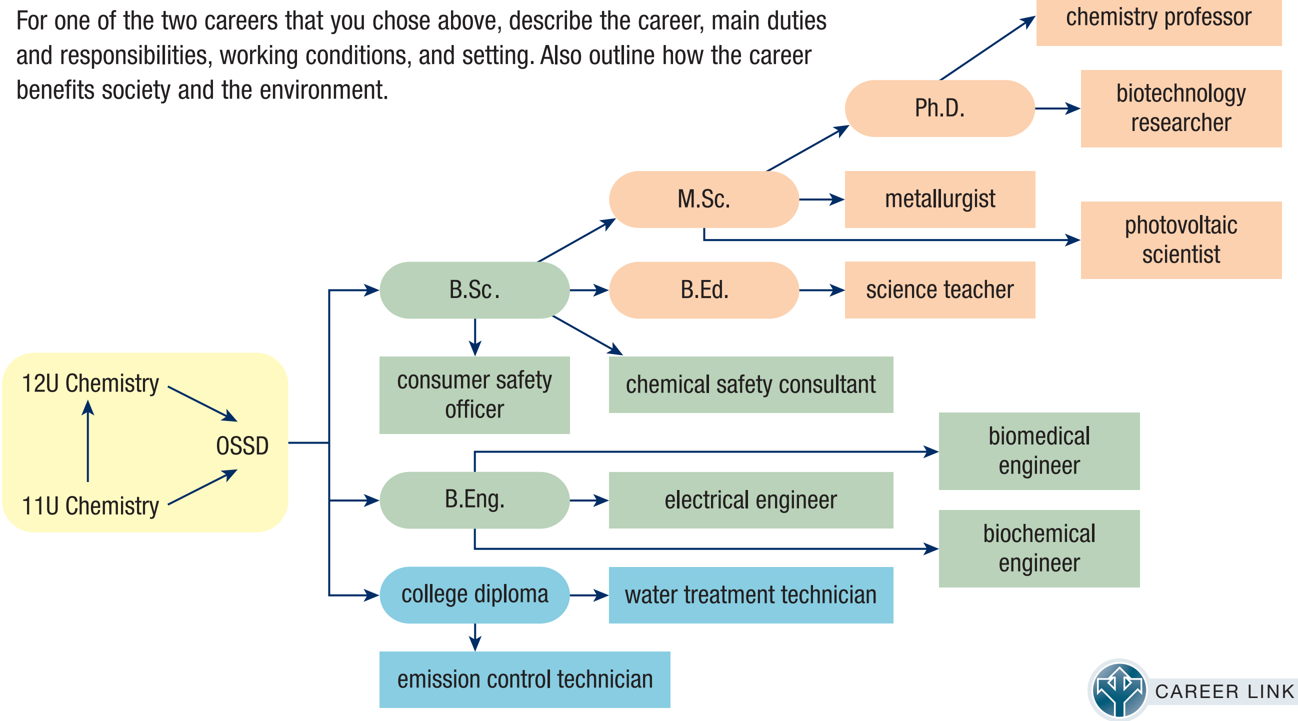
oxidation (p. 600)
reduction (p. 600)
oxidation–reduction (redox) reaction (p. 600)
half-reaction equation (p. 600)
oxidation number (p. 602)
oxidizing agent (p. 605)
reducing agent (p. 605)
redox table (p. 620)

CAREER PATHWAYS

SKILLS HANDBOOK A7

Grade 12 Chemistry can lead to a wide range of careers. Some require a college diploma or a B.Sc. degree. Others require specialized or postgraduate degrees. This graphic organizer shows a few pathways to careers mentioned in this chapter.

1. Select two careers related to Oxidation–Reduction Reactions that you find interesting. Research the educational pathways that you would need to follow to pursue these careers. What is involved in the required educational programs? Prepare a brief report of your findings.
2. For one of the two careers that you chose above, describe the career, main duties and responsibilities, working conditions, and setting. Also outline how the career benefits society and the environment.



CAREER LINK

CHAPTER 9 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. Which of the following statements is true for a redox reaction? (9.1) K/U
   (a) A substance undergoing oxidation gains electrons and a substance undergoing reduction loses electrons.
   (b) A substance undergoing reduction gains electrons and a substance undergoing oxidation loses electrons.
   (c) The oxidizing agent is oxidized.
   (d) The substances always change their physical state.
2. What is the oxidation number of C in CH_2O? (9.1) K/U
   (a) -2
   (b) -1
   (c) 0
   (d) 2
3. How many electrons are transferred in the reaction represented by the following equation? (9.1) K/U
   $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$
   (a) 0
   (b) 2
   (c) 4
   (d) 8
4. Which of the following statements is NOT true of an oxidizing agent? (9.1) K/U
   (a) It becomes reduced.
   (b) It causes the reduction of another entity.
   (c) Its oxidation number decreases.
   (d) It gains electrons.
5. Which of the following is a balanced chemical equation correctly representing the reaction between copper(II) ions and hydrogen gas? (9.2) K/U
   (a) $Cu(s) + H_2(g) \rightarrow Cu^{2+}(aq) + 2\ H^+(aq)$
   (b) $Cu(s) + 2\ H^+(aq) \rightarrow Cu^{2+}(aq) + 2\ H_2(g)$
   (c) $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2\ H^+(aq)$
   (d) $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + H^+(aq)$
6. Which of the following metals is the strongest reducing agent? (9.3) K/U
   (a) Cr(s)
   (b) Fe(s)
   (c) Au(s)
   (d) Ni(s)
7. Which of the following lists reducing agents from strongest to weakest? (9.3) K/U
   (a) Al(s), Pb(s), Sn(s), Cu(s)
   (b) Al(s), Sn(s), Pb(s), Cu(s)
   (c) Cu(s), Al(s), Pb(s), Sn(s)
   (d) Cu(s), Al(s), Sn(s), Pb(s)
8. Which of the following redox reactions is NOT spontaneous? (9.3) K/U
   (a) $Ni^{2+}(aq) + Ca(s) \rightarrow Ca^{2+}(aq) + Ni(s)$
   (b) $Pb^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Pb(s)$
   (c) $Ni^{2+}(aq) + Pb(s) \rightarrow Pb^{2+}(aq) + Ni(s)$
   (d) $Pb^{2+}(aq) + Sn(s) \rightarrow Sn^{2+}(aq) + Pb(s)$

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

9. In the perchlorate ion, $ClO_4^-(aq)$, the chlorine atom has an oxidation number of +5. (9.1) K/U
10. In the molecule CH_3CH_2OH, carbon has an oxidation number of -2. (9.1) K/U
11. In the combustion of methane, $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$, oxygen is oxidized. (9.1) K/U
12. In the oxidation of iron, $4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$, the metal is the reducing agent. (9.1) K/U
13. A chemical equation is said to be balanced if the number of electrons lost by oxidation is equal to the number of electrons gained by reduction. (9.2) K/U
14. Using the oxidation numbers method to balance a redox reaction, you must assign oxidation numbers to the atoms in the reaction. (9.2) K/U
15. The reaction between nickel metal and magnesium ions is spontaneous. (9.3) K/U
16. Silver, Ag(s), is a stronger reducing agent than nickel, Ni(s). (9.3) K/U
17. The following is a list of oxidizing agents from strongest to weakest: $Ag^+(aq)$, $Mg^{2+}(aq)$, $Cu^{2+}(aq)$, and $Pb^{2+}(aq)$. (9.3) K/U

Go to Nelson Science for an online self-quiz.
WEB LINK

CHAPTER 9 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Which of the following equations represents an oxidation half-reaction? (9.1) K/U
   (a) $Na(s) \rightarrow Na^+(aq) + e^-$
   (b) $e^- + Ag^+(aq) \rightarrow Ag(s)$
   (c) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
   (d) $Cu(s) + 2\ Ag^+(aq) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$
2. How many electrons are transferred in the reaction of nickel with copper(II) chloride?
   $Ni(s) + CuCl_2(aq) \rightarrow Cu(s) + NiCl_2(aq)$ (9.1) K/U
   (a) 0
   (b) 1
   (c) 2
   (d) 3
3. What is the oxidation number of carbon in $CH_3OH(l)$? (9.1) K/U
   (a) −2
   (b) −1
   (c) 1
   (d) 2
4. Which of the following chemical equations correctly represents the balanced chemical reaction between lead(II) oxide and ammonia? (9.2) K/U
   (a) $3\ PbO(s) + 2\ NH_3(g) \rightarrow N_2(g) + H_2O(l) + Pb(s)$
   (b) $PbO(s) + NH_3(g) \rightarrow N_2(g) + H_2O(l) + Pb(s)$
   (c) $3\ PbO(s) + 2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2O(l) + 3\ Pb(s)$
   (d) $PbO(s) + 2\ NH_3(g) \rightarrow N_2(g) + H_2O(l) + 3\ Pb(s)$
5. Which of the following chemical equations correctly represents the redox reaction of permanganate ions, $MnO_4^-(aq)$, with iodide, $I^-(aq)$, under acidic conditions? (9.2) K/U
   (a) $2\ I^-(aq) + 2\ MnO_4^-(aq) \rightarrow I_2(s) + 8\ H_2O(l) + 2\ Mn^{2+}(aq)$
   (b) $10\ I^-(aq) + 16\ H^+(aq) + 2\ MnO_4^-(aq) \rightarrow 5\ I_2(s) + 8\ H_2O(l) + 2\ Mn^{2+}(aq)$
   (c) $I^-(aq) + MnO_4^-(aq) \rightarrow I_2(s) + 2\ Mn^{2+}(aq)$
   (d) $2\ I^-(aq) + 2\ MnO_4^-(aq) \rightarrow I_2(s) + 8\ O_2(g) + 2\ Mn^{2+}(aq)$
6. Which is the correct balanced half-reaction equation for the reduction of gold from its ion, $Au^{3+}(aq)$, to its solid metallic form? (9.2) K/U
   (a) $Au^{3+}(aq) \rightarrow Au(s)$
   (b) $Au^{3+}(aq) \rightarrow 3\ e^- + Au(s)$
   (c) $Au^{3+}(aq) + 2\ e^- \rightarrow Au^+(s)$
   (d) $Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$
7. Which of the following elements is the strongest oxidizing agent? (9.3) K/U
   (a) $F_2(g)$
   (b) $Cl_2(g)$
   (c) $Br_2(l)$
   (d) $I_2(s)$
8. Which of the following equations represents the oxidation reaction of the strongest reducing agent? (9.3) K/U
   (a) $Au(s) \rightarrow Au^{3+}(aq) + 3\ e^-$
   (b) $Ca(s) \rightarrow Ca^{2+}(aq) + 2\ e^-$
   (c) $Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$
   (d) $Ca^{2+}(aq) + 2\ e^- \rightarrow Ca(s)$
9. Which of the following equations represents a spontaneous redox reaction? (9.3) K/U
   (a) $Ni^{2+}(aq) + Cd(s) \rightarrow Cd^{2+}(aq) + Ni(s)$
   (b) $Ni^{2+}(aq) + Sn(s) \rightarrow Sn^{2+}(aq) + Ni(s)$
   (c) $Cd^{2+}(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + Cd(s)$
   (d) $Cd^{2+}(aq) + Sn(s) \rightarrow Sn^{2+}(aq) + Cd(s)$

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

10. In the carbonate ion, $CO_3^{2-}(aq)$, carbon has an oxidation number of +2. (9.1) K/U
11. In the reaction of iron with oxygen to produce solid iron(III) oxide, iron is oxidized. (9.1) K/U
12. In the combustion of methane, oxygen is the reducing agent. (9.1) K/U
13. In all redox reactions, the number of electrons lost by oxidation is equal to the number of electrons gained by reduction. (9.2) K/U
14. The following net ionic equation is balanced: (9.2) K/U
    $Cr_2O_7^{2-}(g) + 14\ H^+(aq) + 3\ Cu(s) \rightarrow 3\ Cu^{2+}(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O(l)$
15. Redox reactions can be balanced using the oxidation numbers method or the net ionic equation method. (9.2) K/U
16. The reaction of $Cu^{2+}(aq)$ and $I^-(aq)$ is spontaneous. (9.3) K/U
17. Zinc sulfate, $ZnSO_4(aq)$, is a stronger oxidizing agent than iron(II) chloride, $FeCl_2(aq)$. (9.3) K/U
18. In a redox table, the strongest reducing agent is located on the bottom right side of the table. (9.3) K/U

Match each term on the left with the most appropriate description on the right.

19. (a) oxidation
    (b) reduction
    (c) metal ion
    (d) oxidation number
    (e) oxidizing agent
    (f) reducing agent
    (g) redox reaction

(i) a substance that causes oxidation
(ii) what happens to metal ions when they become elements
(iii) the part of a reaction in which the oxidation number increases
(iv) a reaction in which electrons are exchanged between entities
(v) usually an oxidizing agent
(vi) a substance that is oxidized
(vii) a way of keeping track of electrons (9.1) K/U

Write a short answer to each question.

20. Write the oxidation and reduction half-reaction equations for the reactions represented by each of the following equations: (9.1) T/I
    (a) $Cu^{+}(aq) + Cr^{2+}(aq) \rightarrow Cu(s) + Cr^{3+}(aq)$
    (b) $Fe(s) + Au^{3+}(aq) \rightarrow Au(s) + Fe^{3+}(aq)$
    (c) $Br_2(l) + 2\,NaI(aq) \rightarrow I_2(s) + 2\,NaBr(aq)$

21. Determine the oxidation number of the specified element in each of the following compounds: (9.1) T/I
    (a) Br in $AgBr(s)$
    (b) O in $NaOH(s)$
    (c) N in $HCN(g)$
    (d) C in $H_2C_2O_4(aq)$
    (e) S in $H_2SO_3(aq)$

22. Identify the oxidation numbers of all elements in each of the following molecules: (9.1) T/I
    (a) NCl_3
    (b) SeO_2
    (c) SiS_2
    (d) SF_6
    (e) SCl_2

23. Identify the oxidation numbers of all elements in each of the following ions: (9.1) T/I
    (a) OH^-
    (b) ClO_3^-
    (c) ClO_2^-
    (d) SO_4^{2-}
    (e) $S_2O_8^{2-}$
    (f) $C_2H_3O_2^-$

24. Determine which of the following equations represent redox reactions: (9.1) K/U
    (a) $Cu(s) + 2\,Ag^{+}(aq) \rightarrow 2\,Ag(s) + Cu^{2+}(aq)$
    (b) $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$
    (c) $Ca^{2+}(aq) + 2\,NO_3^-(aq) \rightarrow Ca(NO_3)_2(s)$
    (d) $Ca(s) + Fe^{2+}(aq) \rightarrow Fe(s) + Ca^{2+}(aq)$
    (e) sodium metal + chlorine gas → sodium chloride solution
    (f) sodium sulfide solution + copper(II) nitrate solution → solid copper(II) sulfide + sodium nitrate solution

25. Gold(III) ions react with water according to the following unbalanced equation:
    $H_2O(l) + Au^{3+}(aq) \rightarrow O_2(g) + Au(s)$ (9.2) T/I
    (a) Write the half-reaction equations for this reaction.
    (b) Write the balanced net ionic equation.

26. For the following redox reactions, write the two half-reaction equations: (9.2) T/I
    (a) $Cu^{2+}(aq) + Pb(s) \rightarrow Pb^{2+}(aq) + Cu(s)$
    (b) $2\,HNO_2(aq) + 4\,H^{+}(aq) + 2\,Fe(s) \rightarrow 2\,Fe^{2+}(aq) + N_2O(g) + 3\,H_2O(l)$
    (c) $O_2(g) + 2\,H_2O(l) + 2\,Co(s) \rightarrow 2\,Co^{2+}(aq) + 4\,OH^-(aq)$
    (d) $Br_2(l) + Ag(s) \rightarrow 2\,Br^-(aq) + Ag^{+}(aq)$
    (e) $Fe^{2+}(aq) + Al(s) \rightarrow Al^{3+}(aq) + Fe(s)$
    (f) $H_2S(aq) + Na^{+}(aq) \rightarrow S(s) + Na(s)$
    (g) $MnO_4^-(aq) + Zn(s) + 2\,H_2O(l) \rightarrow MnO_2(s) + Zn^{2+}(aq) + 4\,OH^-(aq)$

27. Consider the high-temperature reaction between nickel metal and chlorine gas, to form gaseous nickel(II) chloride. (9.2) T/I
    (a) Using oxidation numbers, determine how many electrons each nickel atom will lose.
    (b) How many electrons will each chlorine atom gain?
    (c) Write the balanced chemical equation for this reaction.

28. Calcium metal reacts spontaneously with water. Write the half-reactions plus the net ionic equation for this reaction. (9.2) T/I

29. Place the following entities in order of increasing strength as oxidizing agents (at SATP): (9.3) K/U T/I
    $Cd^{2+}(aq), IO_3^-(aq), K^{+}(aq), H_2O(l), AuCl_4^-(aq), I_2(s)$

30. Place the following entities in order of increasing strength as reducing agents (at SATP): (9.3) K/U T/I
    $Cu^{+}(aq), F^-(aq), H_2O(l), I_2(s), K(s)$

31. (a) Which of the following pairs of substances, when combined, would result in a spontaneous chemical reaction?
    (i) $K^+(aq)$ and $Na(s)$
    (ii) $Cr^{2+}(aq)$ and $K(s)$
    (iii) $Pb^{2+}(aq)$ and $Fe(s)$
    (iv) $Ag(s)$ and $Sn^{2+}(aq)$
(b) For each reaction above that you predict will occur, write a balanced chemical equation. (9.3) T/I

32. From the redox tables, identify all substances that would be able to react spontaneously with a solution of aluminum ions. (9.3) K/U

Understanding

33. Describe, in three or four sentences, the features of a redox reaction. Include the terms "oxidation," "reduction," "oxidation number," "oxidizing agent," and "reducing agent." (9.1) K/U

34. Is a hydrocarbon combustion reaction a redox reaction? Support your answer using an example, a balanced chemical equation, and reference to oxidation numbers. (9.1) T/I

35. Rank the following compounds from lowest to highest oxidation number of the nitrogen atom: (9.1) T/I

HNO_3, NH_4Cl, N_2O, NO_2, and $NaNO_2$

36. (a) Use a graphic organizer to compare the roles of reducing agents and oxidizing agents in a chemical reaction.
(b) Would you predict that oxygen gas is a reducing agent or an oxidizing agent? Explain. (9.1) K/U T/I C

37. Explain why some reactions involving ions are redox reactions and others are not. Clearly outline how you can tell whether the reaction is a redox reaction. (9.2) K/U T/I

38. When iron metal is placed in silver solution, the following reaction occurs:

$Fe(s) + Ag^+(aq) \rightarrow Fe^{2+}(aq) + Ag(s)$

Is the above equation balanced? Explain your reasoning. (9.2) T/I

39. Is the following chemical equation balanced? Explain. If it is not balanced, write the balanced equation. (9.2) T/I

$AgNO_3(aq) + Cu(s) \rightarrow Ag(s) + Cu(NO_3)_2(aq)$

40. Ammonia gas undergoes a combustion reaction with oxygen to produce gaseous nitrogen dioxide and water vapour. (9.2) T/I
(a) Write an unbalanced (skeleton) equation for this reaction.
(b) Determine the oxidation numbers of each element in the reaction, as reactant and product.
(c) Write the oxidation and reduction half-reactions.
(d) Write the balanced chemical equation for the reaction.

41. A student in your class missed the lesson on how to determine oxidation numbers. Using either a flow chart or a series of steps, outline the procedure for determining oxidation numbers. Use sodium sulfate as the example. (9.1) T/I C

42. For each of the following reactions, write the oxidation half-reaction equation, the reduction half-reaction equation, and the balanced net ionic equation: (9.2) T/I
(a) $Cu^{2+}(aq) + Pb(s) \rightarrow Pb^{2+}(s) + Cu(s)$
(b) $HNO_2(aq) + H^+(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + N_2O(g) + H_2O(l)$
(c) $O_2(g) + H_2O(l) + Co(s) \rightarrow Co^{2+}(aq) + OH^-(aq)$

43. (a) Create a flow chart to illustrate the steps in the oxidation numbers method of balancing redox reaction equations.
(b) Apply your steps to balancing the following equation:
$NO_3^-(aq) + AsO_3^{3-}(aq) \rightarrow NO(g) + AsO_4^{3-}(aq)$
(9.2) T/I C

44. Balance the reactions represented by the following equations: (9.2) T/I
(a) $Ni^{2+}(aq) + Al(s) \rightarrow Al^{3+}(aq) + Ni(s)$
(b) $MnO_4^-(aq) + Ni(s) \rightarrow MnO_2(s) + Ni^{2+}(aq)$ (in basic solution)
(c) $SO_4^{2-}(aq) + Sn^{2+}(aq) \rightarrow SO_3^{2-}(aq) + Sn^{4+}(aq)$ (in acidic solution)
(d) $Br_2(l) + Ag(s) \rightarrow 2\ Br^-(aq) + Ag^+(aq)$
(e) $Fe^{2+}(aq) + Al(s) \rightarrow Al^{3+}(aq) + Fe(s)$
(f) $H_2S(aq) + Na^+(aq) \rightarrow S(s) + Na(s)$ (in acidic solution)
(g) $MnO_4^-(aq) + Zn(s) \rightarrow MnO_2(s) + Zn^{2+}(aq)$ (in basic solution)

45. Balance the following equations using either the oxidation numbers method or the half-reactions method: (9.2) T/I
(a) $MnO_4^-(aq) + C_2O_4^{2-}(aq) \rightarrow Mn^{2+}(aq) + CO_2(g) + H_2O(l)$ (in acidic solution)
(b) $MnO_4^-(aq) + CN^-(aq) \rightarrow MnO_2(s) + OCN^-(aq)$ (in basic solution)
(c) $Pb(s) + PbO_2(s) \rightarrow 2\ Pb^{2+}(aq)$ (in acidic solution)

46. Can the following reaction occur spontaneously? Explain.

$2\ CuNO_3(aq) + Ni(s) \rightarrow 2\ Cu(s) + Ni(NO_3)_2(aq)$
(9.3) K/U

47. Rank the following metals from strongest to weakest reducing agent and explain your reasoning: (9.3) T/I

$Al(s)$, $Pb(s)$, $Cu(s)$, $Ca(s)$, $Cd(s)$, $Cr(s)$

48. If you were testing several metal ions, how would you be able to identify which ion was the strongest oxidizing agent? (9.3) T/I

49. Using a graphic organizer or in point form, summarize the similarities and differences among a strong reducing agent, a weak reducing agent, a strong oxidizing agent, and a weak oxidizing agent. (9.3) T/I C

Analysis and Application

50. For each reaction described by the equations below, determine the oxidation number of each atom in the reactants and products, the number of electrons transferred, and the oxidizing and reducing agents: (9.1) T/I
    (a) $4\,Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$
    (b) $NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(l)$
    (c) $Fe_2O_3(s) + 3\,CO(g) \rightarrow 2\,Fe(s) + 2\,CO_2(g)$
    (d) $Cu(s) + 4\,HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\,H_2O(l) + 2\,NO_2(g)$

51. The atmosphere of Earth contains many oxidizing agents, whereas the atmospheres of many other planets, such as Saturn, are described as "reducing environments." (9.1) T/I A
    (a) Suggest which gases account for the oxidizing or reducing atmospheres of Earth and Saturn.
    (b) Predict how the carbon atom in a compound such as methanol, CH_3OH, would behave in each type of environment.

52. Is the process of photosynthesis a redox reaction? Justify your answer. (9.1) K/U A

53. Indicate the substance that is oxidized and the substance that is reduced in each of the reactions represented by the following unbalanced equations. Include the number of electrons transferred for each half-reaction. (9.1) T/I C
    (a) $AgI(s) + Cr^{2+}(aq) \rightarrow Ag(s) + I^-(aq) + Cr^{3+}(aq)$
    (b) $Ni^{2+}(aq) + Al(s) \rightarrow Al^{3+}(aq) + Ni(s)$
    (c) $MnO_4^-(aq) + Ni(s) \rightarrow MnO_2(s) + Ni^{2+}(aq)$
    (d) $SO_4^{2-}(aq) + Sn^{2+}(aq) \rightarrow SO_3^{2-}(aq) + Sn^{4+}(aq)$

54. A piece of calcium metal is accidentally dropped into a sink full of water in a laboratory (9.3) T/I C A
    (a) Write the half-reactions for the potential reaction.
    (b) Predict whether a reaction will take place. If you think a reaction will occur, write the net ionic equation for the reaction.
    (c) What would you expect to observe in this situation?
    (d) What test could you perform to confirm your predictions?

55. The following chemical equations represent a series of redox reactions: (9.2) T/I
    (i) $AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + Ag(s)$
    (ii) $HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$
    (iii) $Fe_3O_4(s) + CO(g) \rightarrow CO_2(g) + Fe(s)$
    (iv) $HNO_3(aq) + Cu(s) \rightarrow NO(g) + Cu(NO_3)_2(aq) + H_2O(l)$
    (a) For each equation, suggest a laboratory procedure to conduct the reaction.
    (b) Write a balanced chemical equation for each reaction.

56. Chlorine bleach, which is a solution of sodium hypochlorite, $NaOCl(aq)$, and solutions of ammonia, $NH_3(aq)$, may both be used as household cleaners. You should never mix cleaners containing these compounds, since they may react and release dangerous gases. In chlorine bleach, the hypochlorite ion reacts with water to form an equilibrium system involving hypochlorous acid, $HOCl(aq)$:

    $OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$

    Hypochlorous acid reacts with ammonia to produce gaseous or volatile chloroamine compounds such as dichloramine, $NHCl_2$, and nitrogen trichloride (trichloramine), NCl_3. Chloroamines are dangerous because they are strong respiratory irritants. The particular chemical reaction that occurs depends on the pH of the reaction mixture. The following unbalanced equations represent two possible reactions that can occur:

    $HOCl(aq) + NH_3(aq) \rightarrow NHCl_2(g) + H_2O(l)$

    $HOCl(aq) + NH_3(aq) \rightarrow NCl_3(l) + H_2O(l)$

    (9.1, 9.2) K/U T/I
    (a) For each chemical equation, determine the oxidation number of each of the atoms in the reaction, and then balance the equation.
    (b) Predict which of these reactions would occur if equal volumes of household bleach and ammonia solution (of equal concentrations) were mixed.

57. A research technician prepared several solutions to use in chemical analysis, as outlined below. Each of the solutions was stored in a different type of container.
    (i) iron(III) sulfate in a copper flask
    (ii) copper(II) chloride in an iron drum
    (iii) tin(II) chloride in a copper flask
    (iv) silver nitrate in a copper flask (9.3) T/I A
    (a) Predict whether the technician will notice any changes a day later. Explain your reasoning.
    (b) For each solution that you predict will react, what evidence of change do you think the technician will observe?
    (c) Write a balanced equation for each predicted reaction.

58. A chemistry teacher found three unknown pieces of metal in the school cupboard. To identify the metals, the teacher tested each of them in solutions of various metal salts. **Table 1** shows which metals reacted with which metal ion. (9.3) T/I A

Table 1 Summary of Reactions of Metals X, Y, and Z with $Fe^{2+}(aq)$, $Mg^{2+}(aq)$, and $Ag^{+}(aq)$

Metal Ion	X	Y	Z
$Fe^{2+}(aq)$	yes	no	yes
$Mg^{2+}(aq)$	no	no	no
$Ag^{+}(aq)$	yes	yes	yes

(a) According to the evidence, which of the metals is the strongest reducing agent? Explain.

(b) According to the evidence, which of the ions is the strongest oxidizing agent? Explain.

59. Plants require nitrogen for healthy growth (**Figure 1**). They obtain this nitrogen from nitrates and nitrites in the environment. Nitrates are ionic compounds containing the nitrate ion, NO_3^-, and nitrites are ionic compounds containing the nitrite ion, NO_2^-. Nitrates and nitrites arise naturally in the environment through a series of reactions. First, at high temperatures produced by lightning, gaseous nitrogen and oxygen in the atmosphere react and produce nitrogen monoxide, $NO(g)$. Then, nitrogen monoxide reacts with more oxygen gas to produce nitrogen dioxide, $NO_2(g)$. Finally, nitrogen dioxide reacts with water vapour to produce nitric acid, $HNO_3(aq)$, and nitrous acid, $HNO_2(aq)$. Dilute solutions of these acids supply the nitrate and nitrite ions that plants can take up and use. (9.1, 9.3) K/U A

Figure 1 A nitrogen-deficient plant

(a) Determine the oxidation state of nitrogen in each nitrogen-containing compound in this series of reactions.

(b) Is nitrogen oxidized or reduced during this series of reactions?

(c) State the oxidizing agent or reducing agent that acts on the nitrogen atom.

(d) Gardeners often use chemical or organic fertilizers to add nitrates and nitrites to soil. Suggest a reason for this, referring to the reactions that produce these compounds naturally.

60. During an investigation, a forensics technician finds a sample of a pure, grey metal. From its colour, she knows the metal can only be magnesium, aluminum, or nickel. (9.3) T/I

(a) Design an experiment to identify the metal. List all necessary equipment and materials. Identify the manipulated and responding variables. Write a step-by-step procedure that includes any safety precautions.

(b) Write a balanced equation for any chemical reactions that could occur during your experimental procedure.

61. (a) Predict which pure metal would be most resistant to corrosion or oxidation.

(b) Is the metal you identified in (a) useful as a roofing material? Why or why not? (9.3) K/U A

Evaluation

62. Look carefully at **Table 2**. Are all of the compounds in the correct place? If not, identify any substances that are in the wrong location. Be sure to include your reasoning and determine the proper location. (9.3) T/I

Table 2 Ranking of Selected Ionic Compounds as Oxidizing Agents

Compound	
$ZnCl_2(aq)$	**Strongest oxidizing agent**
$CuCl_2(aq)$	
$NiCl_2(aq)$	↓
$CoCl_2(aq)$	
$AlCl_3(aq)$	
$NaCl(aq)$	**Weakest oxidizing agent**

63. You have been asked to select the strongest reducing agent from the following chemicals, using empirical evidence: (9.3) T/I A

$Co(s)$, $Sn(s)$, $Ca(s)$, $Cu(s)$, $H_2(g)$, and $H_2SO_3(aq)$

(a) Predict which substance is the strongest reducing agent. Explain your reasoning.

(b) Design a procedure to collect the necessary evidence. Include safety precautions and expected observations.

64. A fellow student argues that, because all metals (except gold) form oxides, all of the following metals will react spontaneously with oxygen dissolved in water: (9.3) T/I

Ag(s), Cd(s), Al(s), Fe(s)

Is this student correct? Refer to Table 1 in Appendix B7 to support your answer.

Reflect on Your Learning

65. Think about what you already knew about oxidation and reduction before you studied this chapter. Did you have any ideas that were incorrect? If so, what were they? How did the information in this chapter help you identify and correct your misconceptions? A
66. Make a poster, comic strip, or other product to explain to your peers how an understanding of redox reactions could be useful in their everyday lives. C A
67. What concept or concepts in this chapter did you find most interesting? Explain. A
68. List three questions you still have about the information in this chapter. How can you find the answers to your questions? A

Research

WEB LINK

69. Many rocks and soils are a reddish colour because they contain a mineral called magnetite. One of the major components of magnetite is an oxide of iron with the formula unit Fe_3O_4. Look up the common oxidation numbers of iron. Working with a partner, develop an explanation for the formula unit of this compound. T/I A
70. Redox reactions are often used as part of the remediation process to clean up contaminated ecosystems or water sources. One metal that is frequently the focus of this cleanup is chromium. The fully oxidized form of chromium, Cr^{6+}, is extremely harmful and may be a contaminant of waste water from manufacturing facilities. The less oxidized form of the element, Cr^{3+}, is much less toxic than the hexavalent form. However, it is difficult to convert Cr^{6+} into Cr^{3+} to make it safer for the environment. T/I A
    (a) Outline what type of agent will be needed to convert Cr^{6+} into Cr^{3+} in industrial waste water.
    (b) Research the form in which Cr^{6+} usually occurs, and investigate at least two ways of achieving this conversion. Briefly describe each process and evaluate each one.
71. Alkaline batteries have been used to provide energy for electronic devices for decades. Many newer devices, however, are powered by lithium ion batteries. Research the differences between alkaline batteries and lithium batteries. Summarize the advantages and disadvantages of each in a chart. T/I C A CAREER LINK
72. Early coins were made of gold or silver. Since those days, many different metals have been used for coinage. Research at least six different metals and alloys that have been used, and discuss the advantages of each. Which type of metal (or combination of metals) do you think is the best choice for coinage? Explain. T/I A
73. Choose one metal that is important to society. Research how it is processed from the raw ore into a purified metal. Draw a flow chart illustrating the steps in its refinement. T/I C A
74. Sour gas is methane (natural gas) that contains high concentrations of hydrogen sulfide, $H_2S(g)$ (**Figure 2**). Before it can be used, the hydrogen sulfide must be removed from sour gas. As well as having a rotten-egg smell, even low concentrations of hydrogen sulfide gas are toxic. Combustion of sour gas produces sulfur dioxide gas, which is converted in the atmosphere to sulfurous acid, $H_2SO_3(aq)$, a major component of acid rain. One way to remove hydrogen sulfide from sour gas is to bubble it through a slurry of iron(III) oxide, $Fe_2O_3(s)$, and water. The methane molecules in sour gas do not react with the slurry. However, the hydrogen sulfide gas reacts to produce iron(III) sulfide, $Fe_2S_3(s)$, and water. The iron(III) sulfide then reacts with oxygen gas to regenerate iron(III) oxide. These reactions are represented by the following unbalanced chemical equations:

$$Fe_2O_3(s) + H_2O(l) + H_2S(g) \rightarrow Fe_2S_3(s) + H_2O(l)$$

$$Fe_2S_3(s) + O_2(g) + H_2O(l) \rightarrow Fe_2O_3(s) + H_2O(l) + S(s)$$

T/I C A

    (a) Are these reactions oxidation–reduction reactions? Use oxidation numbers to support your answer.
    (b) Balance the given chemical equations.
    (c) Why is this an economical way of removing the hydrogen sulfide from the natural gas?
    (d) Research the effects of different concentrations of hydrogen sulfide gas on humans.

Figure 2 Hydrogen sulfide is highly toxic.

CHAPTER

10 Electrochemical Cells

KEY CONCEPTS

After completing this chapter you will be able to

- explain electrochemical cells (galvanic cells, fuel cells, and electrolytic cells)
- design, build, and test various kinds of electrochemical cells
- describe the operation of electrochemical cells
- predict the cell potential for a galvanic cell using a reference table
- describe methods for preventing corrosion
- identify environmental implications of industrial electrochemical processes

How Are Chemical Energy and Electrical Energy Related?

Luigi Galvani, an Italian biologist, studied the effects of electric current on the nerves of skinned frog legs. According to legend, Galvani's wife was preparing frog legs for her husband's experiments. One day, she accidentally touched the edge of the metal scalpel to a nerve in a frog leg and to the metal of the machine on the table. To her surprise, the frog leg twitched as if the frog were alive. Today, we know that a redox reaction occurred when the two different metals touched the electrolyte in the frog leg. The movement of electrons in this reaction created a small electric current. The current passed through a nerve and stimulated a muscle in the frog leg, causing the leg to move.

Over time, the principles behind Galvani's observations have allowed us to develop portable electrical energy sources, commonly known as batteries. Batteries can be disposable or rechargeable. Batteries come in all shapes and sizes, and are specifically designed for their intended use. For example, batteries used in portable electronic devices, such as cameras and laptops, are designed to be lightweight and compact, and to function for many hours between charges. Batteries for pacemakers, which are used to regulate heart rate, must also be extremely reliable—a person's life depends on it.

From their accidental discovery in Galvani's lab, batteries have become one of the technological success stories of the twenty-first century. Each year, we spend an estimated $50 billion to keep our portable electronic devices going. Today, batteries allow us to do things that were science fiction only a generation ago.

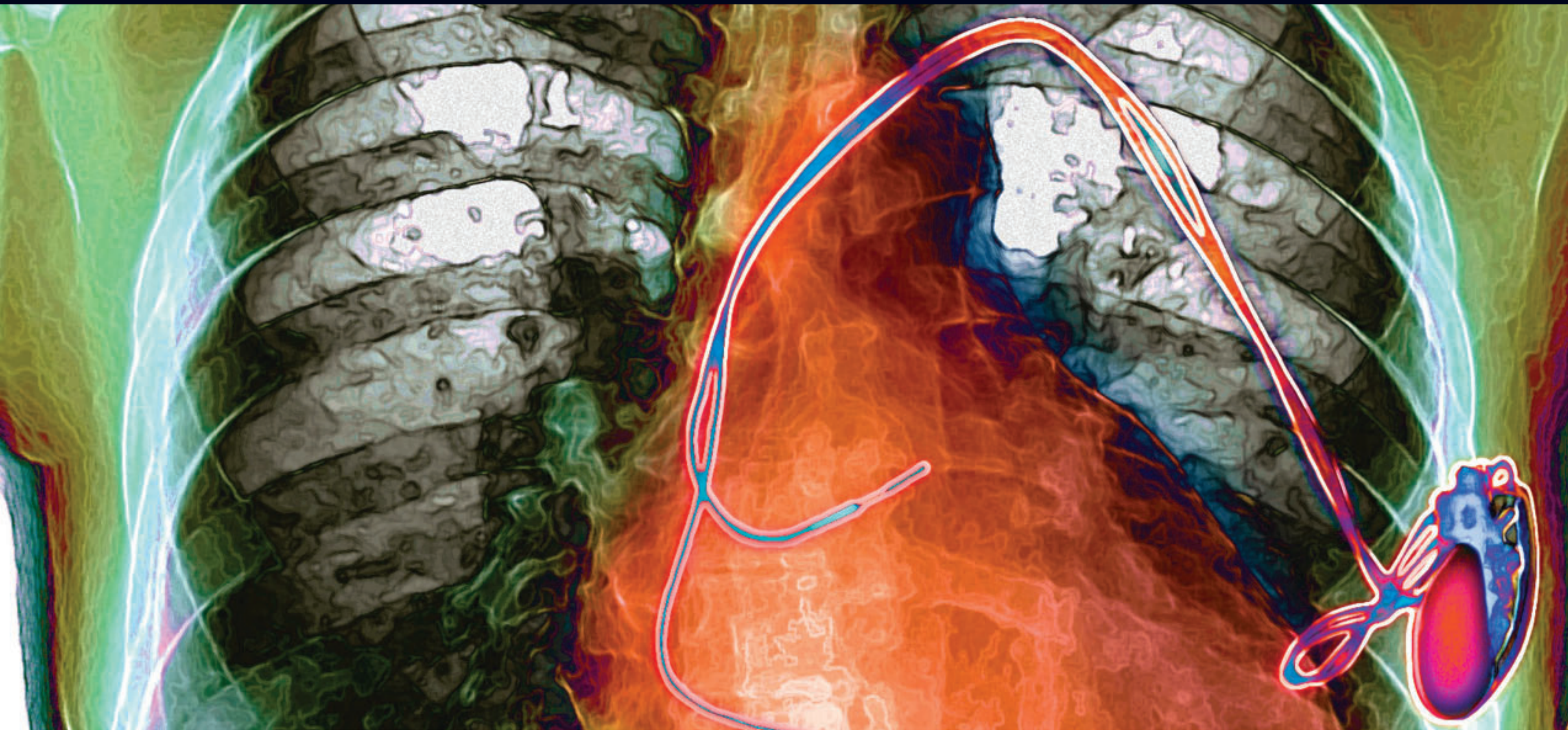
The innovation continues. Engineers are developing creative ways of storing more energy into smaller and more versatile batteries. In the near future, the hard case of your smart phone may provide more than just protection—it could also be the phone's energy source. How about a transparent smart phone? Recent developments in transparent screens, circuitry, and even batteries could make sleek, transparent, and ultrathin gadgets a reality sooner than we think.

No matter how complex their design, all batteries have the same basic components as the twitching frog leg in Galvani's experiments: two different substances undergoing a redox reaction and an electrolyte.

STARTING **POINTS**

Answer the following questions using your current knowledge. You will have a chance to revisit these questions later, applying concepts and skills from the chapter.

1. What characteristics should the ideal source of portable electrical energy have?
2. List the sources of portable electrical energy that you use in your daily life. Evaluate these sources, considering their benefits and drawbacks.
3. Identify the environmental consequences, if any, of the sources of portable electrical energy that you listed in Question 2.
4. What do you think are the limitations of the continued use of batteries? What are possible alternative energy sources for portable devices?



Mini **Investigation**

Harnessing Plant Energy

Skills: Controlling Variables, Performing, Observing, Communicating

SKILLS HANDBOOK A1

How much energy can you get from a slice of watermelon? How much energy can you get from a potato? In this investigation, you will use a fruit or vegetable to supply the electrolyte that enables electrons to move from one piece of metal to another. The circuit will be completed by wires and a small electrical device. The device will only operate if a small electric current flows through it.

Equipment and Materials: voltmeter; zinc strip; copper strip; connecting wires; a small electrical device; variety of fruits and vegetables

1. Use the voltmeter to test the potential difference of each fruit and vegetable provided, as shown in **Figure 1**. Secure the zinc strip and copper strip in the fruit, a few centimetres apart. Connect the wires of the voltmeter to each metal strip (electrode). Be sure to give the voltmeter time to register a consistent reading. Record your observations for each fruit and vegetable you test.
2. Select the fruit or vegetable with the highest potential difference. Insert the metal strips into this fruit or vegetable again.
3. Disconnect the voltmeter from the connecting wires. In its place, attach the small electrical device. Make sure that you have a closed circuit. Record your observations.

A. List the fruits and vegetables that you tested in Step 1, in the order of the potential difference that you observe. T/I

B. Why do you think the potential differences observed for these fruits and vegetables were not all the same? T/I

C. What did you observe in Step 3? Why do you think this occurred? Do you think this would occur if you used other fruits or vegetables? Explain. T/I

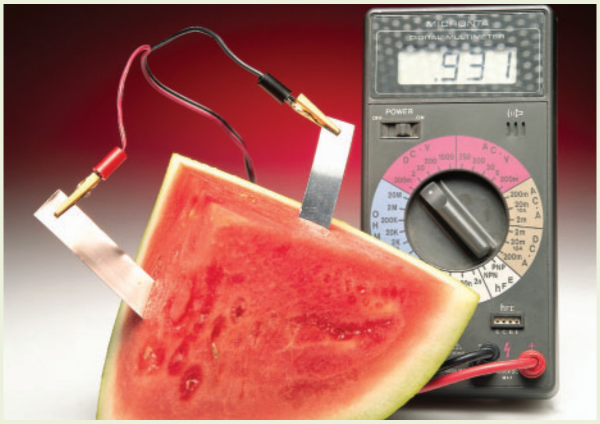


Figure 1 Testing the ability of watermelon to act as an electrolyte for the production of electrical energy

10.1 Galvanic Cells

Figure 1 Dental braces that come in contact with aluminum, such as the aluminum in candy wrappers, can produce a strange tingling sensation.

Have you ever bitten down on aluminum foil accidentally and experienced an unpleasant tingling feeling? Touching aluminum metal against dental work can cause this feeling (**Figure 1**). Touching a gold chain against metal dental braces can produce a similar feeling. The tingling is the result of a small electric current that is generated by an oxidation–reduction or redox reaction. The reaction involves two different metals and electrolytes in your saliva. The batteries that we use to provide energy for portable electrical devices work in a similar way.

Transforming Chemical Energy into Electrical Energy

During a redox reaction, one substance loses electrons while another substance gains electrons. As this occurs, electrons are transferred from the substance that is oxidized to the substance that is reduced. You are likely familiar with the chemical reaction of a strip of zinc metal, Zn(s), with a solution of copper(II) sulfate, $CuSO_4(aq)$ (**Figure 2**):

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

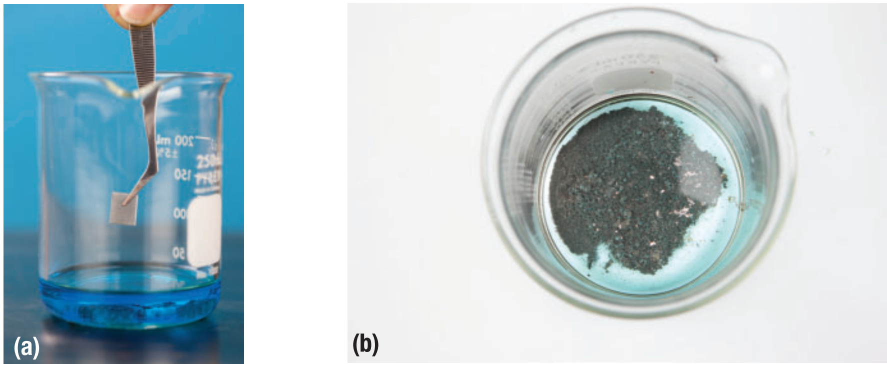


Figure 2 (a) A strip of zinc metal is placed in a solution of copper(II) sulfate. (b) After several hours, the characteristic blue colour of the copper(II) ion, $Cu^{2+}(aq)$, has disappeared, indicating that copper(II) ions are no longer present. Instead, solid copper metal remains in the beaker.

During this chemical reaction, electrons are transferred from the zinc metal to the aqueous copper(II) ions. As a result, the zinc metal is oxidized and the copper(II) ions are reduced. The half-reaction equations for these reactions can be written as follows:

$$\text{Oxidation: } Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$
$$\text{Reduction: } Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

The balanced chemical equation for the redox reaction is the sum of the two half-reaction equations:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Electrons are transferred directly from the zinc atoms to the copper(II) ions when the copper(II) ions collide with the zinc surface. This reaction occurs spontaneously, releasing a small quantity of energy. When the zinc metal and the copper(II) ions are in direct contact, the chemical energy of these transferred electrons cannot be harnessed directly. Instead, it is released to the environment as thermal energy. The key to harnessing the energy is to separate the oxidizing agent from the reducing agent in a way that forces electron transfer to occur through a wire. When electrons flow through a wire, electric current is produced. The current can then be directed through a device, such as an electric motor, a clock, or a music player.

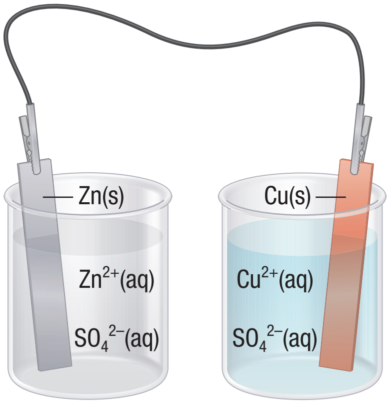


Figure 3 The oxidizing and reducing agents of a redox reaction can be separated by placing them in different containers.

half-cell an electrode and an electrolyte that form half of a complete cell

electrode a solid electrical conductor

cell a system in which two connected electrodes are in contact with an electrolyte

The system illustrated in **Figure 3** is composed of two half-cells connected by a wire. Each **half-cell** consists of an electrode that is in contact with a solution of ions. An **electrode** is a solid electrical conductor. The metal strips in Figure 3 are the electrode. The system in Figure 3 can be called a **cell**, which is a system comprising of two electrodes in contact with appropriate electrolytes.

We might predict that the copper(II) ions in Figure 3 (in the beaker on the right) would attract electrons from the zinc electrode. This would result in a flow of electrons through the wire from the zinc strip to the copper strip. However, careful observation of the cell shows that current flows for an instant and then stops. Why? The current stops flowing because charges build up in the two half-cells. The oxidation of the zinc results in an increase in the concentration of zinc(II) ions in the zinc half-cell. This results in a buildup of positive charge. Similarly, the reduction of copper(II) ions in the copper half-cell reduces the concentration of copper(II) ions in the solution. This results in a buildup of negative charge in the copper half-cell due to the sulfate ions that remain. The buildup of charge in each half-cell prevents further electron transfer from occurring. As a result, the redox reaction stops. This problem can be solved very simply by connecting the solutions so that ions can flow between them to keep the net charge in each half-cell at zero.

UNIT TASK BOOKMARK

Consider what kinds of electrodes and electrolytes you will need to construct a galvanic cell for the Unit Task outlined on page 684.

Transforming Chemical Energy into Electrical Energy

The two half-cells could be connected with a salt bridge. A **salt bridge** is a U-shaped tube that is filled with a non-reactive electrolyte (**Figure 4**). The ends of the tube are plugged with cotton balls. The cotton plugs prevent the solution from falling out of the tube, but they are porous enough to permit some fluid and ions to flow in and out of the tube.

salt bridge a tube that contains an electrolyte solution and connects the two half-cells in a galvanic cell

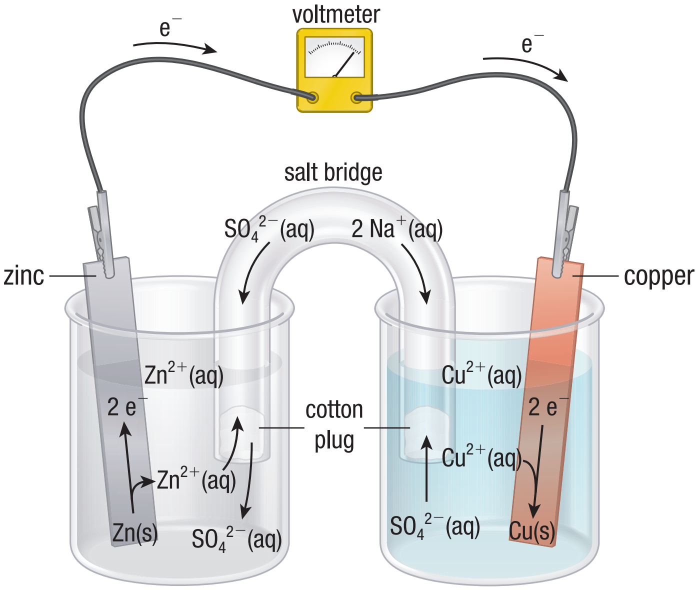


Figure 4 In this galvanic cell, electrons flow from the reducing agent, Zn(s), to the oxidizing agent, $CuSO_4$(aq), through a conducting wire. The flow of ions through the sodium sulfate salt bridge keeps the solution in each half-cell electrically neutral.

THE ROLE OF THE SALT BRIDGE

The salt bridge in Figure 4 consists of a U-shaped tube filled with a sodium sulfate solution. Sodium sulfate is an ideal electrolyte for this salt bridge because it is very soluble and its ions do not react with the electrodes or the electrolyte solutions. The cotton plugs at the ends of the tube are porous enough to allow ions to flow in and out of the tube, but they prevent the solution from pouring out.

As this cell operates, sulfate ions, SO_4^{2-}(aq), spontaneously migrate into the zinc half-cell to offset any buildup of zinc(II) ions. Similarly, sodium ions spontaneously migrate into the copper half-cell to offset the loss of copper (II) ions. As a result of ion migration through the salt bridge, the solutions in each half-cell remain electrically neutral. CAREER LINK

Characteristics of a Galvanic Cell

galvanic cell an arrangement of two connected half-cells that spontaneously produces electric current

anode the electrode where oxidation occurs

cathode the electrode where reduction occurs

If you explored the effect of inserting electrodes into fruits and vegetables at the beginning of this chapter, you made an electric cell. In honour of Luigi Galvani, this cell is called a **galvanic cell**: a device consisting of two connected half-cells that produce current electrical energy spontaneously. The reactions in a galvanic cell occur at the interface between the electrodes and the solutions where the electron transfer occurs. The electrode where oxidation occurs is called the **anode**. The electrode where reduction occurs is called the **cathode** (**Figure 5**). As the cell operates, electrons flow spontaneously from the anode to the cathode through an external path—the conducting wire. In the salt bridge, negatively charged ions, or anions, flow to the anode while positively charged ions, or cations, flow to the cathode.

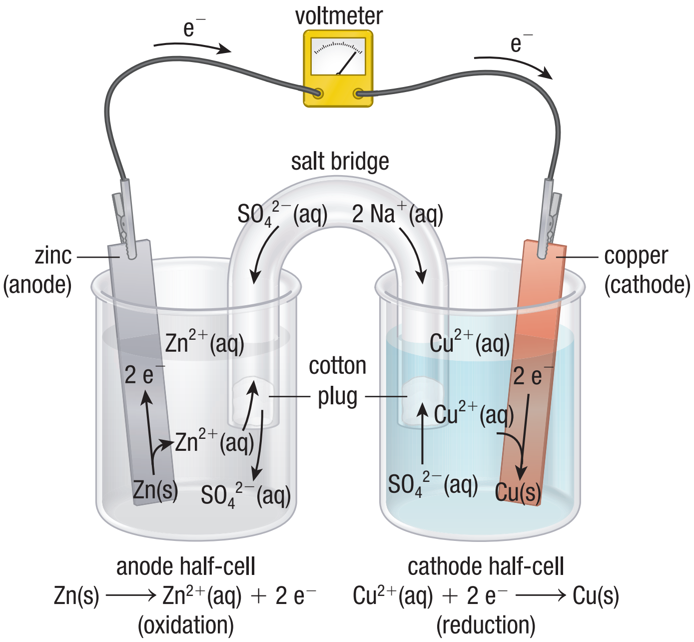


Figure 5 A half-cell reaction takes place in each of these beakers. The wire allows electrons to travel from the anode to the cathode. The salt bridge allows anions to travel from the cathode half-cell to the anode half-cell and allows cations to travel the other way.

What changes might we observe in the galvanic cell in Figure 5? What would we notice if we replaced the voltmeter with an ammeter? **Table 1** shows some typical observations and a theoretical interpretation of these observations.

Table 1 Evidence and Interpretation of the Zinc–Copper Cell

Evidence	Interpretation
The zinc electrode decreases in mass.	Oxidation of the zinc metal is occurring at the zinc anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
The copper electrode increases in mass as copper is deposited on it. The blue colour of the copper(II) solution decreases in intensity.	Copper(II) ions in solution are reduced to copper metal at the copper cathode: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
A voltmeter indicates that the zinc electrode has a negative charge and the copper electrode has a positive charge.	Electrons move from the zinc electrode to the copper electrode.
An ammeter indicates that electric current flows from the zinc electrode to the copper electrode.	Electrons leave the zinc half-cell and enter the copper half-cell.

Predicting Cell Reactions and Equations

The direction of electron flow can be explained in terms of a competition for electrons, much like a "tug of war." Both zinc ions and copper(II) ions are capable of accepting electrons from another substance. In other words, both ions can act as oxidizing agents. According to the table of Standard Reduction Potentials (Table 1 in Appendix B7), $Cu^{2+}(aq)$ ions are a stronger oxidizing agent (SOA) than $Zn^{2+}(aq)$ ions. As a result, we would predict that the copper(II) ions should win the "tug of war" for electrons when the two half-cells in Figure 5 are connected. The source of these electrons is the stronger reducing agent (SRA) in the cell: zinc metal. Our prediction is supported by the evidence: electrons flow spontaneously from the zinc anode to the copper cathode as this cell operates.

The net ionic equation of the reaction in this cell can be determined using the same procedure that was used in Section 9.3 when predicting redox reactions:

Anode (oxidation) half-reaction equation: $Zn(s) \rightarrow Zn^{2+}(aq) + \cancel{2e^-}$

Cathode (reduction) half-reaction equation: $Cu^{2+}(aq) + \cancel{2e^-} \rightarrow Cu(s)$

Net ionic equation: $\underset{\text{(SOA)}}{Cu^{2+}(aq)} + \underset{\text{(SRA)}}{Zn(s)} \rightarrow Cu(s) + Zn^{2+}(aq)$

Galvanic Cells with Inert Electrodes

Chemists are continually exploring the various combinations of oxidizing and reducing agents, electrodes, and electrolytes that could be used to construct an electric cell. In a cell with a metal electrode and metal ions, the metal electrode usually participates in the cell reaction. However, not all galvanic cells are constructed this way. Many of the cells in batteries use an inert solid conductor, such as carbon (graphite), as an electrode. An inert electrode provides a surface on which the oxidation and reduction reactions may occur, but it does not participate in these reactions. An inert electrode is required in cells where the cell reaction involves only entities in the solution, not the electrode itself.

To understand the role of an inert electrode in a galvanic cell, consider the reaction between aqueous permanganate ions, $MnO_4^-(aq)$, and aqueous iron(II) ions, $Fe^{2+}(aq)$:

$$8\,H^+(aq) + MnO_4^-(aq) + 5\,Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4\,H_2O(l)$$

During the reduction half-reaction, the manganese atoms of the permanganate ions are reduced from manganese with an oxidation number of +7 to manganese with an oxidation number of +2:

$$8\,H^+(aq) + MnO_4^-(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

During the oxidation half-reaction equation, iron(II) ions are oxidized to iron(III) ions:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

To balance the two half-reaction equations, first multiply the oxidation reaction by 5:

$$5(Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-)$$

$$5\,Fe^{2+}(aq) \rightarrow 5\,Fe^{3+}(aq) + 5\,e^-$$

Then, add the two half-reaction equations to get the balanced net ionic equation for the overall reaction:

$$8\,H^+(aq) + \underset{\text{(SOA)}}{MnO_4^-(aq)} + \underset{\text{(SRA)}}{5\,Fe^{2+}(aq)} \rightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4\,H_2O(l)$$

In this reaction, permanganate, $MnO_4^-(aq)$, is the stronger oxidizing agent and iron(II) is the stronger reducing agent. The manganese(II) ion, $Mn^{2+}(aq)$, is the reduction product, and iron(III) is the oxidation product. The reduction half-reaction equation represents the reactions occurring at the cathode and the oxidation half-reaction equation represents the reactions occurring at the anode. The inert electrodes provide a place to connect the wire and a surface for the half-reactions to occur.

Line Notation and Galvanic Cells

Line notation is an abbreviated way to describe cells. In line notation, the anode components are listed on the left and the cathode components are listed on the right. They are separated by double vertical lines to indicate a salt bridge. A single vertical line indicates a boundary between two states of matter, such as the interface of an electrode and an electrolyte in a half-cell (**Figure 6**).

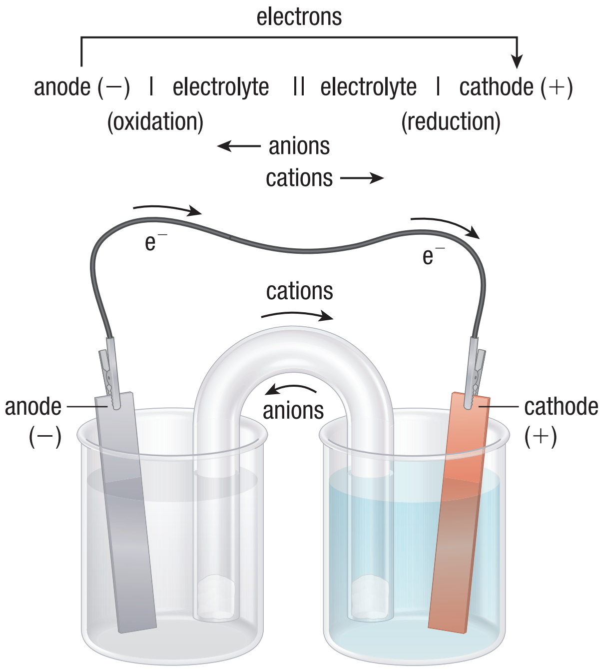


Figure 6 This example shows the general pattern for writing line notation.

Starting with the net ionic equation, we can produce the following line notation for the zinc–copper cell in Figure 5:

Net ionic equation: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Line notation: $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$

Platinum, Pt(s), is the inert electrode that is generally used in the iron(II)–permanganate cell. The net ionic equation and line notation for this cell are written as follows:

Net ionic equation:

$$8\,H^{+}(aq) + MnO_4^{-}(aq) + 5\,Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4\,H_2O(l)$$

Line notation: $Pt(s)|Fe^{2+}(aq)||MnO_4^{-}(aq)|Pt(s)$

Investigation **10.1.1**

Investigating Galvanic Cells (page 671)
In this investigation, you will build three different galvanic cells to determine which cell produces the highest voltage.

10.1 Review

Summary

- A galvanic cell consists of two separated half-cells. The electrodes are connected by a wire. The solutions are connected by a salt bridge.
- In a galvanic cell, reduction occurs at the cathode (the positive electrode) and oxidation occurs at the anode (the negative electrode).
- The stronger oxidizing agent is reduced at the cathode. The stronger reducing agent is oxidized at the anode.
- As the cell operates, electrons travel from the anode to the cathode via the external circuit (the wire). Ions flow through the salt bridge to keep the solutions electrically neutral (anions to the anode, cations to the cathode).

Questions

1. Why is it necessary to separate the oxidizing agent from the reducing agent in a galvanic cell? K/U
2. Identify the two "connections" that are required before a galvanic cell can function. K/U
3. What characteristics should the solution in a salt bridge have? K/U T/I A
4. A galvanic cell is constructed using the following materials: strip of nickel metal; strip of magnesium metal; nickel(II) sulfate, $NiSO_4(s)$; magnesium sulfate, $MgSO_4(s)$; sodium sulfate, $Na_2SO_4(s)$, for the salt bridge; distilled water; connecting wires; U-shaped tube; cotton; 2 beakers; voltmeter. K/U T/I C
   - (a) Draw and label a diagram of the cell.
   - (b) Identify the anode and the cathode in the cell.
   - (c) Label the directions of electron and ion flow.
   - (d) Identify the oxidizing and reducing agents.
   - (e) Write the equations for the half-reactions that occur in the cell.
   - (f) Write the net ionic equation for the cell reaction.
   - (g) Predict how the mass of the electrodes will change as the cell operates.
5. Consider the galvanic cells that are represented by the given line notations. For each cell,
   - (i) identify the stronger oxidizing agent and stronger reducing agent,
   - (ii) write chemical equations to represent the half-reactions at the cathode and anode, and
   - (iii) write the net ionic equation. K/U C
   - (a) $Mg(s)|Mg^{2+}(aq)||Cu^{+}(aq)|Cu(s)$
   - (b) $Fe(s)|Fe^{2+}(aq)||Ag^{+}(aq)|Ag(s)$
6. A galvanic cell has a magnesium electrode in a 1.0 mol/L magnesium nitrate solution and an iron electrode in a 1.0 mol/L iron(II) nitrate solution. T/I C
   - (a) Draw a diagram of the cell. Include the following labels: anode, cathode, salt bridge, electron flow, ion flow.
   - (b) Predict the half-reactions that will occur, and write their equations.
   - (c) Write a net ionic equation for the cell reaction.
   - (d) What visible evidence would you expect to see, indicating that the cell is functioning?
7. **Figure 7** shows a galvanic cell that consists of magnesium and copper electrodes in tap water. This cell generates enough electrical energy to operate a small digital clock. K/U T/I C
   - (a) Compare the design of this cell with the zinc–copper cell in Figure 5.
   - (b) The anode half-reaction in this cell is the oxidation of magnesium. The cathode half-reaction involves the reduction of water. Use the redox table to write equations for both half-reactions and the net ionic equation for the cell reaction.
   - (c) What is the function of the copper electrode in this cell?
   - (d) The cell in Figure 7 works well with tap water but not with distilled water. Why do you think the type of water that is used makes a difference?

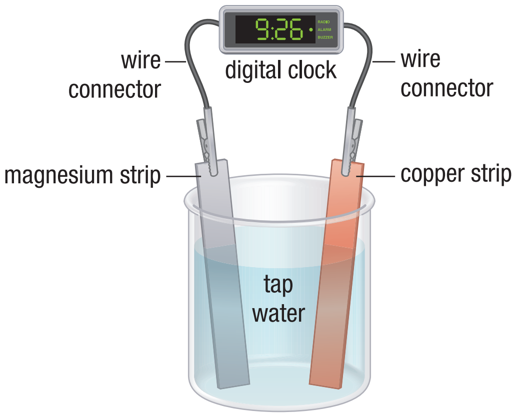


Figure 7

10.2 Standard Reduction Potentials

In Section 10.1, you learned how a galvanic cell, similar to the one in **Figure 1(a)**, converts the chemical energy from a spontaneous redox reaction into electrical energy. Although the design of a galvanic cell makes the cell impractical as an energy source for a portable electronic device, it is useful for showing the chemical processes that are involved. It is also useful for showing how commercial galvanic cells, such as 1.5 V alkaline dry cells (**Figure 1(b)**), work. An important design feature of any galvanic cell is its cell potential.

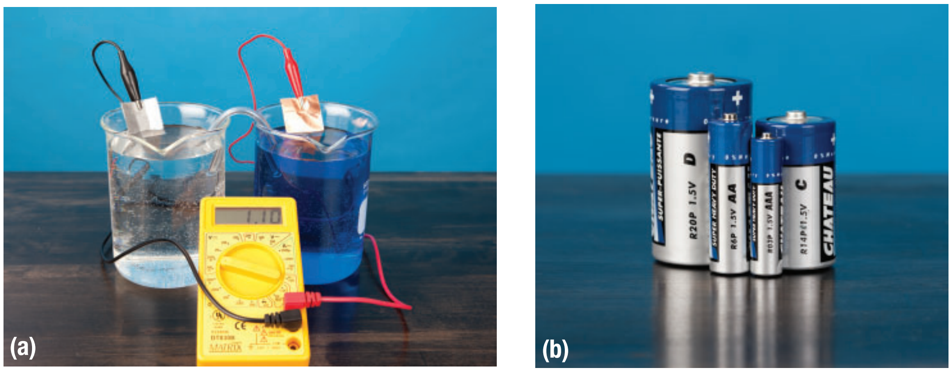


Figure 1 Both (a) an experimental zinc–copper galvanic cell and (b) commercial 1.5 V alkaline dry cells operate on the same principle.

Investigation **10.2.1**

Constructing a Galvanic Cell (page 672)
In this investigation, you will determine how the materials used to construct a cell affect the cell potential.

Cell Potential

cell potential the electric potential difference (voltage) between the two half-cells in a galvanic cell; the SI unit is the volt, and the unit symbol is V (1 V = 1 J/C)

The electrons in each half-cell of a galvanic cell have different amounts of electric potential energy. This is analogous to two apples hanging from a tree. The apple hanging from an upper branch of the tree has more gravitational potential energy than the apple hanging from a lower branch. **Cell potential** is a measure of the electric potential difference or voltage between two half-cells. Cell potential is analogous to the difference in gravitational potential energy between the two apples hanging at different heights on the tree.

The SI unit for cell potential is the volt (symbol: V). One volt is defined as one joule of energy per coulomb of electric charge, or 1 V = 1 J/C. The coulomb is the SI unit for electric charge. (1 C is equivalent to the charge of 6.25×10^{18} electrons.)

Since cell potential is a ratio of energy to charge, it is unaffected by the number of electrons transferred as a galvanic cell operates. For example, an alkaline D cell transfers electrons, and therefore electrical energy, for a longer time than a smaller AAA cell because it contains a greater quantity of reactants. However, the quantity of the energy per charge (in joules per coulomb) transferred by both cells is identical: 1.5 J/C or 1.5 V. Factors that influence cell potential include the design of the cell, the redox reaction involved, and the concentration of the reactants in the cell. For example, the lithium-ion cell and the alkaline cell have different cell potentials because they use different redox reactions.

The cell potential for a galvanic cell is measured using a voltmeter. The magnitude of the reading indicates the difference in the ability of the two half-cells to attract electrons. The sign of the voltmeter reading identifies the anode, the cathode, and the direction of electron flow in the cell. A voltmeter typically has two terminals: a red (positive) terminal and a black (negative) terminal. A positive reading on the voltmeter means that the positive terminal is connected to the cathode of the cell and the negative terminal is connected to the anode. A negative reading means that the connections are reversed. Once the anode and the cathode are determined, the direction of electron flow—from the anode to the cathode, or vice versa—is known. CAREER LINK

LEARNING **TIP**

Electrode Mnemonic
These mnemonics may help you remember the process that occurs at each electrode:

- RED CAT—REDuction always occurs at the CAThode.
- AN OX—OXidation always occurs at the ANode.

Can you think of your own mnemonics?

Standard Cells and Standard Cell Potentials

Cell potential varies depending on the concentration of the chemicals in a cell. To study cells more easily, chemists have defined standard conditions under which cells operate. A **standard cell** is a galvanic cell in which all the entities are at SATP, with a concentration of 1.0 mol/L for solutions. For example, the line notation for a standard zinc–copper cell (Figure 1(a)) is

$$\mathrm{Zn(s)}|\underset{1\ \mathrm{mol/L}}{\mathrm{Zn^{2+}(aq)}}||\underset{1\ \mathrm{mol/L}}{\mathrm{Cu^{2+}(aq)}}|\mathrm{Cu(s)}$$

standard cell a galvanic cell in which all the entities involved in the half-cell reactions are at SATP and the solutions have a concentration of 1.0 mol/L

The **standard cell potential** (**$\Delta E°_{r\ (cell)}$**) is the electric potential difference of a cell that is operating under standard conditions. It is a measure of the potential energy difference, per unit of charge, between the cathode and the anode. The degree symbol is used to indicate standard conditions. The **standard reduction potential** (**$E°_r$**) indicates the ability of a half-cell to attract electrons, and therefore undergo reduction. As a cell operates, the half-cell with the greater (more positive) reduction potential gains electrons from the half-cell with the lower reduction potential. Therefore, the standard cell potential is the difference between the reduction potentials of the two half-cells:

standard cell potential (**$\Delta E°_{r\ (cell)}$**) the electric potential difference of a galvanic cell that is operating under standard conditions

standard reduction potential (**$E°_r$**) the ability of a half-cell to attract electrons in a cell that is operating under standard conditions

$$\Delta E°_{r\ (cell)} = E°_{r\ (cathode)} - E°_{r\ (anode)}$$

Developing a Reduction Potentials Table

Cell potentials are measured with a voltmeter. The electric potential of a half-cell cannot be measured because a half-cell reaction cannot occur on its own. Chemists have overcome the difficulty in predicting cell potentials for combinations of half-cells by assigning the **standard hydrogen half-cell** an electric potential of exactly 0 V (**Figure 2**). The standard hydrogen half-cell consists of an inert platinum electrode in contact with an acidic solution containing 1.0 mol/L hydrogen ions through which hydrogen gas is bubbled at a pressure of 100 kPa. The electric potentials of other half-cells can be determined relative to the standard hydrogen half-cell.

standard hydrogen half-cell the galvanic cell from which all the half-cell potentials are determined; $E°_r = 0$ V (by definition)

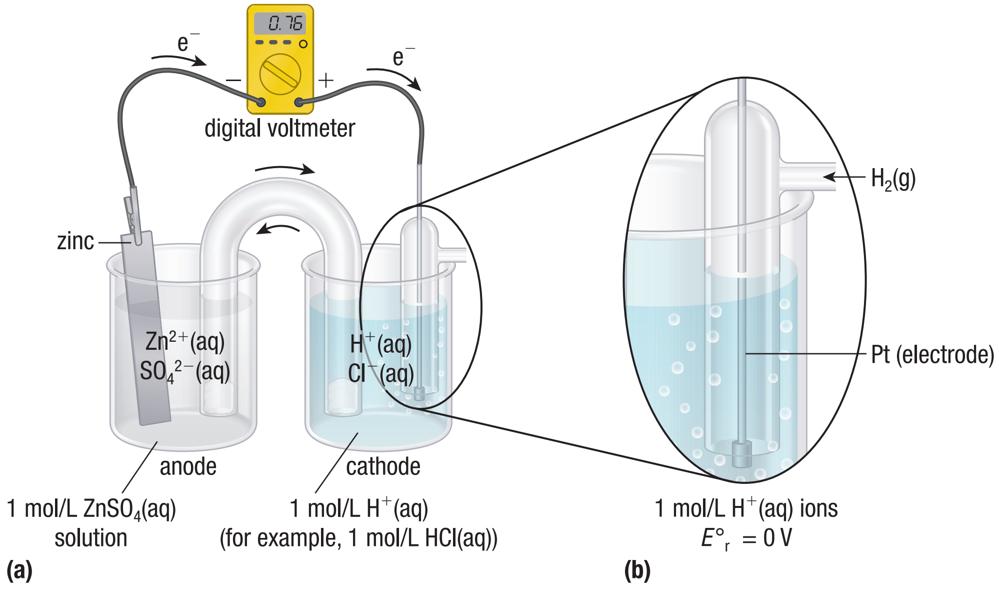


Figure 2 (a) In this galvanic cell, hydrogen is reduced and zinc is oxidized. (b) In the hydrogen half-cell, hydrogen gas at 100 kPa passes over a platinum electrode in a 1 mol/L solution of hydrogen ions. The reduction of hydrogen at this electrode is arbitrarily assigned a value of exactly 0 V.

The cell shown in Figure 2(a) contains zinc ions in one half-cell and hydrogen ions in the other half-cell. Due to their positive charge, both zinc ions and hydrogen ions compete for the electrons—both ions can be oxidizing agents. However, the positive cell potential indicates that electrons flow from the zinc anode to the platinum cathode. Therefore, the hydrogen ion is a stronger oxidizing agent than the zinc ion.

Investigation **10.2.2**

Investigating Cell Potentials (page 673)

In this controlled experiment, you will construct galvanic cells using magnesium, zinc, iron, and copper half-cells.

The cell potential for the zinc–hydrogen cell is 0.76 V. Therefore, the reduction potential of the hydrogen ions is greater than the reduction potential of the zinc ions by 0.76 V. Since the reduction potential of the hydrogen ions is defined as exactly 0 V, the reduction potential of the zinc ions, measured relative to the hydrogen ions, must be −0.76 V. This value is a measure of how much stronger hydrogen ions are as oxidizing agents than zinc ions (**Figure 3**). The two reduction half-reactions can be listed in order of decreasing reduction potential as follows:

$$2\,H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E^\circ_r = 0\ V$$

$$Zn^{2+}(aq) + 2\,e^- \rightleftharpoons Zn(s) \quad E^\circ_r = -0.76\ V$$

If the zinc half-cell in Figure 2 is replaced with a copper half-cell, the reading on the meter changes to –0.34 V. The change in sign means that electrons are now flowing in the opposite direction—from the hydrogen half-cell to the copper half-cell. Therefore, copper is the cathode and platinum is the anode. If the connections to the electrodes are reversed, the reading changes to a positive value of 0.34 V (**Figures 4** and **5**). This means that the copper(II) ion is a better competitor for electrons (a better oxidizing agent) than the hydrogen ion by 0.34 V.

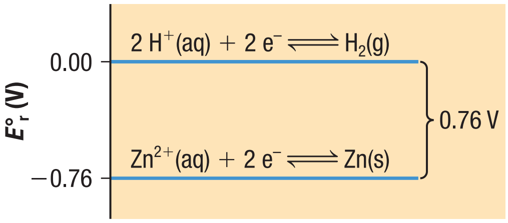


Figure 3 $H^+(aq)$ is a stronger oxidizing agent than $Zn^{2+}(aq)$ by 0.76 V.

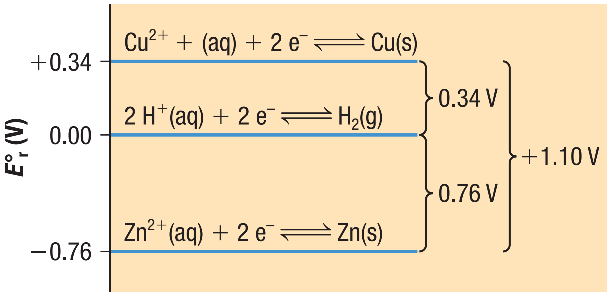


Figure 4 $Cu^{2+}(aq)$ is a stronger oxidizing agent than both $H^+(aq)$ and $Zn^{2+}(aq)$. A standard cell constructed using copper and zinc half-cells has a predicted cell potential of +1.10 V.

We can therefore add copper to our reduction potentials list:

$$Cu^{2+}(aq) + 2\,e^- \rightleftharpoons Cu(s) \quad E^\circ = +0.34\ V$$

$$2\,H^+(aq) + 2\,e^- \rightleftharpoons H_2(g) \quad E^\circ = 0.00\ V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\circ = -0.76\ V$$

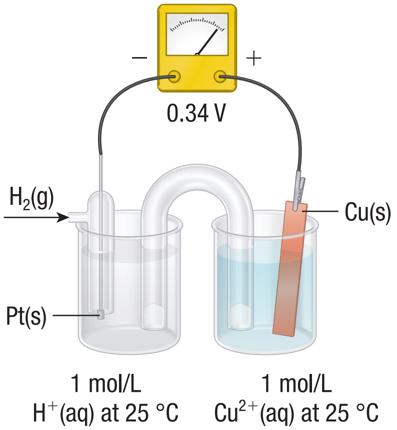


Figure 5 A standard galvanic cell that involves the half-reactions $H_2(g) \rightarrow 2\,H^+(aq) + 2\,e^-$ (at the anode) and $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$ (at the cathode) has a potential of 0.34 V.

These data can be used to predict the net ionic equation for the cell reaction and cell potential for the zinc–copper cell (**Figure 6**, next page):

$$\begin{array}{ll} \text{Reduction (cathode): } & Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s) \\ \text{Oxidation (anode): } & Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \\ \hline \text{Net ionic equation: } & Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq) \end{array}$$

The standard cell potential ($\Delta E^\circ_{r\,(cell)}$) is the difference between the reduction potentials of the two half-cells:

$$\begin{aligned} \Delta E^\circ_{r\,(cell)} &= E^\circ_{r\,(cathode)} - E^\circ_{r\,(anode)} \\ &= +0.34\ V - (-0.76\ V) \\ &= +1.10\ V \end{aligned}$$

If we continued measuring the standard reduction potentials of many other half-cells against the hydrogen half-cell, we could add them to our ranked list of reduction potentials. We would then be able to predict the cell potentials for a variety of cells.

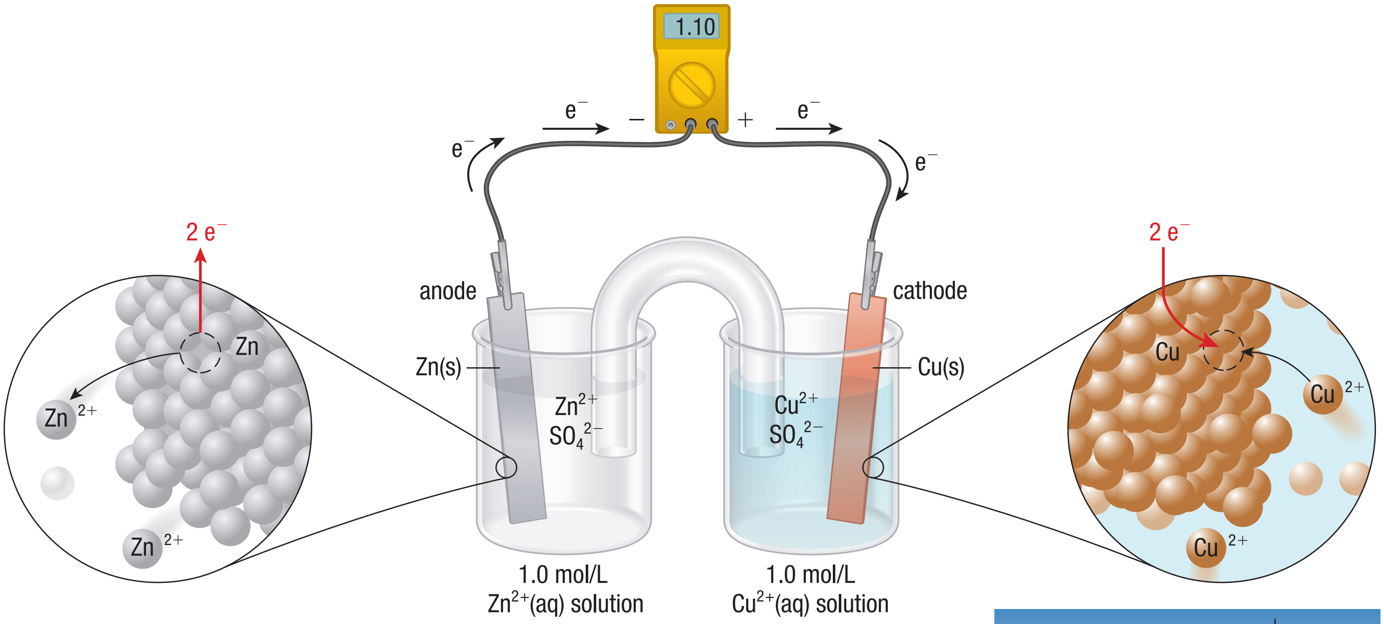


Figure 6 In a galvanic cell that involves the half-reactions $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$ (at the anode) and $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$ (at the cathode), $E°_{r\,(cell)} = 1.10$ V.

$\Delta E°_{r\,(cell)}$ and Spontaneity

The sign and magnitude of a predicted cell potential provide important information about the operation of a galvanic cell.

SPONTANEOUS REACTION, $\Delta E°_{r\,(cell)} > 0$

A positive value for the cell potential means that the cell reaction occurs spontaneously. The magnitude of the cell potential, however, does not indicate how quickly the reaction occurs. This can only be determined experimentally. The largest potential is observed when the contents of the cell are at standard conditions. As the cell operates, the observed potential gradually decreases. This occurs because the chemicals within the cell are being used up and are no longer at standard concentrations.

REACTION AT EQUILIBRIUM, $\Delta E°_{r\,(cell)} = 0$

Eventually, the cell potential for an operating cell decreases to zero. At this point, the forward and reverse reactions are occurring at the same rate. In other words, the reaction inside the cell has reached chemical equilibrium. To continue functioning, the cell must be recharged. If this is not possible, the cell can no longer be used and must be discarded.

NON-SPONTANEOUS REACTION, $\Delta E°_{r\,(cell)} < 0$

A negative value for the cell potential means that the cell reaction does not occur spontaneously. As you will learn in Section 10.7, however, the cell reaction can be made to occur by applying energy from an external source.

A Water Analogy for a Galvanic Cell

A water analogy may help explain changes in cell potential as a galvanic cell operates. Consider the water in a lock (**Figure 7(a)**). Each millilitre of surface water on the right side of the gate is higher, and therefore has more gravitational potential energy, than each millilitre of surface water on the left side. When the small sluice gates are opened, potential energy is converted to kinetic energy as water flows to the lower side. As the water level drops (**Figure 7(b)**), the difference between the potential energies of the two sides decreases. The flow of water stops once the potential energies of the two sides are equal (**Figure 7(c)**).

Similarly, the anode is the "high side" of a galvanic cell, while the cathode is the "low side." As the cell operates, electrons flow spontaneously "downhill" from anode to cathode. The cell potential is the measure of the electric potential energy difference (or potential difference) across the two half-cells. Gradually, the cell potential

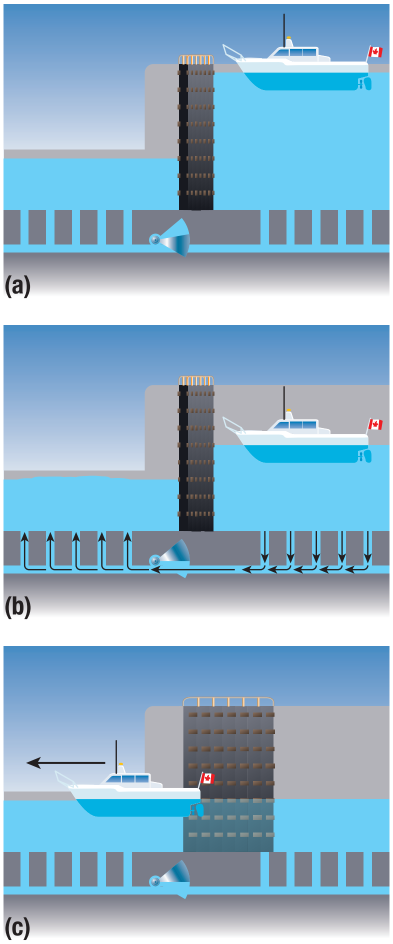


Figure 7 (a) The water behind the main gates in a lock has a certain potential energy, ΔE, relative to the bottom of the canal. (b) When the sluice gates at the bottom are opened, water flows to the lower level on the other side. The potential energy of the stationary water is converted to kinetic energy of flowing water. The flowing water is analogous to electron flow. (c) Water stops flowing when the two levels are equal.

decreases until it reaches zero. At this point, the electron flow has stopped and the cell is considered "dead" because its cell reaction has reached chemical equilibrium.

Predicting Standard Cell Potentials

Table 1 below and Table 1 in Appendix B7 both list the standard reduction potentials of many half-cells, measured relative to the standard hydrogen half-cell. By convention, we always write the equations for these half-cell reactions from left to right as reduction reactions. The reduction potentials can be used to predict the cell potential for a galvanic cell that involves any pair of these half-cell reactions.

Table 1 Standard Reduction Potentials at 25 °C (298 K) for Many Common Half-Reactions

Half-reaction	E°_r (V)	Half-reaction	E°_r (V)
Strongest Oxidizing Agent; Weakest Reducing Agent			
$F_2(g) + 2\ e^- \rightleftharpoons 2\ F^-(aq)$	2.87	$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	0.52
$Ag^{2+}(aq) + e^- \rightleftharpoons Ag^+(aq)$	1.99	$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightleftharpoons 4\ OH^-(aq)$	0.40
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	1.82	$Cu^{2+}(aq) + 2\ e^- \rightleftharpoons Cu(s)$	0.34
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons 2\ H_2O(l)$	1.78	$Hg_2Cl_2(aq) + 2\ e^- \rightleftharpoons 2\ Hg(l) + 2\ Cl^-(aq)$	0.34
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	1.70	$AgCl(aq) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	0.22
$PbO_2(s) + 4\ H^+ + SO_4^{2-}(aq) + 2\ e^- \rightleftharpoons PbSO_4(s) + 2\ H_2O(l)$	1.69	$SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	0.20
$MnO_4^-(aq) + 4\ H^+(aq) + 3\ e^- \rightleftharpoons MnO_2(s) + 2\ H_2O(l)$	1.68	$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	0.16
$IO_4^-(aq) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons IO_3^-(aq) + H_2O(l)$	1.60	$2\ H^+(aq) + 2\ e^- \rightleftharpoons H_2(g)$	0
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightleftharpoons Mn^{2+}(aq) + 4\ H_2O(l)$	1.51	$Fe^{3+}(aq) + 3\ e^- \rightleftharpoons Fe(s)$	−0.036
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	1.50	$Pb^{2+}(aq) + 2\ e^- \rightleftharpoons Pb(s)$	−0.13
$PbO_2(s) + 4\ H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2\ H_2O(l)$	1.46	$Sn^{2+}(aq) + 2\ e^- \rightleftharpoons Sn(s)$	−0.14
$Cl_2(g) + 2\ e^- \rightleftharpoons 2\ Cl^-(aq)$	1.36	$Ni^{2+}(aq) + 2\ e^- \rightleftharpoons Ni(s)$	−0.23
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightleftharpoons 2\ Cr^{3+}(aq) + 7\ H_2O(l)$	1.33	$PbSO_4(aq) + 2\ e^- \rightleftharpoons Pb + SO_4^{2-}(aq)$	−0.35
$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightleftharpoons 2\ H_2O(l)$	1.23	$Cd^{2+}(aq) + 2\ e^- \rightleftharpoons Cd(s)$	−0.40
$MnO_2(s) + 4\ H^+(aq) + 2\ e^- \rightleftharpoons Mn^{2+}(aq) + 2\ H_2O(l)$	1.21	$Fe^{2+}(aq) + 2\ e^- \rightleftharpoons Fe(s)$	−0.44
$IO_3^-(aq) + 6\ H^+(aq) + 5\ e^- \rightleftharpoons \frac{1}{2}\ I_2(s) + 3\ H_2O(l)$	1.20	$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$	−0.50
$ClO_4^-(aq) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons ClO_3^-(aq) + H_2O(l)$	1.19	$Cr^{3+}(aq) + 3\ e^- \rightleftharpoons Cr(s)$	−0.73
$Br_2(l) + 2\ e^- \rightleftharpoons 2\ Br^-(aq)$	1.09	$Zn^{2+}(aq) + 2\ e^- \rightleftharpoons Zn(s)$	−0.76
$VO_2^+(aq) + 2\ H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	1.00	$2\ H_2O(l) + 2\ e^- \rightleftharpoons H_2(g) + 2\ OH^-(aq)$	−0.83
$AuCl_4^-(aq) + 3\ e^- \rightleftharpoons Au(s) + 4\ Cl^-(aq)$	0.99	$Mn^{2+}(aq) + 2\ e^- \rightleftharpoons Mn(s)$	−1.18
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightleftharpoons NO(g) + 2\ H_2O(l)$	0.96	$Al^{3+}(aq) + 3\ e^- \rightleftharpoons Al(s)$	−1.66
$ClO_2(g) + e^- \rightleftharpoons ClO_2^-(aq)$	0.954	$H_2(g) + 2\ e^- \rightleftharpoons 2\ H^-(aq)$	−2.23
$2\ Hg^{2+}(aq) + 2\ e^- \rightleftharpoons Hg_2^{2+}(aq)$	0.91	$Mg^{2+}(aq) + 2\ e^- \rightleftharpoons Mg(s)$	−2.37
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	0.80	$La^{3+}(aq) + 3\ e^- \rightleftharpoons La(s)$	−2.37
$Hg_2^{2+}(aq) + 2\ e^- \rightleftharpoons 2\ Hg(l)$	0.80	$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	0.77	$Ca^{2+}(aq) + 2\ e^- \rightleftharpoons Ca(s)$	−2.76
$O_2(g) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons H_2O_2(aq)$	0.68	$Ba^{2+}(aq) + 2\ e^- \rightleftharpoons Ba(s)$	−2.90
$MnO_4^-(aq) + e^- \rightleftharpoons MnO_4^{2-}(aq)$	0.56	$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$I_2(s) + 2e^- \rightleftharpoons 2\ I^-(aq)$	0.54	$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05
		Weakest Oxidizing Agent; Strongest Reducing Agent	

Tutorial 1 Predicting Standard Cell Potentials

This tutorial shows how to use a standard reduction potentials table to determine the standard cell potential and the net ionic equation for a cell reaction.

Sample Problem 1: Determining a Standard Cell Potential and Net Ionic Equation

Determine the standard cell potential and the net ionic equation for a redox reaction that involves silver and zinc half-cells.

Given: Look up the two reduction half-cell reactions and their standard reduction potentials in Table 1:

$$Ag^+(aq) + e^- \rightarrow Ag(s) \quad E°_r = 0.80\ V$$

$$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s) \quad E°_r = -0.76\ V$$

Required: $\Delta E^o_{r\ (cell)}$ and the net ionic equation for the cell reaction

Analysis: Use the following equation to calculate the standard cell potential:

$$\Delta E°_{r\ (cell)} = E°_{r\ (cathode)} - E°_{r\ (anode)}$$

Solution:

Step 1. Write the equation for the half-cell reaction that has the more positive reduction potential as a forward reaction. Write the equation for the half-cell reaction that has less positive (or negative) reduction potential as a reverse reaction.

The half-cell reaction with more positive potential is the reduction half-reaction. In this case, the reduction of silver ions occurs at the cathode:

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

Zinc is oxidized at the anode. Write its equation as an oxidation reaction:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

Step 2. Balance the number of electrons involved in the two half-cell reactions.

The reduction half-reaction requires 1 electron, and the oxidation half-reaction produces 2 electrons. To balance the number of electrons, the silver half-reaction needs to be multiplied by 2:

$$2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)$$

The zinc equation stays the same because it already involves 2 electrons.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$$

Step 3. Combine the two half-reactions to give the balanced net ionic equation:

$$\begin{aligned} 2\ Ag^+(aq) + \cancel{2\ e^-} &\rightarrow 2\ Ag(s) \\ Zn(s) &\rightarrow Zn^{2+}(aq) + \cancel{2\ e^-} \\ \hline 2\ Ag^+(aq) + Zn(s) &\rightarrow Zn^{2+}(aq) + 2\ Ag(s) \end{aligned}$$

Step 4. Use the formula $\Delta E°_{r\ (cell)} = E°_{r\ (cathode)} - E°_{r\ (anode)}$ to determine the standard cell potential.

Note that the silver half-cell potential is not multiplied by 2 because the cell potential represents a ratio of energy per coulomb of charge and is therefore unaffected by the number of electrons in the half-cell reaction equation.

$$\Delta E°_{r\ (cell)} = +0.80\ V - (-0.76\ V)$$

$$\Delta E°_{r\ (cell)} = +1.56\ V$$

Statement: The net ionic equation and the standard cell potential for a cell involving the zinc and silver half-cells are

$$2\ Ag^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2\ Ag(s)$$
$$\Delta E°_{r\ ((cell)} = +1.56\ V$$

Practice

1. Galvanic cells that involve the following pairs of half-reactions are constructed. Write the net ionic equation and determine the standard cell potential for each galvanic cell. Assume that all the entities are in their standard states. K/U
   (a) $MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightleftharpoons Mn^{2+}(aq) + 4\ H_2O(l)$
   $IO_3^-(aq) + 6\ H^+(aq) + 5\ e^- \rightleftharpoons \frac{1}{2}\ I_2(s) + 3\ H_2O(l)$ [ans: 0.31 V]
   (b) $O_2(g) + 2\ H_2O(l) + 4e^- \rightleftharpoons 4\ OH^-(aq)$
   $Al^{3+}(aq) + 3\ e^- \rightleftharpoons Al(s)$ [ans: 2.06 V]

10.2 Review

Summary

- All the entities in the cell equation for a standard cell are pure substances under SATP and/or solutions with a concentration of 1.0 mol/L.
- The standard hydrogen half-cell, by definition, has a reduction potential of exactly 0 V. All other potentials are measured relative to this reduction potential.
- The standard cell potential, $\Delta E°_{r\ (cell)}$, can be predicted from the reduction potentials listed in a standard reduction potentials table, using the formula $\Delta E°_{r\ (cell)} = E°_{r\ (cathode)} - E°_{r\ (anode)}$.
- By convention, standard half-cell potentials are written as reduction potentials. This indicates the tendency of a half-cell to undergo reduction.
- The value of the standard cell potential ($\Delta E°_{r\ (cell)}$) is positive if the cell reaction occurs spontaneously.

UNIT TASK BOOKMARK

Use what you have learned about standard cell potentials to choose the best components for your galvanic cell for the Unit Task outlined on page 684.

Questions

1. Why was it necessary to use the standard hydrogen half-cell as a reference? K/U
2. Describe how to predict the spontaneity of the redox reaction in a galvanic cell. K/U
3. Explain why the cell potential for an operating galvanic cell decreases over time but does not change from a positive value to a negative value. T/I A
4. The following half-reactions are combined in a galvanic cell. Write the net ionic equation and determine the standard cell potential for the cell. Assume that all the concentrations are 1.0 mol/L and all the partial pressures are 1.0 atm. K/U

   $Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq)\quad E°_r = 1.36\ V$

   $Br_2(g) + 2\ e^- \rightarrow 2\ Br^-(aq)\quad E°_r = 1.09\ V$

5. The following unbalanced equation shows the reactants and products that are involved in a galvanic cell: K/U T/I

   $Fe^{3+}(aq) + Mg(s) \longrightarrow Mg^{2+}(aq) + Fe^{2+}(aq)$

   (a) Write the anode half-reaction equation, the cathode half-reaction equation, and the net ionic equation. Assume that all the concentrations are 1.0 mol/L.
   (b) Calculate the standard cell potential for the overall cell reaction. (Refer to Table 1, page 646)

6. This equation provides information about a reaction that takes place in a galvanic cell:

   $2\ Ag^+(aq) + X(s) \rightarrow 2\ Ag(s) + X^{2+}(aq)\quad \Delta E°_r = 1.03\ V$

   Use reduction potentials from Table 1 (page 646) to determine the reduction potential for the half-cell involving X, and to identify X if possible. K/U

7. A student assembled and tested the cell potentials of three different galvanic cells. **Table 2** lists the student's observations. K/U T/I

Table 2 Cell Potential Data

Negative electrode	Positive electrode	$\Delta E°_{r\ (cell)}$(V)
$Pd(s) \mid Pd^{2+}(aq)$	$Cr_2O_7^{2-}(aq), H^+(aq) \mid C(s)$	$+ 0.28$
$Ti(s) \mid Ti^{2+}(aq)$	$Tl^+(aq) \mid Tl(s)$	$+1.29$
$Tl(s) \mid Tl^+(aq)$	$Pd^{2+}(aq) \mid Pd(s)$	$+1.29$

   (a) Determine the reduction potential for each half-cell. (You may look up the reduction potential for one half-cell reaction in Table 1, page 646.)
   (b) Using the given evidence, complete a table of relative strengths of oxidizing agents. Justify your prediction.

8. Predict whether each cell will react spontaneously. If it will, write the net ionic equation and determine the standard cell potential for the cell. T/I

   (a) $Mg(s) \mid Mg^{2+}(aq) \parallel Au^{3+}(aq) \mid Au(s)$
   (b) $Cu(s) \mid Cu^+(aq) \parallel Mg^{2+}(aq) \mid Mg(s)$
   (c) $Zn(s) \mid Zn^{2+}(aq) \parallel Sn^{2+}(aq) \mid Sn(s)$

Cells and Batteries

10.3

We use portable electronic devices, such as cellphones and laptops, almost everywhere (**Figure 1**). These devices require reliable, compact, and portable sources of electrical energy to keep them operating. The demand for portable energy has driven rapid advances in the design of cells and batteries.

Figure 1 The batteries for portable electronic devices must be small and lightweight, and they must last for several hours.

The Arrangement of Cells in Batteries

When cells are arranged in series, they are wired like beads in a necklace, with the anode (negative terminal) of one cell connected to the cathode (positive terminal) of the next cell (**Figure 2**). One end of the chain of cells is an anode, and the other end is a cathode. These ends form the terminals of the battery. A **battery** consists of two or more galvanic cells connected in series. Electron flow only occurs when a device that draws electrical energy is attached to the terminals. This explains why unused batteries still work after being stored for months.

battery a group of two or more galvanic cells connected in series

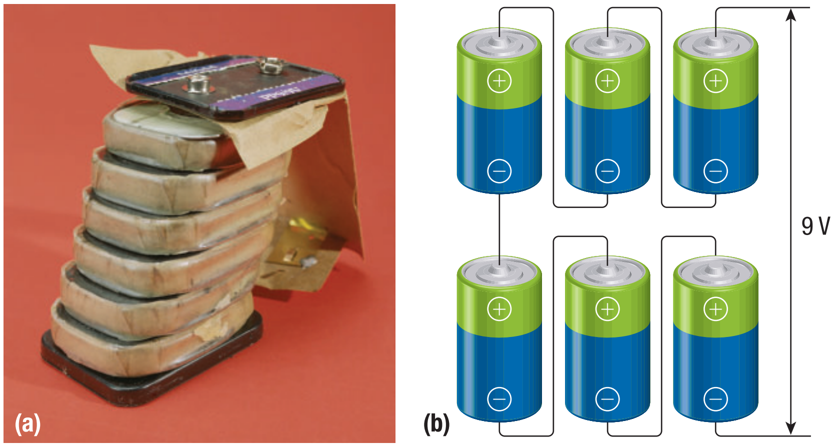


Figure 2 (a) Inside a 9 V battery are six 1.5 V cells wired in series. (b) The voltage of a battery is the sum of the voltages of the cells.

When cells are connected in series, the electric potential difference, or voltage, of the battery is the sum of the cell potentials of its cells (Figure 2(b)). The series arrangement of the six 1.5 V cells in Figure 2 gives the battery a voltage of 6 × 1.5 V, or 9 V. Recall that voltage is the ratio of the joules of energy per coulomb (1 V = 1 J/C). Because of the larger voltage, a 9 V battery transfers more electrical energy than each of its cells individually. This is why a light bulb attached to a 9 V battery glows more brightly than it would if it were attached to a single cell. Batteries with cells connected in series are ideal for devices with high energy demands, such as cordless power tools (**Figure 3**). CAREER LINK

Figure 3 Cordless power tools, such as this drill, use rechargeable batteries. The 18 V battery consists of six 3 V cells connected in series.

Primary and Secondary Cells

One important distinction among cells is whether they are rechargeable. A **primary cell** is a cell that cannot be recharged. A primary cell provides electrical energy until its reactants are used up. The redox reaction that releases electrical energy in a primary cell is not easily reversible. Primary cells are used in disposable batteries.

primary cell a cell that cannot be recharged

secondary cell a cell that can be recharged by being attached to an external source of electrical energy; recharging reverses the chemical reaction that generates the electrical energy

A cell that can be recharged is called a **secondary cell**. To recharge a secondary cell, an external source of electrical energy is used to reverse the redox reaction that is occurring in the cell. The recharging process regenerates the reactants.

Commercial Cells and Batteries

There are several different types of cells and batteries, each with a specific application. Although each is a source of electrical energy, the details of how this energy is provided determine which application is the most suitable.

ALKALINE DRY CELLS

Alkaline dry cells are one of the most common types of primary cells. They are tiny, lightweight, and long-lasting. They are used in many common devices, such as remote controllers for televisions, flashlights, and watches.

The anode of an alkaline dry cell consists of a paste, which contains zinc metal (**Figure 4**). (The alkaline dry cell gets its name from this "dry" paste. Other cells, discussed later in this section, contain a liquid electrolyte.) The electrolyte paste is surrounded by a cathode that contains solid manganese dioxide, $MnO_2(s)$. The anode and cathode chemicals are separated by a porous fabric. This material prevents the chemicals from coming in direct contact, while still allowing ion flow—much like a salt bridge.

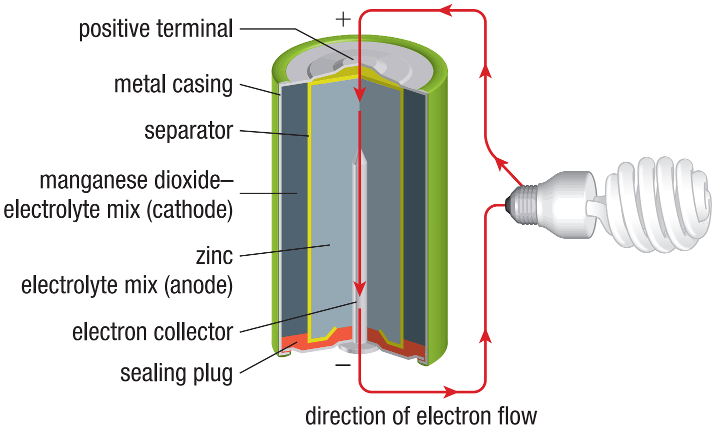


Figure 4 An alkaline dry cell has features that are common to most galvanic cells: separated anode and cathode compartments and electrolytes. Electron flow occurs only when the device that is attached to the cell is turned on, thus completing the circuit.

LEARNING **TIP**

Discharging and Charging
Discharging is a spontaneous process. Charging is a non-spontaneous process, which requires an external source of electrical energy. Discharging a battery is like allowing water to flow spontaneously from an open tap. Charging a battery is like pumping water uphill.

As the cell discharges (generates electrical energy), electrons are released as a result of oxidation. The electrons flow through the central collector. Then, they flow out of the cell via the negative terminal and through the device that requires the electrical energy. The electrons return via the positive terminal to the cathode, where they take part in the reduction half-reaction.

The equations for the half-cell reactions occurring as an alkaline dry cell discharges can be written as follows:

Anode half-reaction equation: $Zn(s) + 2\,OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2\,e^-$
Cathode half-reaction equation:

$$2\,MnO_2(s) + H_2O(l) + 2\,e^- \rightarrow Mn_2O_3(s) + 2\,OH^-(aq)$$

Alkaline dry cells contain strongly basic (alkaline) electrolytes, such as potassium hydroxide. This electrolyte makes the contents of these cells corrosive.

Lead Storage Batteries

The lead storage battery (or lead–acid battery) has been used in vehicles for almost 100 years. This durable battery can function for several years, through temperature extremes ranging from –30 °C to 50 °C and under constant punishment from rough roads. A typical car battery has six cells connected in series. Each cell contains multiple electrodes in the form of grids (**Figure 5**) and has a potential difference of approximately 2 V, giving a total battery potential of about 12 V.

Each cell in a lead storage battery consists of a lead cathode coated with lead(IV) oxide and a lead anode. The electrolyte is a concentrated solution of sulfuric acid. Because of the liquid electrolyte, this cell is known as a wet cell.

The electrode reaction equations can be written as follows:

Anode (oxidation) half-reaction equation:

$$\mathrm{Pb(s)} + \mathrm{HSO_4^-(aq)} \rightarrow \mathrm{PbSO_4(aq)} + \mathrm{H^+(aq)} + 2\,\mathrm{e^-}$$

Cathode (reduction) half-reaction equation:

$$\mathrm{PbO_2(s)} + \mathrm{HSO_4^-(aq)} + 3\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{PbSO_4(s)} + 2\,\mathrm{H_2O(l)}$$

Net ionic equation:

$$\mathrm{Pb(s)} + \mathrm{PbO_2(s)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{HSO_4^-(aq)} \xrightarrow{\text{discharging}} 2\,\mathrm{PbSO_4(s)} + 2\,\mathrm{H_2O(l)}$$

The net ionic equation represents the spontaneous discharging reaction of the battery.

Under normal driving conditions, an electrical device called an alternator continually recharges the battery in the vehicle. Electrical energy from the alternator makes the cell reaction proceed in the reverse direction:

Charging reaction:

$$2\,\mathrm{PbSO_4(s)} + 2\,\mathrm{H_2O(l)} \xrightarrow{\text{charging}} \mathrm{Pb(s)} + \mathrm{PbO_2(s)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{HSO_4^-(aq)}$$

A car with a "dead" battery can be "jump-started" by connecting its battery to a fully charged battery in another automobile using jumper cables, and then starting the engine (**Figure 6**). The "good" battery provides enough electrical energy to start the dead battery. This can be dangerous, however, because the applied current causes water in the dead battery to decompose and produce gaseous hydrogen and oxygen. Disconnecting the jumper cable after the disabled car starts may create a spark that can ignite the gaseous mixture. The battery may explode, ejecting corrosive sulfuric acid. This problem can be avoided by connecting the ground jumper cable to a part of the engine that is remote from the battery. Any spark that is produced when the ground jumper cable is disconnected will then be harmless. It is important to allow the engine to run for several minutes before disconnecting to recharge the dead battery fully.

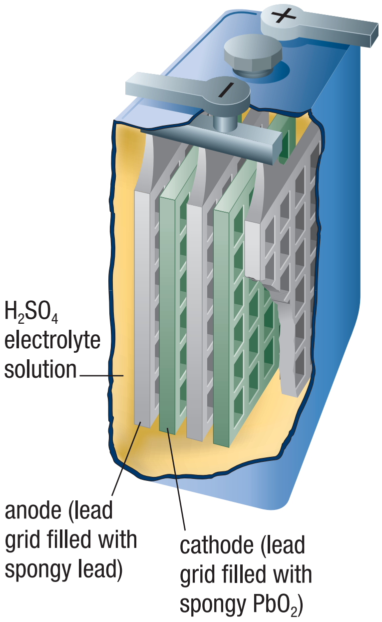


Figure 5 This diagram shows one of the six cells in a 12 V lead storage battery. The anode is filled with a type of lead called spongy lead. The cathode is filled with lead(IV) oxide. The battery also contains 38 % (by mass) sulfuric acid.

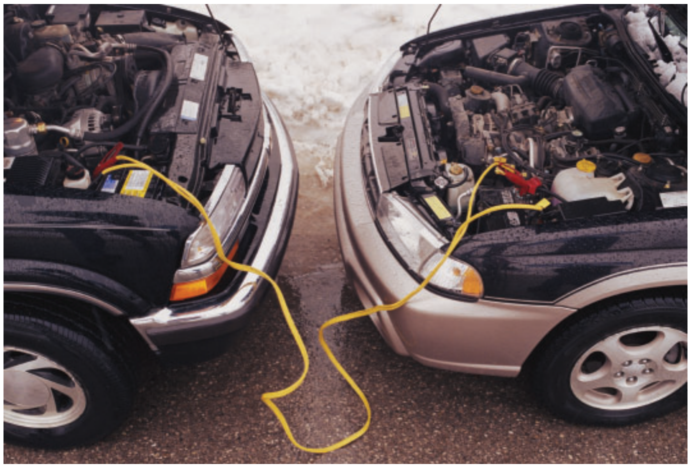


Figure 6 A jumper cable connects a vehicle's "dead" battery to a functioning battery to boost the vehicle back to life.

UNIT TASK BOOKMARK

What characteristics should your cell have, for the Unit Task outlined on page 684?

Although a lead storage battery does provide excellent service, it has a useful lifetime of about five years in a vehicle. While it might seem to have the ability to undergo an indefinite number of discharge/charge cycles, physical damage and chemical side-reactions eventually cause it to fail. Lead storage batteries contain toxic and corrosive ingredients, such as lead and sulfuric acid. Lead is a neurotoxin and can affect brain development and functioning. Sulfuric acid is highly corrosive and, if spilled, can lead to the release of toxic ions in the environment. Recycling of lead storage batteries is therefore important. According to Tonolli Canada Ltd., a leader in battery recycling, about 98 % of used car batteries in Ontario are successfully recycled. WEB LINK

LITHIUM-ION CELLS AND BATTERIES

Lithium-ion cells are one of the most popular types of secondary, or rechargeable, cells. Batteries made from these cells are commonly used in cordless tools, cellphones, laptops, and some electric cars (**Figure 7**). A lithium-ion cell may be cylindrical or rectangular. The outside of the cell is metal, with a pressure-sensitive vent hole. Inside the cell are several sheets of material that are pressed together. The sheets are arranged in sets of three: an anode, a cathode, and a separator. The separator sheet is made of porous plastic to allow ions to flow from one half-cell to the other.

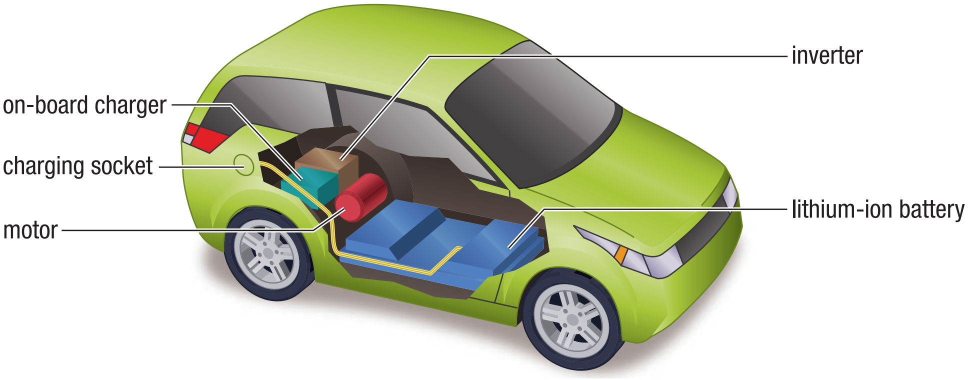


Figure 7 The energy for this electric car is supplied by a lithium-ion battery. The battery in an electric car may contain several thousand cells. By comparison, the battery in a laptop computer may contain only 12 cells.

The chemistry of lithium-ion cells is quite complex, and the composition of these cells varies a great deal. One of the more common designs has an anode of lithium metal, Li(s), mixed with graphite, C(s), and a cathode of metal oxide, such as cobalt (IV) oxide, $CoO_2(s)$. The electrolyte is a lithium compound, such as lithium bromide, dissolved in a polar organic solvent, $Li^+(solv)$.

Lithium-ion cells have several advantages over other types of cells. They have a larger cell potential than other cells. It can be as high as 3.7 V—more than double the cell potential of alkaline cells. This is a result of lithium being one of the strongest reducing agents on the standard reduction potentials table. Lithium is also the lightest metal on the periodic table. These features mean that a lithium-ion cell generates more energy per gram than most other cells, making it ideal for portable devices such as laptops and cellphones.

UNIT TASK BOOKMARK

How will your cell, constructed for the Unit Task outlined on page 684, compare to a commercial battery?

FUEL CELLS

fuel cell a galvanic cell for which the reactants are continuously supplied

Fuel cells are gaining attention in the media as a new energy source for vehicles. A **fuel cell** is a galvanic cell for which the reactants are continuously supplied. To show how fuel cells work, consider the exothermic redox reaction of methane with oxygen:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) + \text{energy}$$

This reaction is probably familiar: it is a complete combustion reaction. When it occurs in a furnace or a generator, the resulting energy is used to warm homes or run tools and appliances. However, in a fuel cell designed to use this reaction, the energy is used to produce an electric current. The electrons flow from the reducing agent, $CH_4(g)$, to the oxidizing agent, $O_2(g)$, through a conductor.

The U.S. space program has supported extensive research to develop fuel cells (**Figure 8**). NASA spacecraft have used hydrogen fuel cells for decades to generate electrical energy. As a hydrogen fuel cell operates, hydrogen and oxygen react to form water:

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$$

The half-reaction equations can be written as follows:

Anode half-reaction equation: $2\,H_2(g) + 4\,OH^-(aq) \rightarrow 4\,H_2O(l) + 4\,e^-$

Cathode half-reaction equation: $4\,e^- + O_2(g) + 2\,H_2O(l) \rightarrow 4\,OH^-(aq)$

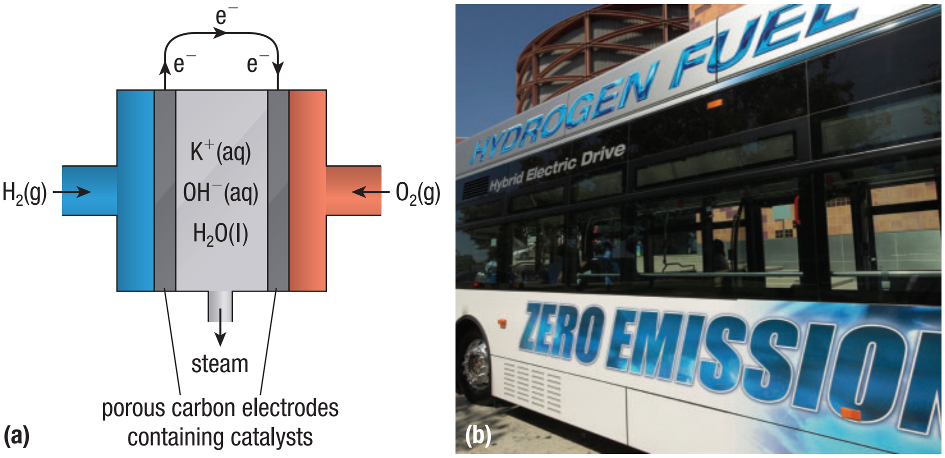


Figure 8 (a) A hydrogen–oxygen fuel cell is continually re-supplied with the reactant for the redox reaction. (b) During the 2010 Winter Olympics, visitors to Vancouver, British Columbia, were transported in buses with hydrogen fuel cells.

The hydrogen fuel cell designed for space vehicles weighs about 225 kg, but this is obviously not practical for general use as a source of portable energy.

In Ontario, fuel cells—particularly portable fuel cells—are heading toward commercialization. Many designs for hydrogen fuel cells currently use hydrocarbons as a source of hydrogen. Newer designs can use fuels such as methane and diesel directly, without having to produce hydrogen first.

At first glance, the hydrogen fuel cell appears to be the ideal way to eliminate air pollutants emitted by vehicles. The only waste product emitted by a hydrogen fuel cell is water vapour. However, several technical hurdles must be overcome before the widespread use of hydrogen-powered vehicles becomes a reality. For example, elemental hydrogen, $H_2(g)$, is quite rare in the atmosphere. Instead, it is found in compounds, such as water, $H_2O(l)$, and methane, $CH_4(g)$. These compounds must first be decomposed to liberate their hydrogen—a process that requires energy. Consequently, the hydrogen that is used in fuel cells is only as environmentally "clean" as the energy that was used to produce it. Other technical hurdles include the fact that hydrogen is highly explosive, and therefore difficult to store and transport safely in large quantities. CAREER LINK

10.3 Review

Summary

- A battery consists of two or more galvanic cells connected in series. The voltage of the battery is the sum of the voltages of the cells.
- Primary cells are non-rechargeable cells that run until their reactants are used up. Disposable batteries contain primary cells. Secondary cells can be recharged by the addition of electrical energy.
- Commercially available cells and batteries include the alkaline dry cell (a primary cell); the lead storage battery (a secondary battery commonly used in vehicles); the lithium-ion battery (a common secondary battery with many applications); the fuel cell (a galvanic cell receiving a continuous supply of reactants).

Questions

1. Draw a diagram that shows a battery made of three galvanic cells. How does the voltage of the battery compare with the voltage of its cells? K/U C
2. Compare and contrast the following terms. K/U
   (a) cell and battery
   (b) primary cell and secondary cell
3. Nickel metal hydride (NiMH) batteries were once used in power tools. A 14.4 V NiMH battery contains 12 cells connected in series. What is the voltage of each cell? T/I
4. **Figure 9** shows a clock that is operated with energy from two potatoes. K/U T/I C

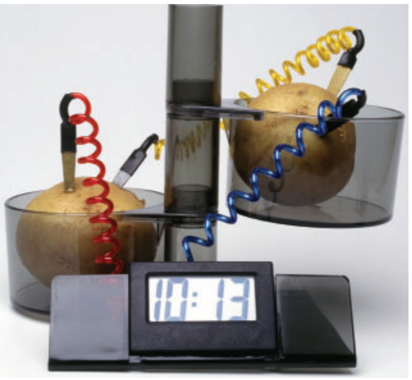


Figure 9 A potato “battery” with copper and steel (iron) electrodes

   (a) Use the terms “cell” and “battery” to describe the device in Figure 9.
   (b) Identify the anode and cathode in each cell.
   (c) Compare the voltage of one potato cell with the voltage of the two connected potatoes. Justify your answer.
   (d) What would happen if all four metal strips were made of copper? Explain.
   (e) Sketch a diagram that shows three potatoes connected in a similar way.
5. Both the alkaline dry cell and the lithium-ion cell have a component called a “separator.” K/U
   (a) What is the function of the separator?
   (b) Why must the separator be porous?
6. As lead storage batteries age, some of the lead(II) sulfate that is produced in the cathode reaction falls off the surface of the electrode to the bottom of the battery. Why do you think this might limit the life of the battery? K/U T/I A
7. Most batteries that are used in personal electronic equipment are secondary cells. A
   (a) Explain why secondary cells are appropriate for personal electronic equipment.
   (b) What other characteristics should the ideal battery for a camera have? Why?
8. One design of the lithium-ion cell uses lithium metal as the anode. Use the standard reduction potentials table to explain each of the following statements: K/U T/I A
   (a) An aqueous solvent cannot be used in this cell.
   (b) The potential for this cell is greater than the potential for a cell constructed using any other reducing agent.
9. Much of the world’s lithium supply comes from Chile. How might this affect the widespread use of lithium-ion batteries to supply energy for electric cars? A
10. Research the current status of vehicles powered by hydrogen fuel cells. T/I A
11. Research how fuel cells are being used as permanent energy sources for ground-based transportation and how fuels such as methane and diesel can be used directly as sources of chemical energy for fuel cells. Present your findings in a format of your choice. T/I A

WEB LINK

10.4 Explore an Issue in Electrochemistry

Pick Your Energy Source: Lithium or Hydrogen?

SKILLS MENU

- Defining the Issue
- Researching
- Identifying Alternatives
- Analyzing
- Defending a Decision
- Communicating
- Evaluating

Many automotive experts agree that the future of the gasoline-powered automobile is limited. Gasoline is becoming more and more expensive, and the world's oil deposits will someday be depleted. Also, the combustion of fossil fuels, such as gasoline, is a major source of air pollution and a major contributor to climate change.

So what is next? Two contenders as sources of energy for the future automobile are the lithium-ion battery and the hydrogen fuel cell. Each technology has significant benefits, drawbacks, and limitations. CAREER LINK

The Issue

You are an environmental consultant who has been hired by the manager of a fleet of 50 automobiles used by a parcel delivery company. The entire fleet must be replaced in five years by more economical and less polluting vehicles (**Figure 1**). Which technology best suits the company's needs: lithium-ion batteries or fuel cells? Is there a better alternative?

Figure 1 Would you rather drive a car that gets its energy from (a) a lithium-ion battery or (b) a hydrogen fuel cell?

Goal

To advise a parcel delivery company on the best choice of vehicle.

Research

SKILLS HANDBOOK A5

Research lithium-ion batteries and hydrogen fuel cells, as well as potential alternatives. The goal of your research is to provide the information that you will need to determine which technology best meets the needs of the company. Consider the following factors in your research:

- the availability of fuel or recharging stations
- the initial cost and the ongoing cost of repairs and maintenance
- tax breaks or incentives (Does the Canadian government provide tax breaks or incentives to owners of vehicles that have less environmental impact?)
- environmental impact of the vehicle (Which vehicle has the least environmental impact? What evidence can you find to support this?) WEB LINK

Possible Solutions

Compare the advantages and disadvantages of lithium-ion batteries and fuel cells as energy sources for delivery vehicles. Are there better alternatives to these technologies?

Decision

Review your research, and come to a decision that you can take to the manager.

Communicate

Prepare a report that you can present to a meeting of the company's board of directors for approval. You must be able to respond to any questions that the board members may have about your final decision.

Plan for **Action**

Write a commercial, create a website, or produce a brochure to encourage people to invest in the type of vehicle you have chosen.

Cold Fusion: The Discovery That Never Happened

SKILLS HANDBOOK A4

ABSTRACT

Nuclear fusion releases an enormous amount of energy. This energy could potentially be harnessed to generate electrical energy. So far, however, fusion only occurs at extremely high temperatures, such as the temperature in a star.

In 1989, chemists Martin Fleischmann and Stanley Pons claimed to have discovered an inexpensive way to conduct fusion at room temperature, using an electrochemical cell. If their so-called "cold fusion" process had been valid, it would have been the most important scientific discovery of the century. Caught up in the excitement of their "discovery," Fleischmann and Pons chose to release their preliminary findings to the public. The usual practice is to have scientific work checked by other scientists first. After Fleischmann and Pons released their findings, other research labs attempted to duplicate cold fusion using the same method, with little success.

What Is Nuclear Fusion?

Nuclear fusion is a process in which small atoms combine to form larger atoms. Fusion requires extremely high temperatures and pressures, such as those that occur in a star. These conditions overcome the repulsions of the hydrogen nuclei, allowing them to merge to form a heavier element, such as helium. In a typical fusion reaction, two isotopes of hydrogen, hydrogen-2 and hydrogen-3, combine to form an atom of helium and a neutron:

$$^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}\text{n}$$

Fusion is a very exothermic process. The energy that is emitted by stars, including the Sun, is released during fusion reactions.

Fusion is the opposite of fission. Fusion is the combining of atoms, whereas fission is the splitting of atoms. During fission, atoms of heavy elements, such as uranium, are bombarded with neutrons travelling at high speeds. When the neutrons collide with the uranium, the uranium nuclei break apart. Like fusion, fission is highly exothermic. Energy from the fission of uranium is used in nuclear power plants to generate electrical energy. One disadvantage of fission is that its waste is radioactive and requires long-term storage.

Fusion has the potential to be an ideal energy source. The hydrogen that is required for fusion is readily available in water. Fusion produces enormous amounts of energy—the fusion of the hydrogen atoms in one cup of water releases as much energy as the combustion of two tonnes of coal. Unlike fission or the combustion of fossil fuels, the products of fusion do not pose a threat to the environment.

Billions of dollars have already been spent on fusion research, but scientists have been unable to recreate fusion in a laboratory (**Figure 1**).

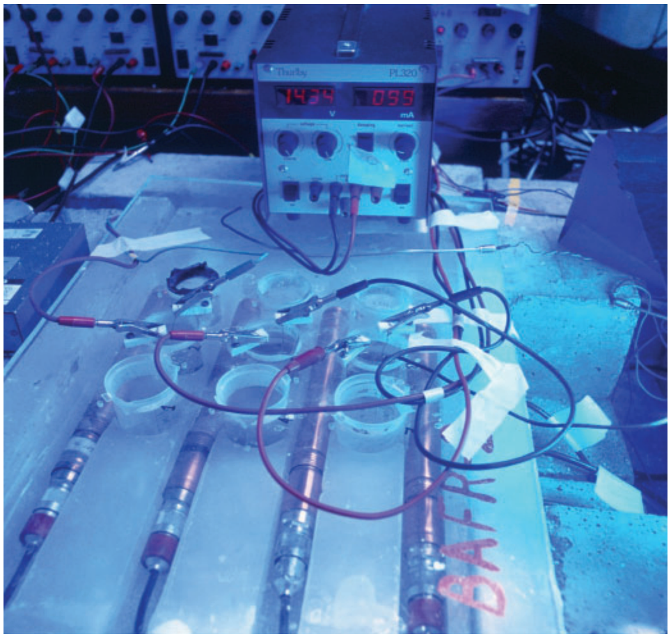


Figure 1 This experimental apparatus was used by the Physics Department at Birmingham University, U.K., in an attempt to replicate Fleischmann and Pons's "discovery."

What Is "Cold Fusion"?

In 1989, Martin Fleischmann and Stanley Pons, chemists at the University of Utah, claimed to have observed fusion occurring at room temperature. In their experiment, Fleischmann and Pons used a relatively inexpensive electrochemical cell to pass an electric current through heavy water. In heavy water, many of the water molecules include an isotope of hydrogen called deuterium, $^{2}_{1}\text{H}$. Fleischmann and Pons claimed that they detected an increase in the temperature of the water in the electrochemical cell, as well as some stray neutrons. According to Fleischmann and Pons, these observations could not be the result of an electrochemical process. They believed that the applied current forced deuterium atoms into the crystalline structure of the palladium electrode of the cell. There, the deuterium atoms were compressed until they underwent fusion. CAREER LINK

Fraud or Bad Science?

Scientific discoveries are usually first published in scientific journals for peer review (review by other experts in the field) before being announced to the public. However, peer reviews take time. Fleischmann and Pons were concerned that a competing researcher was about to announce the same discovery. Could they risk waiting to publish when cold fusion had the potential to be the most important discovery of the twentieth century? They would likely be recognized with a Nobel Prize for their work.

Finally, the intense pressure to be the first to publish their "discovery" convinced Fleischmann and Pons to bypass the peer review process and release their findings directly to the public. Soon after the release, other research labs attempted to replicate their work. This is an important part of testing new discoveries and theories. However, the other researchers announced that they were unable to obtain results that matched those of Fleischmann and Pons. The "discovery" was not supported by evidence. With this announcement, the promise of cold fusion soon fizzled back into science fiction.

Was the cold fusion fiasco fraud or just bad science? According to some science historians, Fleischmann and Pons did not intentionally lie to the scientific community. Instead, they were so convinced of the validity of their evidence and the need to get the news out that they took the risk of publishing prematurely. It was a gamble—and they lost!

Further Reading

Browne, M.W. (1989, May 3). Physicists debunk claim of a new kind of fusion. *The New York Times*.

Goldstein, D. (2010). *On fact and fraud: Cautionary tales from the front lines of science*. Princeton, N.J.: Princeton University Press.

10.5 Questions

1. Describe the process that Fleischmann and Pons used to try to create fusion. What makes their process different from other fusion processes? T/I
2. In your opinion, did Fleischmann and Pons commit fraud or just conduct bad science? Explain your reasoning. Provide information about the process of science to support your conclusion. Is it more or less likely that something similar could happen today? A
3. Billions of dollars have already been spent on fusion research, with very limited success. Billions more will be needed for the research to continue. Given the potential benefits of fusion, do you think this expenditure is warranted? T/I
4. Suppose that you were the head of the Chemistry Department at the University of Utah, where Fleischmann and Pons worked. If cold fusion had been valid, the discovery would have brought a great deal of recognition and millions of dollars of research grants to the university. T/I A
   (a) What advice would you have given Fleischmann and Pons: Make the announcement quickly, or wait for the peer review? Explain your reasoning.
   (b) Would you have recommended disciplinary action against Fleischmann and Pons after other scientists determined that cold fusion did not occur? Explain.

10.6 Corrosion

There are an estimated 9000 shipwrecks corroding on the seabed (**Figure 1**). About one-sixth of these vessels are oil tankers that were sunk during World War II. As the steel in the hulls of these ships corrodes, the oil will leak and pollute local ecosystems. In this section, you will examine corrosion, its causes, and how it can be prevented.

Figure 1 A diver peers through the rusty porthole of a sunken ship.

The Oxidation of Metals

corrosion the deterioration of a metal by a redox reaction

You can consider corrosion to be the process of metals returning to their natural state—the ores from which the metals were originally obtained. **Corrosion** can be defined as the breakdown or deterioration of a metal by a redox reaction. Since corroded metal often loses its strength and attractiveness, this spontaneous process has a great environmental and economic impact. Approximately one-fifth of the iron and steel that is produced annually is used to replace rusted metal. Although steel is infinitely recyclable, replacing corroded steel and iron uses additional resources and energy. WEB LINK

Figure 2 A freshly cut piece of sodium metal reacts almost instantly with oxygen to form dull-grey sodium oxide, $Na_2O(s)$.

Metals corrode because they oxidize easily. With the exception of gold, all the metals that are commonly used for structural and decorative purposes have standard reduction potentials below (less positive than) the reduction potential of oxygen gas. (Refer to the Standard Reduction Potentials table in Appendix B7.) When the half-reaction for any of these metals is reversed (to show the oxidation of the metal) and combined with the reduction half-reaction for oxygen, the result is a positive $E°_r$ value. Thus, the oxidation of most metals by oxygen is spontaneous. We cannot, however, tell from the reduction potential how fast the oxidation will occur (**Figure 2**).

Considering the large difference between the reduction potentials for oxygen and most metals, it is rather surprising that the problem of corrosion in air does not completely prevent us from using metals. With a reduction potential of −1.66 V, for example, aluminum should be easily oxidized by $O_2(g)$. Based on aluminum's low reduction potential, an aluminum airplane should dissolve in a rainstorm. Why, then, is this very active metal used as a structural material? The reason is due to a thin, adherent layer of aluminum oxide, $Al_2O_3(s)$, that forms on the surface of the aluminum. This layer protects the internal atoms from further oxidation. Iron also forms an oxide coating when exposed to oxygen in moist air. However, unlike the oxide that forms on aluminum, the resulting oxide does not adhere well to the underlying metal. As a result, the oxide flakes off and exposes new metal to corrosion. This is why iron and steel are so seriously affected by corrosion, or rust. CAREER LINK

Investigation **10.6.1**

Testing the Corrosion of Iron (page 674)

In this controlled experiment, you will test the effects of several factors on the corrosion of iron.

The corrosion products of "noble" metals, such as copper and silver, are complex and affect the use of these metals as decorative materials. Under normal atmospheric conditions, copper forms a layer of greenish copper carbonate (**Figure 3**). Silver tarnish is black silver sulfide, $Ag_2S(s)$. Gold does not corrode in air because it has a positive standard reduction potential of 1.50 V, greater than that of oxygen (1.23 V).

Figure 3 The green colour of copper carbonate, sometimes called verdigris, can be clearly seen on the copper rooftop of the Peace Tower at the Parliament Buildings in Ottawa.

Rusting: The Corrosion of Iron

Steel is a metal alloy that is composed mainly of iron, with a small percentage of carbon. Depending on the type of steel and the intended application, other small percentages of other elements are also included in the steel alloy, such as manganese, vanadium, chromium, and nickel. Stainless steel is an exception. Stainless steel may contain up to 18 % chromium and up to 10 % nickel.

Since steel is the main structural material for bridges, buildings, and automobiles, and iron is a large component of steel, controlling the corrosion of iron is extremely important. Instead of being a direct oxidation process, the processes that occur as iron corrodes are similar to those in a galvanic cell. The corrosion of iron is an electrochemical process (**Figure 4**).

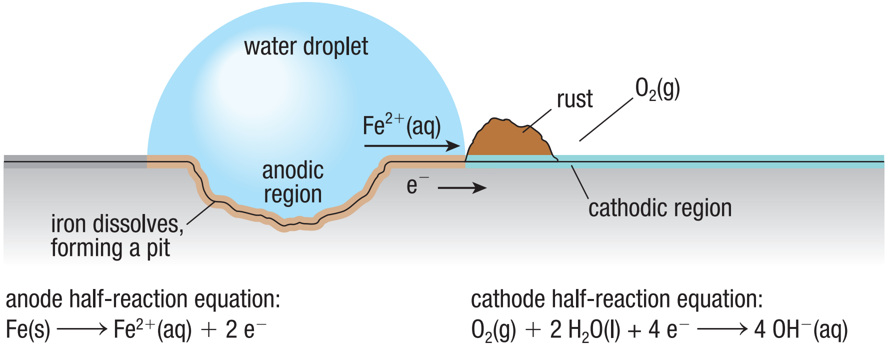


Figure 4 The electrochemical corrosion of iron

The chemical composition of steel is not quite homogeneous. It has a slightly non-uniform surface. As well, bending the steel causes physical strains and leaves stress points in it. The iron is more easily oxidized at these non-uniformities and stress points (anodic regions) than it is in other parts of the steel (cathodic regions). In an anodic region, each iron atom gives up two electrons to form an iron(II) ion:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-$$

The electrons that are released flow through the steel, as they do through the wire of a galvanic cell, to a cathodic region. At the cathodic region, they are involved in the reduction of oxygen:

$$O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$$

The iron(II) ions that are formed in the anodic region travel to the cathodic region through the moisture on the surface of the steel, just as ions travel through a salt bridge in a galvanic cell. In the cathodic region, iron(II) ions react with oxygen to form rust. Rust is a hydrated form of iron(III) oxide, $Fe_2O_3{\bullet}nH_2O(s)$, where n can vary depending on the conditions for the reaction.

Because of the migration of ions and electrons, rust often forms some distance away from where the iron was oxidized. The degree of hydration of the iron oxide affects the colour of the rust, which may vary from black to yellow to the familiar reddish brown.

The electrochemical nature of the corrosion of iron explains the importance of moisture in the corrosion process. Water is a reactant in the reduction half-reaction. It also acts much like a salt bridge in a galvanic cell, connecting the anodic and cathodic regions. Steel does not rust in dry conditions, which explains why vehicles remain corrosion-free in dry climates (**Figure 5**).

Figure 5 Hundreds of old airplanes are stored at this airplane graveyard in Arizona, U.S., until they can be stripped of any usable parts. The dry desert air prevents the airplanes from rusting.

Salt does not actually cause corrosion. However, salt definitely accelerates corrosion by providing ions—much like the salt bridge in a galvanic cell. Vehicle owners in regions of Canada where salt is used on roads to melt snow and ice are very aware of this fact. The severity of rusting is greatly increased because the dissolved salt on the moist steel surface increases the conductivity of the aqueous solution formed, and thus accelerates the electrochemical corrosion process.

Corrosion Prevention

Preventing corrosion is an important way to conserve energy and metals. The primary method of prevention is the application of a coating, such as paint, to protect the metal from oxygen and moisture. The metal remains protected as long as the coating remains intact. However, even a tiny pinhole in the coating could become a corrosion site.

galvanizing the process in which steel is coated with a thin layer of zinc to protect the steel from corrosion

Plating steel with other metals provides longer-lasting protection than painting. Chromium and tin are often used to plate steel because they oxidize to form a durable, effective oxide coating. In a process called **galvanizing**, zinc is also used to coat steel. Zinc forms a mixed oxide–carbonate coating (**Figure 6**).

Since zinc is a more active metal than iron, any oxidation that occurs involves zinc rather than iron. Consider the reduction half-reaction potentials for iron and zinc:

$$\mathrm{Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)} \quad E^\circ_{\mathrm{r}} = -0.44\ \mathrm{V}$$

$$\mathrm{Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)} \quad E^\circ_{\mathrm{r}} = -0.76\ \mathrm{V}$$

Recall that the strongest reducing agents are near the bottom of the right side of the standard reduction potentials table. Therefore, zinc is a stronger reducing agent than iron, so it is oxidized before iron. Once zinc is oxidized, its oxide–carbonate coating clings tightly to the iron beneath it, isolating iron from the environment. Unlike painting, galvanizing continues to provide corrosion protection even if the metal surface is scratched.

Alloying, the process of combining two or more metals, is also used to prevent corrosion. Stainless steel, as noted earlier, contains chromium and nickel. Both of these metals form oxide coatings that help the steel resist corrosion. In some applications, such as surgical implants, it is critical that the metals do not corrode (**Figure 7**).

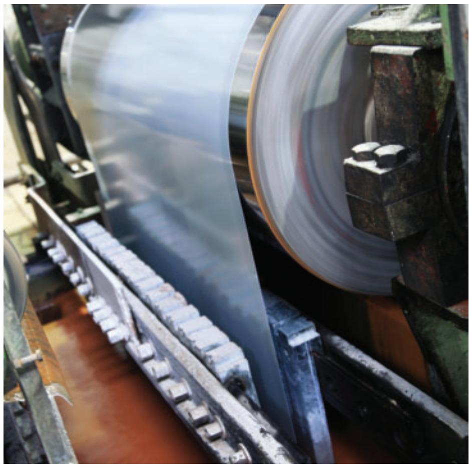


Figure 6 Steel is galvanized by rolling it through a solution of zinc ions. As electricity is passed through the solution, zinc is deposited on the surface of the steel, galvanizing it.

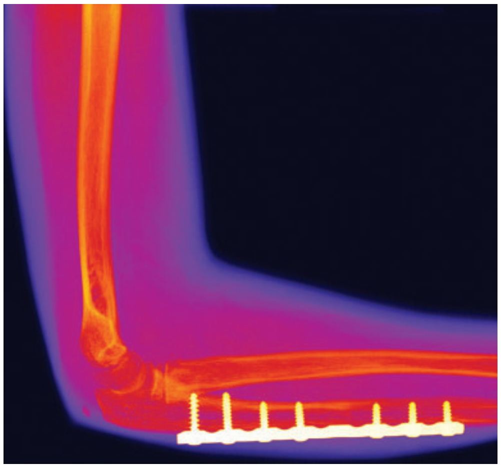


Figure 7 This coloured X-ray image of an arm shows how the ulna was repaired using a surgical-steel implant secured with screws.

cathodic protection a form of corrosion prevention in which electrons are continually supplied to the metal that is being protected, making the metal a cathode

Cathodic protection is the most common form of corrosion prevention for steel in buried fuel tanks and pipelines. The two methods that are used to provide cathodic protection are the sacrificial anode (active metal) method and the impressed current method. Both methods work the same way—by supplying the metal to be protected with electrons so that it cannot be oxidized. As a result, the metal becomes the cathode of the corrosion cell.

The **sacrificial anode** method involves attaching a more active metal, such as magnesium, to the steel. The active metal is connected by a wire to the pipeline or tank that needs to be protected (**Figure 8(a)**). This method may be used in your home to protect the water heater from corrosion. Since the magnesium is a better reducing agent than iron, electrons are supplied by the magnesium rather than the iron, keeping the iron from being oxidized. As oxidation occurs, the magnesium anode is used up, so it must be replaced periodically. The hull of a ship may be protected in a similar way, by attaching bars of zinc to the steel hull. In salt water, the zinc acts as the anode and is oxidized instead of the steel hull (the cathode).

sacrificial anode a form of cathodic protection in which the oxidation of a more active metal that is attached to the steel prevents the iron in the steel from being oxidized

The **impressed current** method involves attaching the object to be protected to the negative terminal of a DC power supply (**Figure 8(b)**). An inert electrode, such as graphite, is attached to the positive terminal. When the power is turned on, electrons are pumped into the steel object, making it the cathode of the cell. As long as the steel object is receiving electrons, it cannot be oxidized. Impressed current is often used for structures that are too large to make the use of the sacrificial anode economically feasible. For example, many of Canada's oil and natural gas pipelines are protected using impressed current.

impressed current a form of cathodic protection in which electrons from a DC power source are pumped into the metal that is being protected

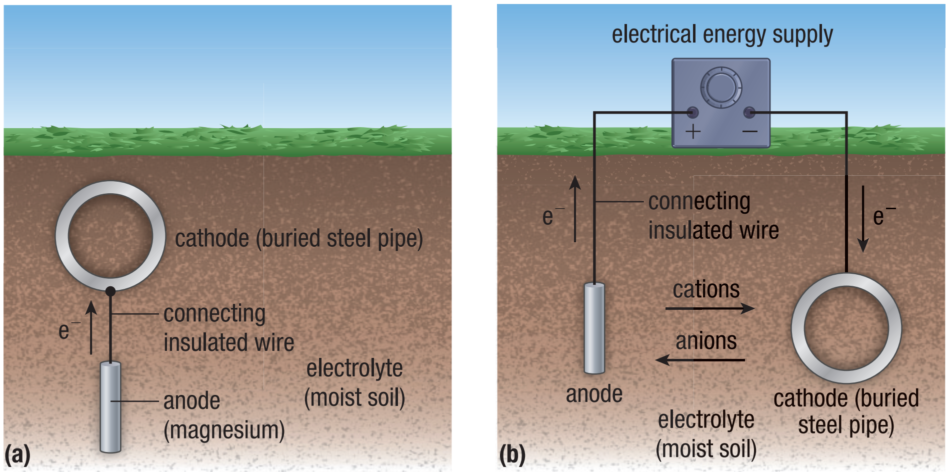


Figure 8 Two methods of cathodic protection that can be used to reduce the corrosion of a buried pipeline by supplying electrons: (a) attaching a sacrificial anode and (b) impressing a current

Research This

Corrosion and Health

Skills: Researching, Defining the Issue, Identifying Alternatives, Defending a Decision

SKILLS HANDBOOK A5.1

Prior to 1960, builders frequently used lead in home construction and decoration. At the time, it was considered a safe and practical material, with many useful applications. Lead has since been linked to several health problems. Many owners of older homes would like to remove the source(s) of lead contamination. In practice, however, this may not always be a viable or economical option.

1. Research sources of lead contamination in older homes.
2. Research the health risks associated with exposure to lead.

A. What are the most likely places where lead may be encountered in a home? K/U

B. How does lead from these places enter the human body? K/U

C. What effects can lead have on a person? Are certain segments of the population more vulnerable to the negative effects of lead? Explain. K/U

D. Why is lead removal sometimes impractical? K/U A

E. Other than removing the lead altogether, what other treatments or processes can be used to reduce human exposure to lead in an older home? K/U A

F. Given that lead was once thought to be safe and is now known to cause health problems, what steps would you recommend to ensure the safety of the materials used in home construction today? Why? K/U A

WEB LINK

10.6 Review

Summary

- Corrosion is the breakdown or deterioration of a metal by a redox reaction.
- Most metals spontaneously corrode when exposed to oxygen and water.
- Dissolved salt allows corrosion to occur faster, but it does not cause corrosion.
- A corroding piece of iron is similar to a galvanic cell. Oxygen is reduced at the cathodic region, and iron is oxidized at the anodic region. Electrons travel through the metal from anode to cathode, while dissolved ions travel through the water to maintain neutrality.
- Corrosion prevention methods include coating with paint or a corrosion-resistant metal layer, such as galvanizing with zinc; using corrosion-resistant alloys; and using cathodic protection (with a sacrificial anode or an impressed current).

Questions

1. Use Table 1 in Appendix B7 to answer the following questions. K/U T/I
   (a) Which metal, zinc or tin, best protects iron against corrosion?
   (b) Why does iron corrode readily in acidic solutions, while gold and silver do not?
2. What substances must be present for iron to corrode? K/U
3. (a) Rank the following metals in terms of their tendency to oxidize, based on your knowledge of the metals and their uses in everyday life: gold, zinc, magnesium, iron.
   (b) Rank the metals in Part (a) using a redox table. Try to account for any differences from your ranking in Part (a). T/I A
4. Why do many Canadians have the underside of their cars sprayed with oil before each winter? T/I A
5. Explain why galvanized steel nails are suitable for exterior use, while regular steel nails are not. T/I A
6. (a) Use a Venn diagram to compare the mechanisms by which sacrificial anodes and impressed current prevent corrosion.
   (b) What do you think is a significant limitation for the use of impressed current to protect a steel structure from corrosion? K/U C A
7. To investigate the effects of corrosion, steel nails were exposed to different conditions in four test tubes:

   Test tube A: steel nails in water and air

   Test tube B: steel nails in a drying agent

   Test tube C: steel nails in distilled water and oil

   Test tube D: steel nails in salt water

   Figure 9 shows the results of the investigation. Explain why some of the nails had evidence of corrosion, while others did not. T/I

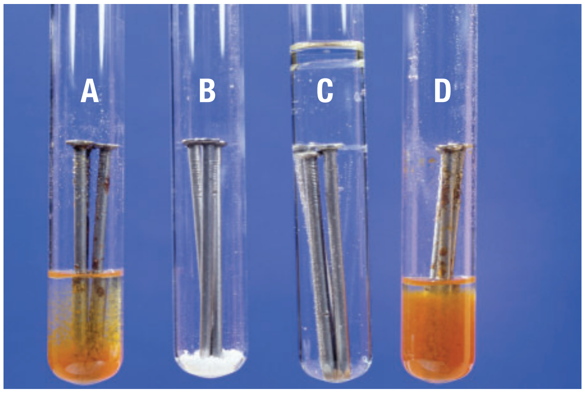


Figure 9 Testing corrosion under different conditions

8. What are rusticles, and how are they formed? Why are they a cause for concern among scientists? Research "rusticles from the sunken hull of the *Titanic*" to find articles that answer these questions. T/I

WEB LINK

Electrolysis

10.7

As discussed in Section 10.6, corrosion is the outcome of a spontaneous redox reaction. An impressed current (one method that is used to provide cathodic protection) can stop corrosion by reversing the spontaneous corrosion reaction and driving it in the non-spontaneous direction. An impressed current passes an electric current through the structure being protected, such as a pipeline. An external electrical source supplies the current.

Other non-spontaneous redox reactions can be forced to occur in a similar way. One example is recharging the secondary cells in a battery. A battery uses a spontaneous redox reaction to produce an electric current. Recharging a battery involves applying an external energy source to drive the redox reaction in the reverse, non-spontaneous direction. For example, a lead storage battery in a car can be recharged by applying a current to it (**Figure 1**). In this section, you will learn how some useful non-spontaneous reactions can be forced to occur. Many of these reactions have important consumer and industrial applications.

Figure 1 A car with a "dead" battery can be restarted by connecting the dead battery to a working battery. It is important to follow the manufacturer's directions when setting up jumper cables. Otherwise, a spark might cause the hydrogen gas that is produced to explode.

Electrolytic Cells

A galvanic cell produces a current when an oxidation–reduction reaction happens spontaneously. Another kind of cell, called an **electrolytic cell**, uses a current from an outside source to make an electrolytic reaction occur. In a process called **electrolysis**, the current is forced through the cell to produce a chemical change for which the cell potential is negative. That is, electrical energy causes an otherwise non-spontaneous chemical reaction to occur. Electrolysis has great practical importance. For example, electrolysis is used to recharge a battery, produce aluminum metal, and cover objects with a layer of chrome.

electrolytic cell a cell that uses electrical energy to produce a chemical change that would not occur spontaneously

electrolysis the application of current through a cell to produce a chemical change

Figure 2 shows the differences between a galvanic cell and an electrolytic cell. The galvanic cell (Figure 2(a)) runs spontaneously to produce 1.10 V.

Anode half-reaction equation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$

Cathode half-reaction equation: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$

Figure 2(b) shows an external energy source forcing electrons through the cell in the direction opposite to that shown in Figure 2(a). This requires an external potential greater than 1.10 V, because the external potential must be applied in opposition to the natural cell potential. The device in Figure 2(b) is an electrolytic cell. Notice that the anode and the cathode are reversed in Figures 2(a) and 2(b). In a galvanic cell, zinc is the anode. In an electrolytic cell, copper is the anode. Also, ions flow through the salt bridge in opposite directions in the two cells.

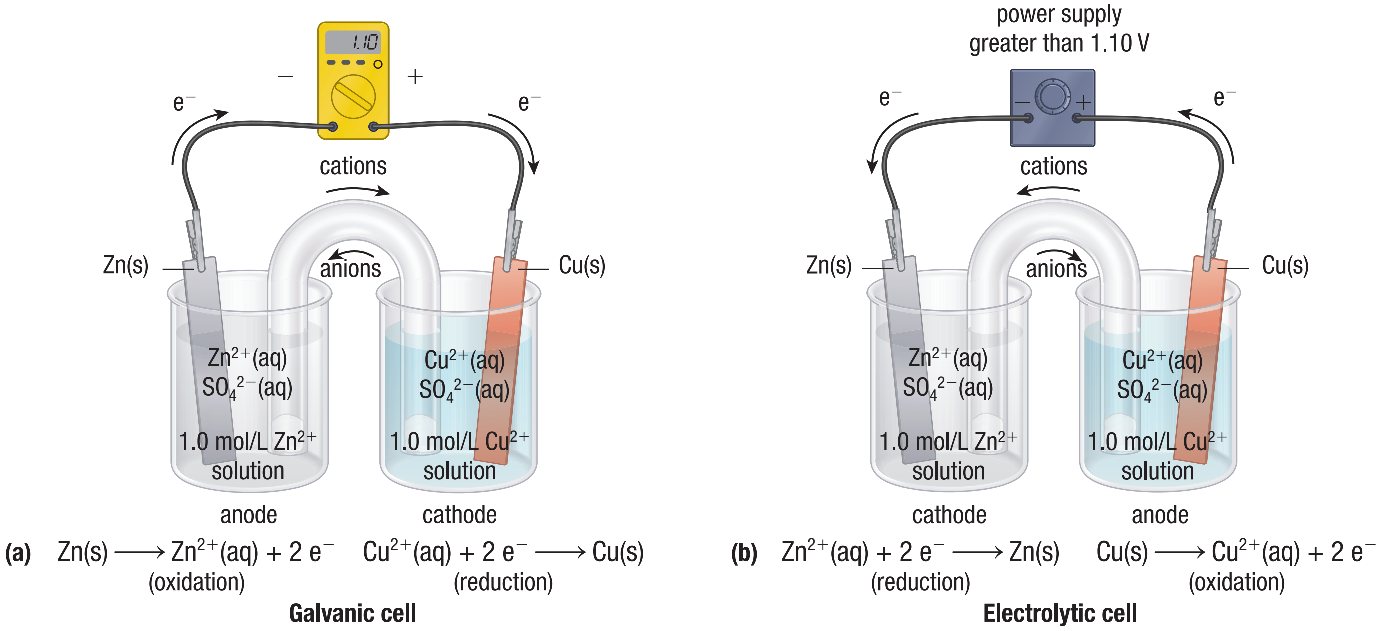


Figure 2 (a) A galvanic cell produces a current from a spontaneous redox reaction:
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
(b) An electrolytic cell requires a power source to drive the opposite, non-spontaneous reaction:
$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$

Electrolysis of Water

In Section 10.3, you learned that the reaction in which hydrogen and oxygen combine spontaneously to form water can be used to produce an electric current in a fuel cell. The reverse reaction is non-spontaneous and is an example of electrolysis. Electric current must be supplied to carry out the electrolysis of water. During electrolysis, water is oxidized at the anode and reduced at the cathode. Therefore, water is both the oxidizing agent and the reducing agent in this reaction. Only two equations in Table 1, Appendix B7, involve just water as an oxidizing agent or a reducing agent:

$$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(l) \quad E°_r = +1.23\ V$$
$$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq) \quad E°_r = -0.83\ V$$

Note that the water in these two equations forms an upward diagonal to the right. This means that the electrolysis reaction is non-spontaneous. However, we can force it to occur by applying a current. The reaction equations can be written as follows:

Anode half-reaction equation: $2\ \text{H}_2\text{O(l)} \rightarrow \text{O}_2\text{(g)} + 4\ \text{H}^+\text{(aq)} + 4\ \text{e}^-$

Cathode half-reaction equation: $4\ \text{H}_2\text{O(l)} + 4\ \text{e}^- \rightarrow 2\ \text{H}_2\text{(g)} + 4\ \text{OH}^-\text{(aq)}$

[multiply by 2 to balance electrons]

Net ionic equation: $$6\ \text{H}_2\text{O(l)} \rightarrow 2\ \text{H}_2\text{(g)} + \text{O}_2\text{(g)} + \underbrace{4\ \text{H}^+\text{(aq)} + 4\ \text{OH}^-\text{(aq)}}_{4\ \text{H}_2\text{O(l)}}$$

or $$2\ \text{H}_2\text{O(l)} \rightarrow 2\ \text{H}_2\text{(g)} + \text{O}_2\text{(g)}$$

The standard cell potential for the electrolysis of water can be determined using the same equation that is used for galvanic cells:

$$\begin{aligned}\Delta E^\circ_{\text{r (cell)}} &= E^\circ_{\text{r (cathode)}} - E^\circ_{\text{r (anode)}}\\ &= -0.83\ \text{V} - (+1.23\ \text{V})\\ \Delta E^\circ_{\text{r (cell)}} &= -2.06\ \text{V}\end{aligned}$$

If you tried to electrolyze pure water by using platinum electrodes connected to a 6 V battery, you would observe no reaction. This is because pure water contains so few ions that almost no current can flow. However, dissolving even a small amount of an electrolyte, such as a soluble salt or a strong acid, in the water causes the immediate production of bubbles of hydrogen and oxygen (**Figure 3**). The electrolysis of water supplies oxygen to submarine crews and to astronauts in the International Space Station.

Figure 3 The electrolysis of water produces hydrogen gas at the cathode (on the right) and oxygen at the anode (on the left). Note that twice as much hydrogen as oxygen is produced.

Comparing Galvanic and Electrolytic Cells

A galvanic cell and an electrolytic cell are both types of **electrochemical cell**. They have some characteristics in common and some differences. The main characteristics of galvanic cells and electrolytic cells are compared in **Table 1**.

electrochemical cell a general term that is used to refer to both a galvanic cell and an electrolytic cell

A galvanic cell converts chemical energy into electrical energy through a spontaneous chemical reaction that takes place at the electrodes. Oxidation occurs at the anode, giving the anode a negative charge. Reduction occurs at the cathode, giving the cathode a positive charge. A wire connects the anode and the cathode, allowing electrons to move from the anode to the cathode. The electrodes are also connected by a salt bridge or a similar ionic conductor, which permits ions to flow between them. The flow of ions prevents a charge from building up in one of the electrodes. Since the redox reaction that takes place in a galvanic cell is spontaneous, a galvanic cell can be used as an energy source for an electrical device.

In contrast, an electrolytic cell requires an external energy source to operate. The basis for an electrolytic cell is a non-spontaneous redox reaction. Therefore, energy must be provided to drive the reaction. Like a galvanic cell, an electrolytic cell has an anode (the site of oxidation) and a cathode (the site of reduction). Electrons leave the anode along the wire, pass through the source of electrical energy, and travel to the cathode.

Table 1 Comparison of Galvanic and Electrolytic Cells

<table>
<tr><th>Galvanic cell</th><th>Electrolytic cell</th></tr>
<tr><td>involves a spontaneous redox reaction</td><td>involves a non-spontaneous redox reaction</td></tr>
<tr><td>produces electrical energy</td><td>requires electrical energy to drive the reaction</td></tr>
<tr><td>uses a salt bridge to prevent a charge buildup</td><td>may or may not use a salt bridge</td></tr>
<tr><td>results in oxidation at the anode and reduction at the cathode</td><td>results in oxidation at the anode and reduction at the cathode</td></tr>
<tr><td colspan="2">The electrode that would be the anode of a galvanic cell is the cathode of an electrolytic cell.</td></tr>
<tr><td colspan="2">The electrode that would be the cathode of a galvanic cell is the anode of an electrolytic cell.</td></tr>
</table>

Commercial Electrolytic Processes

An important characteristic of metals is their ability to donate electrons (become oxidized) to form ions. Since metals are usually good reducing agents, most are found in nature in ores. Ores are mixtures of ionic compounds, which often contain oxide, sulfide, and silicate anions. The noble metals, such as gold, silver, and platinum, are more difficult to oxidize and are more often found as pure metals.

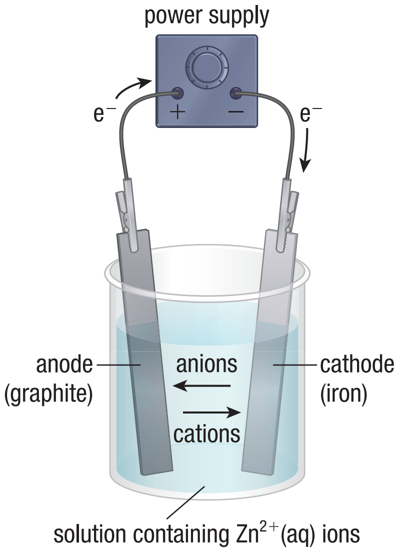


Figure 4 A model of the electrolytic cell that is used industrially to electroplate zinc onto iron

Electrolysis of Aqueous Solutions

Many industries use electrolytic cells. One important application of electrolysis involves plating one metal onto another metal. For example, in Section 10.6 you learned that an effective way to prevent iron from corroding is to coat it with zinc. In this process, called galvanizing, the metal object to be plated is made the cathode of the electrolytic cell by attaching it to the positive terminal of the electrical energy supply (**Figure 4**). An inert electrode, such as graphite, is often used as the anode. The electrodes are then placed in an aqueous solution that contains cations of the metal to be plated onto the cathode.

For galvanizing, a zinc sulfate solution is used. As the cell operates, a shiny layer of zinc precipitates onto the iron cathode. Bubbles of oxygen rise from the anode, suggesting that the water is oxidized. The reaction equations are given below:

Anode half-reaction equation: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$

Cathode half-reaction equation: $2\ Zn^{2+}(aq) + 4\ e^- \rightarrow 2\ Zn(s)$

[multiply by 2 to balance electrons]

Net ionic equation: $2\ H_2O(l) + 2\ Zn^{2+}(aq) \rightarrow 2\ Zn(s) + \underbrace{O_2(g) + 4\ H^+(aq)}_{4\ H_2O(l)}$

The standard cell potential for this cell is

$$\Delta E^\circ_{r\ (cell)} = -0.76\ V - (+1.23\ V)$$

$$\Delta E^\circ_{r\ (cell)} = -1.99\ V$$

In practice, a potential difference of more than 1.99 V must be applied for zinc to plate onto iron.

Mini **Investigation**

Pencil Electrolysis

Skills: Performing, Observing, Analyzing

SKILLS HANDBOOK A1

In this investigation, you will use electrical energy to make a non-spontaneous reaction occur. The graphite in pencil "lead" serves as the electrode for both anode and cathode half-reactions.

Equipment and Materials: chemical safety goggles; lab apron; Petri dish; 2 small pencils sharpened at both ends; 2 connecting wires with alligator clips; 9 V battery; 0.5 mol/L potassium iodide, KI(aq); dropper bottle of phenolphthalein indicator

1. Put on your chemical safety goggles and lab apron.
2. Half-fill the Petri dish with the potassium iodide solution.
3. Add about 10 drops of phenolphthalein to the solution.
4. Place one end of each pencil in the dish. Keep the pencils far apart from each other.
5. Use the connecting wires to connect the dry end of each pencil to a terminal on the battery.
6. After about 30 s, disconnect the pencils from the battery.
7. Look for evidence of chemical change. Remove each pencil, and check for an odour.
8. Dispose of the contents of the dish according to your teacher's instructions.

A. Identify the anode and the cathode of this cell. T/I

B. What evidence of chemical change did you observe while the pencils were connected? T/I

C. Based on your evidence, predict the identity of one substance that was produced at the anode and one substance that was produced at the cathode. Justify your predictions. T/I

Aluminum Production

Since aluminum is a very active metal, it occurs naturally as an oxide in an ore called bauxite. The production of aluminum metal from its ore proved to be more difficult than the production of most other metals. In 1854, a process for producing metallic aluminum using sodium was discovered. However, aluminum remained extremely expensive.

In 1886, Charles M. Hall in the United States and Paul Héroult in France almost simultaneously discovered a practical electrolytic process for producing aluminum. The key factor in the Hall–Héroult process is the use of molten cryolite, $Na_3AlF_6(l)$, as the solvent for the aluminum oxide (also called alumina). Today, aluminum is relatively inexpensive and has a wide variety of applications, such as building materials (**Figure 5**).

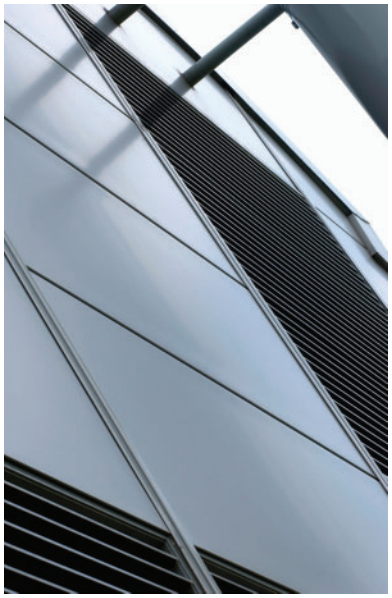


Figure 5 The low mass, the lustre, and the corrosion resistance of aluminum make it a useful material for cladding the outsides of buildings.

Electrolysis is possible only if ions can move to the electrodes. A common method for making ions mobile is to dissolve the substance to be electrolyzed in water. However, water cannot be used for the electrolysis of the aluminum salt because water is more easily reduced than aluminum ions:

$$2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + OH^-(aq) \quad E°_r = -0.83\text{ V}$$

$$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s) \quad E°_r = -1.66\text{ V}$$

Thus, aluminum metal cannot be plated out of an aqueous solution of aluminum ions.

Generally, ions can be made mobile by melting the salt. However, the melting point of aluminum oxide, Al_2O_3, is much too high (2050 °C) for electrolysis of the molten oxide to be practical. A mixture of aluminum oxide and cryolite, however, has a melting point of 1000 °C, and the resulting molten mixture can be electrolyzed to obtain aluminum metal. As a result of the Hall–Héroult discovery, the price of aluminum plunged and its widespread use became economically feasible. The industrial production of aluminum still uses the Hall–Héroult process.

Bauxite is not pure aluminum oxide. It also contains oxides of iron, silicon, and titanium, along with various silicate materials. To obtain the pure hydrated aluminum oxide, $Al_2O_3 \cdot nH_2O$, the bauxite is treated with aqueous sodium hydroxide. Aluminum oxide is amphoteric and thus reacts in a basic solution:

$$Al_2O_3(s) + 2\,OH^-(aq) \rightarrow 2\,AlO_2^-(aq) + H_2O(l)$$

The other metal oxides, which are basic, remain as solids. (Recall Section 8.6.) The solution that contains the aluminate ion, $AlO_2^-(aq)$, is separated from the sludge of the other oxides and is acidified with carbon dioxide gas, causing the hydrated alumina to re-form:

$$2\,CO_2(g) + 2\,AlO_2^-(aq) + (n + 1)H_2O(l) \rightarrow 2\,HCO_3^-(aq) + Al_2O_3 \cdot nH_2O(s)$$

Then, the purified aluminum oxide is mixed with cryolite, Na_3AlF_6, and melted at about 1000 °C. The dissociated aluminum ions are reduced to aluminum metal in an electrolytic cell (**Figure 6**).

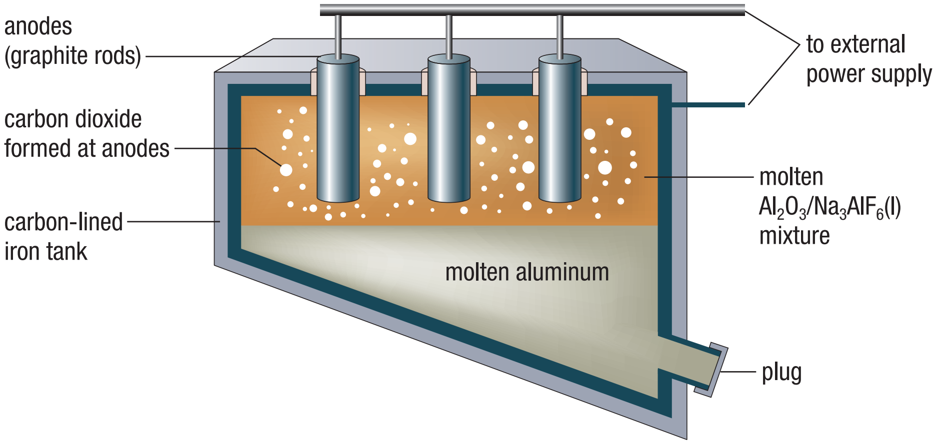


Figure 6 This electrolytic cell is used to produce aluminum by the Hall–Héroult process. Since molten aluminum is denser than the molten mixture of cryolite and alumina, the metal settles to the bottom of the cell and is drawn off periodically.

The electrolyte solution in the Hall-Héroult cell includes many different ions that contain aluminum, so the chemistry is not completely clear. However, aluminum oxide probably reacts with the cryolite anion:

$$Al_2O_3(s) + 4\ AlF_6^{3-}(l) \rightarrow 3\ Al_2OF_6^{2-}(l) + 6\ F^-(l)$$

The following half-cell reactions are also thought to occur:

Cathode half-reaction equation: $AlF_6^{3-}(l) + 3\ e^- \rightarrow Al(s) + 6\ F^-(l)$

Anode half-reaction equation:

$$2\ Al_2OF_6^{2-}(l) + 12\ F^-(l) + C(s) \rightarrow 4\ AlF_6^{3-}(l) + CO_2(g) + 4\ e^-$$

The overall cell reaction equation can be written as

$$2\ Al_2O_3(s) + 3\ C(s) \rightarrow 4\ Al(s) + 3\ CO_2(g)$$

The aluminum produced in this electrolytic process is 99.5 % pure.

Most applications of aluminum use alloys that include other metals. For example, to be useful as a structural material, aluminum is alloyed with metals such as zinc (for trailer and aircraft construction) and manganese (for cooking utensils, storage tanks, and highway signs).

Unfortunately, the production of aluminum has negative effects on the environment. Since a great deal of energy is consumed during the process of aluminum refining, aluminum production contributes to greenhouse gas emissions, such as perfluorocarbons (PFCs), polycyclic aromatic hydrocarbon (PAH), fluoride, $F^-(aq)$, sulfur dioxide, $SO_2(g)$, and carbon dioxide, $CO_2(g)$. Placing aluminum smelting plants near renewable sources of electrical energy, such as waterfalls, reduces the emissions from electricity production. However, the consumption of the carbon electrodes during the electrolytic process also produces PAH and carbon dioxide.

Recycling used aluminum requires only about 5 % of the energy that is used to make new aluminum. Effective recycling programs not only reduce manufacturing costs, but also reduce the harmful emissions associated with producing aluminum.

Electrorefining Metals

The purification of metals is another important application of electrolysis. Impure copper from the chemical reduction of copper ore is cast into large slabs that serve as the anodes for electrolytic cells. Aqueous copper sulfate is the electrolyte. Thin sheets of ultrapure copper function as the cathodes (**Figure 7**). When a potential difference is applied across the electrodes, only copper is deposited on these cathodes. All the

Figure 7 Ultrapure copper sheets, which serve as the cathodes of an electrolytic cell, are lowered between slabs of impure copper, which serve as the anodes. It takes about four weeks for the anodes to dissolve and for the pure copper to be deposited on the cathodes.

other impurities are left as sludge in the cell. Ultrapure copper is important for the production of semiconductors and other electronic components.

The main anode half-reaction equation can be written as follows:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

Other metals, such as zinc and iron, are also oxidized from the impure anode:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^- \text{ and } Fe(s) \rightarrow Fe^{2+} + 2e^-$$

Noble metal impurities in the anode, such as silver, gold, and platinum, are not oxidized at the voltage used. They fall to the bottom of the cell to form a sludge, which is then processed to remove them. The copper(II) ions from the solution are reduced and deposited onto the cathode:

Anode half-reaction equation: $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$

This process produces copper metal that is 99.95 % pure. High-purity gold is also produced by electrorefining.

Electroplating Metals

Metals that readily corrode can often be protected by applying a thin coating, or "plating," of a metal that resists corrosion. Examples are "tin" cans (which are actually steel cans with a thin coating of tin), chrome-plated steel car bumpers, and silver-plated jewellery and decorative items.

An object can be plated by making it the cathode in a tank that contains ions of the plating metal. Silver plating is an example of this electrolytic process (**Figure 8**). The silver plating solution contains ions that form complexes with the silver ion. By lowering the concentration of available silver ions, a smooth, even coating of silver forms over the surface of the object (**Figure 9**). CAREER LINK

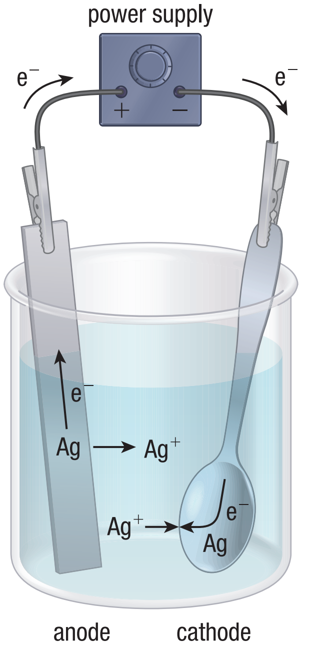


Figure 8 In an electroplating cell, the item to be plated (the spoon) is the cathode and a silver bar is the anode. Silver is plated out at the cathode:
$Ag^+(aq) + e^- \rightarrow Ag(s)$
Note that a salt bridge is not needed because silver ions are involved at both electrodes.

Figure 9 Silver plating is often used to beautify and protect cutlery and tableware, such as this elegant tea set.

Metal plating processes have brought many benefits but also pose a range of environmental concerns. Heavy metals, such as chromium, lead, and cadmium, are used in these processes. Cyanide is a poisonous compound that is used in plating baths. The release of any of these toxic metals or their ions into the environment can cause serious health problems for organisms and persistent damage to ecosystems.

10.7 Review

Summary

- Electrolysis involves forcing a current through a cell to cause a non-spontaneous redox reaction to occur.
- Electrolytic and galvanic cells are both electrochemical cells. They contain an anode where oxidation occurs and a cathode where reduction occurs.
- An electrolytic cell, unlike a galvanic cell, requires an external energy source and involves a non-spontaneous redox reaction rather than a spontaneous redox reaction.
- Industrial applications of electrolysis include the electrolysis of water and other aqueous solutions, as well as recharging batteries, producing aluminum, electrorefining metals, and electroplating.

Questions

1. Explain, using a graphic organizer of your choice, the differences between a galvanic cell and an electrolytic cell. Refer to type of reaction and energy flow. K/U
2. Describe a consumer product that contains a galvanic cell or battery and is sometimes used as part of an electrolytic cell. A
3. Predict the half-reaction that will take place at the cathode and anode when each salt is melted and electrolyzed. T/I
   (a) $NiBr_2(l)$
   (b) $AlF_3(l)$
   (c) $MnI_2(l)$
4. Explain why aluminum recycling can be good for both business and the environment. T/I
5. A steel ring can be electroplated with gold in an aqueous solution that contains gold(III) ions. Sketch and label a diagram of a cell that could be used to produce gold-plated steel. Identify the anode and the cathode in the cell. Indicate the direction of electron flow. T/I
6. Draw a diagram of a process that can be used to electroplate copper onto a steel object, such as a coin. Include in your diagram suggested electrodes, the ions in solution, power supply and connectors, the sign of the electrodes, and the direction of electron and ion flow. T/I C
7. During the electrolysis of a tin(II) chloride solution, $SnCl_2(aq)$, a silver-coloured metal, is deposited onto the cathode. Bubbles of a gas are observed at the anode. A bleach-like odour is detected. Use a redox table to predict the anode, the cathode, and the net ionic equation. T/I C
8. An electrolytic cell is set up using inert electrodes in an aqueous copper(II) sulfate solution. After an hour of electrolysis, the solution is tested. The concentration of copper(II) ions has decreased, while the concentration of hydrogen ions has increased. The mass of one electrode has also increased. Explain these observations using the half-reaction equation for each electrode. T/I
9. Consider the equations for the anode and cathode half-reactions for the Hall–Héroult process, given in this section. T/I A
   (a) Combine these two equations to determine the overall cell reaction equation.
   (b) Combine your answer in (a) with the equation for the reaction of aluminum oxide with the cryolite ion, $AlF_6^{3-}(l)$, to give the overall equation for the production of aluminum:
   $2\ Al_2O_3(s) + 3\ C(s) \rightarrow 4\ Al(s) + 3\ CO_2(g)$
10. Research and explain the steps involved in removing tarnish from a silver object using aluminum foil and baking soda. Include the equation for the chemical reaction. T/I
11. Electroplating companies use a variety of hazardous substances. Research answers to the following questions, and summarize your findings in a brief report: T/I A C
    - What environmental hazards are associated with the electroplating industry?
    - What health and safety hazards are associated with the waste that is generated by electroplating companies?
    - What steps do electroplating companies take to minimize any negative health or environmental effects of their industry?

WEB LINK

CHAPTER 10 Investigations

Investigation 10.1.1 OBSERVATIONAL STUDY

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Investigating Galvanic Cells

In this investigation, you will test three different cell designs. Your goal is to determine which cell design produces the highest voltage. To make your comparison fair, you will use the same electrodes and electrolytes for all three designs.

Purpose

To determine which cell design results in the greatest voltage

Equipment and Materials

- chemical safety goggles
- lab apron
- protective gloves
- 4 medium-sized beakers or a well plate
- U-tube
- voltmeter
- connecting leads
- zinc and copper strips
- emery paper
- cotton plugs
- tap water
- solutions (0.1 mol/L) of
  - potassium sulfate, $K_2SO_4(aq)$
  - copper(II) sulfate, $CuSO_4(aq)$
  - zinc sulfate, $ZnSO_4(aq)$

Copper(II) sulfate is toxic and an irritant. Avoid skin and eye contact. If you spill copper(II) sulfate solution on your skin, wash the affected area immediately with plenty of cool water. Report any spills to your teacher.

Procedure

SKILLS HANDBOOK A1, A2.3

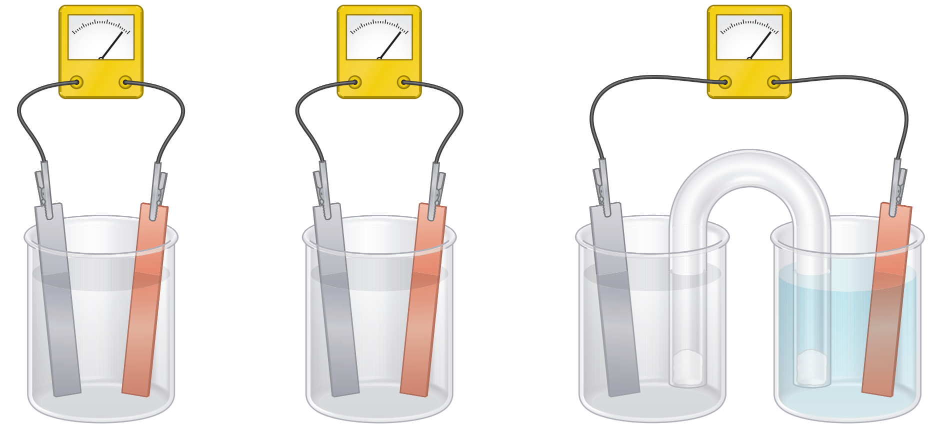
1. Put on your chemical safety goggles, lab apron, and protective gloves.
2. Construct the three galvanic cells shown in **Figure 1**. Use tap water for cell (a). Follow your teacher's instructions for filling the U-tube in cell (c). Keep the electrodes as clean as possible.
3. Connect the voltmeter to each cell, in turn, so that the cell potential has a positive value. Record the cell potential.
4. Investigate the effect of removing the salt bridge on the cell potential in cell (c).

Observations

Create a data table to record your observations.

Analyze and Evaluate

(a) What were the manipulated variables in this investigation? What were the responding variables? Which variables were held constant? T/I



(a) Zn(s) | $H_2O(l)$ | Cu(s) **(b)** Zn(s) | $K_2SO_4(aq)$ | Cu(s) **(c)** Zn(s) | $ZnSO_4(aq)$ || $CuSO_4(aq)$ | Cu(s)

Figure 1 Three different galvanic cell designs

(b) Which cell design produced the highest voltage? T/I

(c) Which cell design produced the lowest voltage? Explain. T/I

(d) Predict the effect of replacing tap water with distilled water on the potential for cell (a). Justify your prediction. T/I

(e) Why do you think all the solutions that you used in this investigation are sulfates? T/I

(f) Identify the anode and the cathode. Justify your choices. T/I

(g) What effect did removing the salt bridge have on the cell potential? Explain. T/I

Apply and Extend

(h) Design an investigation to test the effect of decreasing the cation concentration on cell potential in cell (c). (*Hint*: Add an appropriate precipitating agent to one half-cell and then the other.) Have your design approved by your teacher, then perform the investigation. T/I

(i) Provide an explanation for your observations in (h). T/I

Investigation 10.2.1 CONTROLLED EXPERIMENT

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Constructing a Galvanic Cell

In this investigation, you will determine the effects of the materials used to construct a cell on the cell potential. The cell you will construct has a simple yet unusual design.

Testable Question

Which combination of electrode and electrolyte, when combined in a galvanic cell with an aluminum electrode, gives the greatest cell potential?

Hypothesis

SKILLS HANDBOOK A2.2

Write a hypothesis to predict which of the available electrodes will result in the greatest cell potential. Justify your prediction.

Variables

Read the procedure, and identify the manipulated and responding variables in Part A and Part B. Identify the variables that must be controlled.

Experimental Design

An aluminum pop can serves a dual purpose as the container and as one of the electrodes in this investigation (**Figure 1**). Other electrodes will be tested to discover which electrode results in the highest cell potential. When the best electrode has been selected, a variety of electrolytes (a salt solution, an acidic solution, and a basic solution) will be tested to discover which electrolyte results in the highest cell potential.

Equipment and Materials

- chemical safety goggles
- lab apron
- protective gloves
- voltmeter
- connecting leads with alligator clips
- one empty aluminum pop can with the top removed
- graphite, iron, magnesium, zinc, and copper electrodes
- emery paper
- solutions (0.1 mol/L) of
  - hydrochloric acid, HCl(aq)
  - sodium hydroxide, NaOH(aq)
  - sodium chloride, NaCl(aq)

The acids and bases that are used in this investigation are corrosive. Avoid skin and eye contact. In case of contact, wash the affected area immediately with plenty of cool water. Report any spills to your teacher.

Procedure

SKILLS HANDBOOK A1

Part A: Testing Electrodes

1. Put on your chemical safety goggles, lab apron, and protective gloves.
2. The aluminum can is one of the electrodes in **Figure 1**. To enable the connecting wire to make contact, scrape some of the paint off the can.

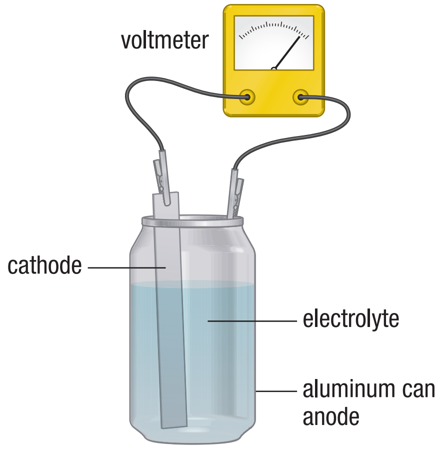


Figure 1 A pop-can cell

3. Use the sodium chloride solution as the electrolyte and the aluminum can as one electrode. Test each possible electrode (in the materials list), in turn, to determine which electrode produces a cell with the greatest cell potential. Keep the electrodes as clean as possible.

Part B: Testing Electrolytes

4. Use the electrode that produced the greatest cell potential in Step 3. Test each of the three solutions (in the materials list), in turn, to determine which electrolyte produces a cell with the greatest cell potential.
5. Dispose of the solutions as directed by your teacher.

Observations

Create data tables to record your observations in Part A and Part B.

Analyze and Evaluate

(a) Which electrode combination produced the greatest cell potential? T/I

(b) Which electrolyte produced the greatest cell potential? T/I

(c) Answer the testable question. T/I

(d) Which variables were measured/recorded and/or manipulated in this experiment? Which variables were held constant? T/I

(e) Using standard reduction potentials, calculate the theoretical (expected) voltage for each cell that you tested. Determine the percentage difference between your experimental value and the theoretical voltage. Account for any differences. T/I

(f) Identify any sources of error in this investigation. What effect could each source of error have on the voltage of the cell? T/I

(g) How suitable is the pop-can cell for commercial development? Consider a variety of factors in your analysis. T/I A

Apply and Extend

(h) Design and (with your teacher's approval) construct a battery by connecting two pop cans in series. Measure and record its voltage. What effect does the cell arrangement have on voltage? T/I

Investigation 10.2.2 CONTROLLED EXPERIMENT

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Investigating Cell Potentials

In this investigation, you will construct galvanic cells using magnesium, zinc, iron, and copper half-cells (**Figure 1**). Then, you will compare the observed cell potential for each cell you constructed with the theoretical cell potential, as predicted using Table 1 in Appendix B7.

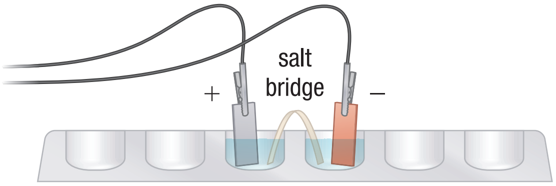


Figure 1 A galvanic cell in a well plate

Testable Question

What are the standard cell potentials of all the cells that can be constructed using the magnesium, zinc, iron, and copper half-cells?

Prediction

SKILLS HANDBOOK A2.2

In a table, list all the galvanic cells that can be constructed using the four half-cells above. Use a redox table to predict the cell potential for each cell. Predict the identity of the anode and cathode in each cell.

Variables

Record the manipulated, responding, and controlled variables for this investigation.

Experimental Design

You will measure the cell potential for each galvanic cell you construct and compare this cell potential with the theoretical cell potential, as predicted in a redox table.

Equipment and Materials

- chemical safety goggles
- lab apron
- protective gloves
- well plate
- tweezers
- voltmeter
- connecting leads
- strips of magnesium, zinc, iron, and copper metal
- emery paper
- strip of filter paper soaked in potassium sulfate solution, $K_2SO_4(aq)$ (1.0 mol/L)
- solutions (0.1 mol/L) of
  - magnesium sulfate, $MgSO_4(aq)$
  - zinc sulfate, $ZnSO_4(aq)$
  - iron(II) sulfate, $FeSO_4(aq)$
  - copper(II) sulfate, $CuSO_4(aq)$

Copper(II) sulfate is toxic and an irritant. The other solutions are irritants. Avoid skin and eye contact. If you spill copper(II) sulfate on your skin, wash the affected area immediately with plenty of cool water. Report any spills to your teacher.

Procedure

SKILLS HANDBOOK A1

1. Put on your chemical safety goggles, lab apron, and protective gloves.
2. Clean the metal strips thoroughly with emery paper.
3. Construct each half-cell using four adjacent wells of the well plate, as shown in Figure 1.
4. Use tweezers to link two half-cells with a filter-paper strip, which acts as a salt bridge.
5. Use the voltmeter reading to determine the anode and the cathode of the cell. Measure the cell potential for the first two half-cells. Record your observations.
6. Dispose of the salt bridge after use.
7. Repeat Steps 4 and 5 for the remaining half-cell combinations.
8. Collect or dispose of the solutions as directed by your teacher.

Analyze and Evaluate

(a) Summarize your observations in a well-organized data table. Use cell notation to describe each cell in your table. C

(b) Answer the testable question. T/I

(c) Identify the manipulated, responding, and controlled variables in this investigation. T/I

(d) Identify the anode and the cathode for each cell in your data table. T/I

(e) Write the half-reaction equations and the net ionic equation for each cell reaction. T/I

(f) A 5 % difference between observed and predicted data is often unavoidable, due to the limitations of an experiment or the materials used. Using this criterion, is the agreement between the observed and predicted cell potentials acceptable? T/I

(g) What sources of error could account for any differences you observed? T/I

(h) If you had not cleaned the metals, how do you think this would have affected the observed cell potentials? Justify your reasoning. T/I

Apply and Extend

(i) Suppose that the magnesium half-cell had been selected as the reference standard half-cell instead of the standard hydrogen half-cell. If the reduction potential for the magnesium half-cell is considered to be 0 V, use your observations to predict the standard reduction potentials of the zinc, iron, and copper half-cells relative to the magnesium half-cell. T/I

(j) Use your predicted reduction potentials in (i) to predict the cell potential for the following cell:

$Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Cu^{2+}(aq)\ |Cu(s)$

Compare your predicted cell potential with your observed potential. Is this difference acceptable? Justify your answer. T/I

Investigation 10.6.1 CONTROLLED EXPERIMENT

SKILLS MENU

- Questioning
- Researching
- Hypothesizing
- Predicting
- Planning
- Controlling Variables
- Performing
- Observing
- Analyzing
- Evaluating
- Communicating

Testing the Corrosion of Iron

Recall, from Section 10.6, that corrosion is a complex electrochemical process. The corrosion of iron begins with the oxidation of iron to iron(II) ions. The oxidizing agent can vary. For example, oxygen can act as the oxidizing agent for neutral or basic solutions, according to the following half-reaction:

$$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$$

Diagnostic tests, such as those shown in **Figure 1**, can be used to detect the presence of hydroxide ions and iron(II) ions. Potassium hexacyanoferrate(III) can be used as an indicator, since it changes from yellow to blue when iron(II) ions are present. Phenolphthalein changes from colourless to pink when hydroxide ions are present.

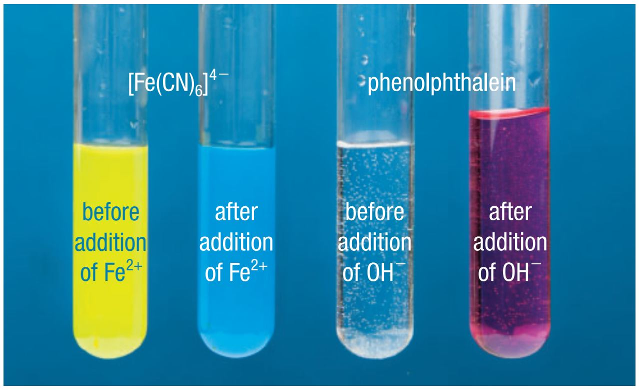


Figure 1 Diagnostic tests for Fe^{2+} and OH^- ions

In this investigation, you will design mini investigations to answer three testable questions. The list of equipment and materials will help you decide how to design your mini investigations. Be sure to include a control in each mini investigation.

Testable Questions

(a) How does the pH of the electrolyte affect corrosion?

(b) How does the presence of both oxygen and water affect corrosion?

(c) How does contact with other metals affect corrosion?

Prediction

SKILLS HANDBOOK A2.2

Predict how each variable in each testable question will affect corrosion. Record your predictions.

Variables

Record the independent variable, the dependent variable, and the control for each part of this investigation.

Experimental Design

You will design a procedure to answer each testable question using the equipment and materials provided.

Equipment and Materials

- chemical safety goggles
- lab apron
- protective gloves
- cleaned nails
- test tubes
- test-tube rack
- stoppers
- dropper bottle solutions of
  - phenolphthalein indicator
  - potassium hexacyanoferrate(III) indicator
- 10 mL of each of the following solutions (0.1 mol/L):
  - sodium chloride, NaCl(aq)
  - hydrochloric acid, HCl(aq)
  - sodium hydroxide, NaOH(aq)
- tap water
- freshly boiled tap water from your teacher's kettle (to remove dissolved oxygen)
- copper wire
- strips of magnesium ribbon

Phenolphthalein is flammable. Keep it away from open flames.

Hydrochloric acid and sodium hydroxide solutions are corrosive. If you spill either of these solutions on your skin, wash the affected area immediately with plenty of cool water. Report any spills to your teacher.

Procedure

SKILLS HANDBOOK A1

1. Study the list of equipment and materials. Design a mini investigation to answer each testable question using the equipment and materials. Include a control in each mini investigation. Specify safety precautions.
2. Once they are approved, conduct your mini investigations.

Observations

Create a data table to record your observations.

Analyze and Evaluate

(a) Determine the variables that were manipulated in each mini investigation. T/I

(b) Which variables were controlled? T/I

(c) Provide an answer to the testable question for each mini investigation. Include evidence that supports your answer. T/I

(d) Evaluate your procedure for each mini investigation. If you were to repeat the investigations, what would you do differently to improve your results? T/I

(e) Why was it necessary to design a control for each mini investigation? K/U

Apply and Extend

(f) A graphite electrode and a nail are immersed in a sodium sulfate solution, $Na_2SO_4(aq)$. The two electrodes are attached to a direct-current energy supply. Design an investigation to determine the effect of the connection (positive or negative) on the rate of corrosion. Outline diagnostic tests to detect the reaction products. T/I

CHAPTER 10 SUMMARY

Summary Questions

1. Review the Key Concepts on page 634. "Unpack" each concept, and list all the sub-ideas you need to know in order to understand it fully. Include diagrams and at least one example of each concept in action in your "unpacking" of the concept.
2. Look back at the Starting Points questions on page 634. Answer these questions again, based on what you have learned in the chapter. Then review your original answers. Complete the following statement for each question: "At first I thought . . . but now I know . . . "

Vocabulary

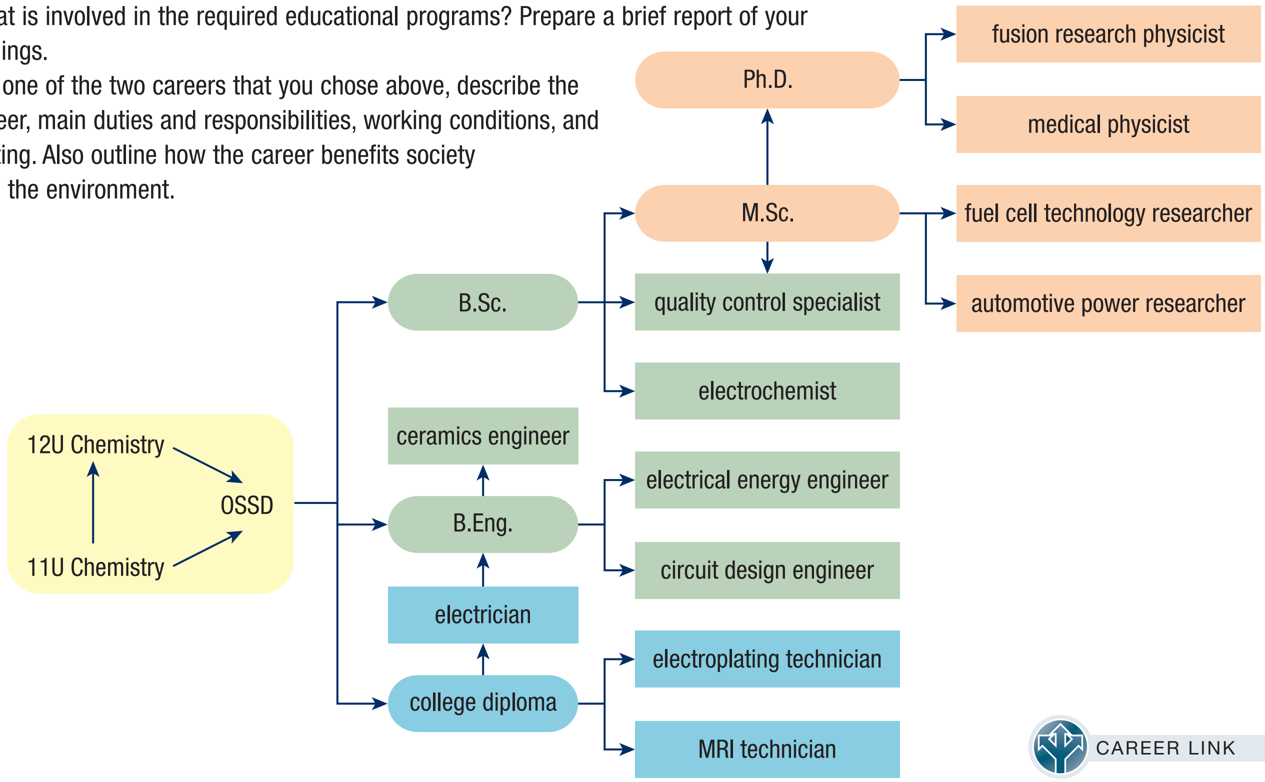
half-cell (p. 636)
electrode (p. 636)
cell (p. 636)
salt bridge (p. 637)
galvanic cell (p. 638)
anode (p. 638)
cathode (p. 638)
cell potential (p. 642)
standard cell (p. 643)
standard cell potential ($\Delta E^\circ_{\text{r (cell)}}$) (p. 643)
standard reduction potential (E°_{r}) (p. 643)
standard hydrogen half-cell (p. 643)
battery (p. 649)
primary cell (p. 649)
secondary cell (p. 650)
fuel cell (p. 652)
corrosion (p. 658)
galvanizing (p. 660)
cathodic protection (p. 660)
sacrificial anode (p. 661)
impressed current (p. 661)
electrolytic cell (p. 663)
electrolysis (p. 663)
electrochemical cell (p. 665)

CAREER PATHWAYS

SKILLS HANDBOOK A7

Grade 12 Chemistry can lead to a wide range of careers. Some require a college diploma or a B.Sc. degree. Others require specialized or postgraduate degrees. This graphic organizer shows a few pathways to careers mentioned in this chapter.

1. Select two careers related to Electrochemical Cells that you find interesting. Research the educational pathways that you would need to follow to pursue these careers. What is involved in the required educational programs? Prepare a brief report of your findings.
2. For one of the two careers that you chose above, describe the career, main duties and responsibilities, working conditions, and setting. Also outline how the career benefits society and the environment.



CAREER LINK

CHAPTER 10 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. The essential components of a galvanic cell are
   (a) two different metals and an electrolyte
   (b) two identical metals and an electrolyte
   (c) two different metals and two different electrolytes
   (d) two different metals and distilled water (10.1) K/U
2. Which statement best describes the route of electrons in a galvanic cell? (10.1) K/U
   (a) Electrons flow through the solution from the anode to the cathode.
   (b) Electrons flow through the solution from the cathode to the anode.
   (c) Electrons flow through a wire from the cathode to the anode.
   (d) Electrons flow through a wire from the anode to the cathode.
3. Why must many galvanic cells have a salt bridge in order to function? (10.1) K/U
   (a) Salt bridges conduct electrons from the anode to the cathode.
   (b) Salt bridges transfer ions between the half-cells.
   (c) Salt bridges keep electrodes from coming into contact with each other.
   (d) Salt bridges provide for standard conditions.
4. What is the value of $\Delta E^\circ_{\text{r (cell)}}$ for the cell with the following overall reaction equation?
   $Fe(s) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn(s)$ (10.2) T/I
   (a) $+0.30$ V
   (b) -0.30 V
   (c) $+0.58$ V
   (d) -0.58 V
5. A 9 V battery is most likely
   (a) 6 cells, each 1.5 V, joined in series
   (b) 9 cells, each 1 V, joined in parallel
   (c) a single cell with a large reduction potential
   (d) used in automobiles (10.3) K/U
6. Which of the following accelerates the corrosion of iron? (10.5) K/U
   (a) warm, dry climates
   (b) lack of oxygen
   (c) water
   (d) paint or oil coatings
7. Which of the following is true of the cathodic protection of iron? (10.6) K/U
   (a) Iron is the anode of the cell.
   (b) Iron is the cathode of the cell.
   (c) Iron is no longer a part of the cell.
   (d) Iron atoms cannot lose electrons.
8. Which process occurs at the cathode, in an electrolytic cell? (10.7) K/U
   (a) Metal atoms become ions.
   (b) Metal ions are reduced.
   (c) Anions lose electrons.
   (d) The electrode loses mass.
9. Which of the following statements describes how an electrolytic cell differs from a galvanic cell? (10.7) K/U
   (a) Electrolytic cells require electrodes.
   (b) Electrolytic cells use a redox reaction.
   (c) Electrolytic cells have a commercial use.
   (d) Electrolytic cells require a source of energy.

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

10. Oxidation of a substance corresponds to losing electrons. (10.1) K/U
11. An oxidizing agent loses electrons and causes another substance to lose electrons. (10.1) K/U
12. The strongest reducing agent in a galvanic cell has the largest positive reduction potential. (10.2) K/U
13. The standard reduction potential of any entity is based on the reduction potential of the weakest available reducing agent. (10.2) K/U
14. The hydrogen fuel cell is an alternative source of energy for road transportation. (10.3) K/U
15. The alkaline battery has been used in vehicles for over 80 years. (10.3) K/U
16. Corrosion is an electrochemical process. (10.6) K/U
17. The electrolysis of water provides energy to the International Space Station. (10.7) K/U

Go to Nelson Science for an online self-quiz.

WEB LINK

CHAPTER 10 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Which of the following statements is true for a zinc–copper galvanic cell? (10.1) K/U
   (a) Electrons flow from the copper electrode to the zinc electrode.
   (b) Electrons flow from the zinc electrode to the copper electrode.
   (c) The anions in the salt bridge move toward the copper electrode.
   (d) The cations in the salt bridge move toward the zinc electrode.
2. The standard reduction potentials of two half-cells are given below:

   $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E°_r = -0.25$ V

   $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E°_r = -0.77$ V (10.2) K/U

   The voltage of the cell formed by combining the above two half-cells would be
   (a) −1.02
   (b) +0.52
   (c) +1.02
   (d) −0.52
3. Which of the following is always a consequence of corrosion? (10.6) K/U
   (a) The metal is eventually eaten away.
   (b) One metal is oxidized and another is reduced.
   (c) Water is produced.
   (d) A metal oxide forms.
4. The process of covering iron with a protective coating of zinc is called
   (a) oxidation
   (b) condensation
   (c) galvanization
   (d) precipitation (10.6) K/U
5. Which of the following statements is true for an electrolytic cell? (10.7) K/U
   (a) Reduction occurs at the cathode.
   (b) Reduction occurs at the anode.
   (c) Electrons flow from the positive terminal of the power supply.
   (d) The cathode is eventually depleted.
6. The electrorefining of copper
   (a) produces highly pure copper
   (b) involves electrolysis
   (c) may produce gold as waste
   (d) all of the above (10.7) K/U

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

7. In a galvanic cell, electrons travel from the cathode to the anode via the external circuit. (10.1) K/U
8. In a galvanic cell, chemical energy is converted to electrical energy. (10.1) K/U
9. The standard cell potential, $\Delta E°_{r\ (cell)}$, can be predicted using the cell potentials of each half-reaction. (10.2) K/U
10. The redox reaction in a secondary cell is irreversible when a current runs through the cell. (10.3) K/U
11. The rising cost of energy from hydrogen has consumers looking at alternative sources of energy. (10.4) K/U
12. Fission is the nuclear process in which small atoms combine to form larger atoms under conditions of very high temperature and pressure. (10.5) K/U
13. Steel rusts more slowly in salt water than in tap water. (10.6) K/U
14. Metals that readily corrode can often be protected by the application of a thin coating of a metal that is less easily oxidized. (10.6) K/U
15. Electrolysis involves applying a current to an electrolytic cell to cause a non-spontaneous reaction to occur. (10.7) K/U

Match each term on the left with the most appropriate description on the right.

16. (a) galvanic cell
    (b) electrolytic cell
    (c) impressed current
    (d) galvanizing
    (e) series connection
    (f) standard hydrogen half-cell
    (g) cell potential
    (h) secondary cell

    (i) assigned a reduction potential of 0 V
    (ii) a cell designed with a reversible redox reaction
    (iii) a system that uses electricity to make a non-spontaneous reaction occur
    (iv) joined in a continuous row
    (v) an electrochemical cell that produces electricity
    (vi) a form of cathodic protection
    (vii) the difference in the reduction potentials of two half-cells
    (viii) corrosion protection involving zinc (10.1, 10.2, 10.3, 10.6, 10.7) K/U

Write a short answer to each question.

17. A functioning galvanic cell is produced using a silver electrode in a silver nitrate solution and a copper electrode in a copper(II) nitrate solution. (10.1) T/I C
    (a) Sketch the galvanic cell, labelling all parts.
    (b) Write the two half-reactions.
    (c) Write the net ionic equation.
    (d) Describe the cell using line notation.
18. During the operation of a galvanic cell, oxidation occurs at one of the electrodes. (10.1) K/U
    (a) What is the name of this electrode?
    (b) Is this electrode positive or negative?
19. Identify the oxidizing agent and reducing agent in the reaction represented by the following equation: (10.1) K/U
    $\text{Zn(s)} + 2\ \text{Cu}^+\text{(aq)} \rightarrow 2\ \text{Cu(s)} + \text{Zn}^{2+}\text{(aq)}$
20. What energy changes occur during the operation of a galvanic cell? (10.1) K/U
21. The following net ionic equations describe reactions taking place in galvanic cells. Write the standard line notation for each cell. (10.1) K/U
    (a) $\text{Fe}^{2+}\text{(aq)} + \text{Al(s)} \rightarrow \text{Al}^{3+}\text{(aq)} + \text{Fe(s)}$
    (b) $\text{Cu}^{2+}\text{(aq)} + \text{Cr}^{2+}\text{(aq)} \rightarrow \text{Cu}^+\text{(aq)} + \text{Cr}^{3+}\text{(aq)}$ (using inert platinum electrodes)
22. Refer to a redox table to answer the following questions. (Assume that all reactions occur at SATP.) (10.2) K/U
    (a) Are iron(II) ions capable of oxidizing chromium(II) ions to chromium(III) ions?
    (b) Are iron(II) ions capable of oxidizing manganese, Mn?
    (c) Is hydrogen gas, H_2(g), capable of reducing nickel ions, Ni^{2+}(aq)?
23. (a) Name one type of fuel cell used in the U.S. space program.
    (b) What was the product used for? (10.3) K/U
24. Under what circumstances does electrolysis occur? (10.7) K/U
25. List at least three applications of electrolysis. (10.7) K/U

Understanding

26. Briefly describe the purpose of the following components in a galvanic cell: (10.1) K/U
    (a) salt bridge
    (b) wire
    (c) electrolyte
    (d) conductive electrodes
27. Many galvanic cells have the two electrodes in separate beakers with a salt bridge and wire connecting them. However, it is possible to create a galvanic cell by inserting two electrodes, joined by a wire, into a piece of fruit or a vegetable. In this case both electrodes are in the same "container." Explain how both of these arrangements operate to produce electrical energy. (10.1) T/I
28. In a chart, summarize four different factors that will stop a galvanic cell from functioning, and explain why. (10.1) T/I C
29. In a laboratory test, you set up two half-cells. One contains a piece of zinc metal in a zinc nitrate solution; the other contains a piece of nickel metal in a nickel nitrate solution. (10.2) T/I
    (a) Identify the anode and cathode if these half-cells are joined to form a galvanic cell.
    (b) Predict the cell potential, assuming standard conditions.
30. Refer to a redox table to answer the following questions. (Assume that all reactions take place under standard conditions.) Predict the cell potential for all spontaneous reactions. (10.2) K/U T/I
    (a) Is H^+(aq) capable of oxidizing Cu(s) to Cu^{2+}(aq)?
    (b) Is Fe^{3+}(aq) capable of oxidizing I^-(aq)?
    (c) Is H_2(g) capable of reducing Ag^+(aq)?
31. Why is it impossible to obtain the electric potential for a single half-cell? (10.2) K/U
32. What is the function of the platinum wire in a standard hydrogen electrode? (10.2) K/U
33. The standard reduction potential for a half-cell involving zinc metal and aqueous zinc ions is –0.76V. Write equations for the half-reactions occurring at the electrodes when the zinc half-cell is connected to a standard hydrogen electrode. (10.2) T/I
34. For each of the following pairs of half-reaction equations, write the net ionic equation and calculate the standard cell potential, $\Delta E°_{\text{r (cell)}}$: (10.2) K/U T/I
    (a) $\text{Zn}^{2+}\text{(aq)} + 2\text{e}^- \rightarrow \text{Zn(s)}\quad E°_\text{r} = -0.76\ \text{V}$
    $\text{Cd}^{2+}\text{(aq)} + 2\text{e}^- \rightarrow \text{Cd(s)}\quad E°_\text{r} = -0.40\text{V}$
    (b) $\text{Ag}^+\text{(aq)} + \text{e}^- \rightarrow \text{Ag(s)}\quad E°_\text{r} = 0.80\ \text{V}$
    $\text{Al}^{3+}\text{(aq)} + 3\ \text{e}^- \rightarrow \text{Al(s)}\quad E°_\text{r} = -1.66\ \text{V}$
    (c) $\text{Fe}^{2+}\text{(aq)} + 2\ \text{e}^- \rightarrow \text{Fe(s)}\quad E°_\text{r} = -0.44\ \text{V}$
    $\text{Al}^{3+}\text{(aq)} + 3\ \text{e}^- \rightarrow \text{Al(s)}\quad E°_\text{r} = -1.66\ \text{V}$
35. Write the balanced ionic equation and determine $\Delta E°_{\text{r (cell)}}$ for each of the galvanic cells based on the following pairs of half-reaction equations. (Refer to Table 1 in Appendix B7.) (10.2) K/U T/I
    (a) $2\ \text{H}^+\text{(aq)} + 2\ \text{e}^- \rightarrow \text{H}_2\text{(g)}$
    $\text{Al}^{3+}\text{(aq)} + 3\ \text{e}^- \rightarrow \text{Al(s)}$
    (b) $\text{Cr}_2\text{O}_7^{\ 2-}\text{(aq)} + 14\ \text{H}^+\text{(aq)} + 6\ \text{e}^- \rightarrow 2\ \text{Cr}^{3+}\text{(aq)} + 7\ \text{H}_2\text{O(I)}$
    $\text{H}_2\text{O}_2\text{(aq)} + 2\ \text{H}^+\text{(aq)} + 2\ \text{e}^- \rightarrow 2\ \text{H}_2\text{O(l)}$
36. Calculate $\Delta E°_{\text{r (cell)}}$ values for the following cells. Predict which reactions are spontaneous as written (under standard conditions). (Refer to Table 1 in Appendix B7.) (10.2) T/I C
    (a) $\text{Pb}^{2+}\text{(aq)} + \text{Cu(s)} \rightarrow \text{Pb(s)} + \text{Cu}^{2+}\text{(aq)}$
    (b) $\text{Au}^{3+}\text{(aq)} + 3\ \text{Ag(s)} \rightarrow 3\ \text{Ag}^+\text{(aq)} + \text{Au(s)}$
    (c) $2\ \text{Cu}^+\text{(aq)} \rightarrow \text{Cu(s)} + \text{Cu}^{2+}\text{(aq)}$

37. Calculate $\Delta E°_{r\ (cell)}$ values for the cells represented by the following chemical equations. Which reactions are spontaneous as written (under standard conditions)? Balance the equations in acid. (10.2) T/I
    (a) $MnO_4^-(aq) + I^-(aq) \rightarrow I_2(s) + Mn^{2+}(aq)$
    (b) $MnO_4^-(aq) + F^-(aq) \rightarrow F_2(aq) + Mn^{2+}(aq)$

38. (a) What is the electrolyte in a typical alkaline dry cell?
    (b) What safety precautions would you recommend when handling a corroded alkaline dry cell? Explain. (10.3) K/U T/I

39. Rust is a familiar product of a redox reaction. (10.6) K/U
    (a) What two substances must always be present for rusting to occur?
    (b) Explain why rust forms more readily in a damp environment than in dry conditions.

40. Create a graphic organizer, such as a Venn diagram, to communicate the differences between electrochemical cells, galvanic cells, and electrolytic cells. Include at least two examples of chemical reactions in your answer. (10.1, 10.3, 10.7) K/U T/I C

41. Many automobile parts that were once made of steel are now being made of aluminum.
    (a) What effect would this change have on the mass and fuel efficiency of the automobile?
    (b) What positive and negative impacts might this change have on the environment? (10.7) K/U A

42. Ionic compounds can be electrolyzed in much the same way as water. They must first be either dissolved in water or melted until they are liquid, to allow the ions to move freely. Write the half-reaction equations for the reaction that will take place at the anode and the cathode when each of the following molten ionic compounds is electrolyzed using inert electrodes. (Assume SATP.) (10.7) K/U T/I
    (a) potassium fluoride, $KF(s)$
    (b) copper(II) chloride, $CuCl_2(s)$
    (c) magnesium iodide, $MgI_2(s)$

Analysis and Application

43. An electrical load requires at least 1.2 V to operate. (10.1, 10.2) T/I C
    (a) Suggest a galvanic cell that could be used to supply the required potential difference.
    (b) Write the half-reaction equations for the reactions involved, and calculate the standard cell potential, $\Delta E°_{r\ (cell)}$.
    (c) Describe the cell using line notation.

44. For a Unit Task, a student is given strips of silver, zinc, copper, and tin and 500.0 mL each of 1.0 mol/L solutions of silver nitrate, zinc nitrate, copper(II) nitrate, and tin(II) nitrate. The student is required to construct a cell that will produce the maximum potential difference. (10.1, 10.2) T/I C
    (a) Explain how the student could determine experimentally which combination would produce the maximum potential difference.
    (b) What other materials and equipment would the student require, to carry out this task?
    (c) Draw a labelled sketch of the setup necessary to complete this task, and calculate the cell potential.

45. **Figure 1** shows two galvanic cells, each with a platinum electrode. For each cell, write the balanced ionic equation and determine $\Delta E°_{r\ (cell)}$. (10.2) K/U T/I

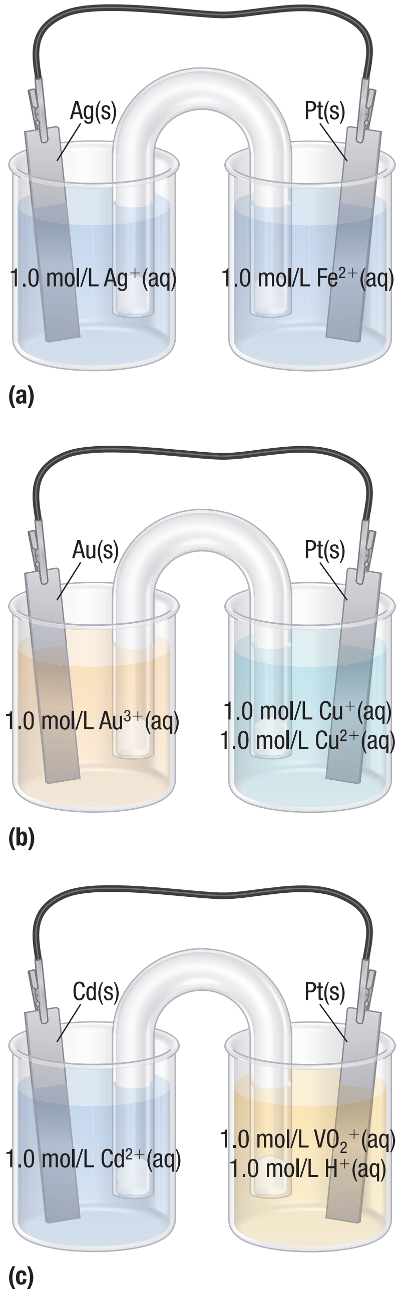


Figure 1

46. For the reaction represented by each of the following unbalanced equations, sketch the galvanic cell in which the reaction occurs. Show the direction of electron flow and the direction of ion migration through the salt bridge, and identify the cathode and anode. Give the overall balanced equation and determine $E°_{r\ (cell)}$. Assume that all reactants are at standard conditions. (10.1, 10.2) K/U
    (a) $IO_3^-(aq) + Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + I_2(aq)$
    (b) $Zn(s) + Ag^+(aq) \rightarrow Zn^{2+}(aq) + Ag(s)$
47. A student has the following materials: a piece of copper metal, a 1.0 mol/L solution of copper(II) nitrate, a piece of an unknown metal, and a 1.0 mol/L solution of the unknown metal's salt. The student uses these materials to set up a galvanic cell, and determines that the cell potential is 2.00 V. (10.1, 10.2) T/I
    (a) What is the unknown metal?
    (b) Write the net ionic equation for the reaction.
48. Consider only the entities in the following list when answering these questions. (Assume that all reactions take place at SATP.)

    $Na^+(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Ag(s)$, $Zn^{2+}(aq)$, $Zn(s)$, $Pb(s)$

    Give reasons for your answers. (10.2) K/U T/I
    (a) Which entity is the strongest oxidizing agent?
    (b) Which entity is the strongest reducing agent?
    (c) Which entities can be oxidized by sulfate ions, $SO_4^{2-}(aq)$, in acid?
    (d) Which entities can be reduced by aluminum metal?
49. Consider only the entities in the following list when answering these questions. (Assume that all reactions take place at SATP.)

    $Br^-(aq)$, $Br_2(l)$, $H^+(aq)$, $H_2(g)$, $La^{3+}(aq)$, $Ca(s)$, $Cd(s)$

    Give reasons for your answers. (10.2) K/U T/I
    (a) Which entity is the strongest oxidizing agent?
    (b) Which entity is the strongest reducing agent?
    (c) Which entities can be oxidized by permanganate ions, $MnO_4^-(aq)$, in acid?
    (d) Which entities can be reduced by zinc metal?
50. Use a redox table to select a reagent that meets each of the following requirements (at SATP in acidic solution): (10.2) K/U T/I
    (a) oxidize bromide ions to bromine gas, $Br_2(g)$, but not oxidize chloride ions to chloride gas
    (b) oxidize magnesium to magnesium(II) ions, but not oxidize iron to iron(II) ions
    (c) reduce copper(II) ions to copper metal, but not to copper(I) ions
51. The saturated calomel electrode (SCE) is often used as a reference electrode for making electrochemical measurements. The SCE is composed of mercury in contact with a saturated solution of calomel (mercury(I) chloride, $Hg_2Cl_2(aq)$). The electrolyte solution is saturated potassium chloride solution, $KCl(aq)$. $\Delta E°_{r\ (SCE)}$ is +0.242 V relative to the standard hydrogen electrode. Calculate the net cell potential, $\Delta E°_{r\ (cell)}$, for each of the following galvanic cells containing a saturated calomel electrode and the given half-cell components at SATP. In each case, indicate whether the SCE is the cathode or the anode. (10.2) K/U T/I
    (a) $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$
    (b) $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}$
    (c) $AgCl(aq) + e^- \rightarrow Ag(s) + Cl^-(aq)$
    (d) $Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$
    (e) $Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$
52. Chlorine dioxide, $ClO_2(g)$, is widely used as a disinfectant for municipal water treatment. Chlorine dioxide is produced by the reaction of sodium chlorite solution with chlorine gas:

    $2\ NaClO_2(aq) + Cl_2(g) \rightarrow 2\ ClO_2(g) + 2\ NaCl(aq)$

    (10.2, 10.3) T/I
    (a) Calculate $\Delta E°_{r\ (cell)}$ at SATP for the production of $ClO_2(g)$.
    (b) Would electrolysis be required for the production of chlorine dioxide? Explain.
53. When jump-starting a car that has a "dead" battery, the ground jumper connection should be attached to a remote part of the engine block. Why? (10.3) K/U T/I A
54. All nuclear power generators currently in operation use fission reactions, in which unstable isotopes of heavy elements break down to release elements with lower atomic masses and a great deal of energy. However, governments around the world are investing billions of dollars in research into fusion as a source of energy. How does fusion differ from fission, and what are the advantages of fusion? (10.5) T/I A
55. Dissolved carbon dioxide is always present in natural water. What effect does dissolved carbon dioxide have on the rusting of metallic iron? (10.6) T/I A
56. A homeowner is building a deck on the side of a house. She uses galvanized nails for most of the deck, but runs out and completes the deck using untreated iron nails. After a few months the ungalvanized nails begin to rust, except for the ones hammered through the aluminum siding to attach the deck to the house. Explain these observations, using terminology that a non-chemist would understand. (10.6) T/I A

57. In theory, we would predict that most metals corrode in air. Observation shows that a few metals, sometimes called the noble metals, rarely corrode in air. The noble metals include gold, platinum, and silver. (10.6) K/U T/I
    (a) Speculate why these elements are called the noble metals.
    (b) Suggest a reason why the noble metals do not generally corrode.

58. Pure silver is too soft to be used to make functional objects such as silverware. Silver is strengthened by alloying it with copper to produce "sterling silver" (92.5% Ag, 7.5 % Cu). Use the standard reduction potentials table to explain why sterling silver corrodes more readily than pure silver or gold. (10.6) K/U A

59. Gold metal does not react or corrode in either concentrated nitric acid or concentrated hydrochloric acid. It will react, however, in *aqua regia*, a mixture of the two concentrated acids. The products of the reaction are $AuCl_4^-(aq)$ ions, water, and gaseous nitrogen monoxide, NO(g). Write a balanced chemical equation for the reaction of gold in *aqua regia*. (10.6) K/U T/I

60. Electroplating involves an electrolytic cell in which the object to be plated is made to be one of the electrodes. What reactions take place at the cathode and the anode when each of the following solutions is used in an electrolytic cell? Write the half-reaction equations for the anode and cathode, and state whether the reaction would result in metal being plated onto the object. (10.7) K/U T/I
    (a) 1.0 mol/L nickel bromide solution, $NiBr_2(aq)$
    (b) 1.0 mol/L aluminum fluoride solution, $AlF_3(aq)$
    (c) 1.0 mol/L manganese iodide solution, $MnI_2(aq)$

Evaluation

61. Hydrazine, $N_2H_4(l)$, is somewhat toxic and flammable. Use the half-reaction equations shown below to decide whether it is safe to mix household bleach (a highly basic solution of sodium hypochlorite, NaClO(aq)) with household ammonia or glass cleaners that contain ammonia. (Assume SATP.) (10.2) K/U T/I A

$$ClO^-(aq) + H_2O(l) + 2\,e^- \rightarrow 2\,OH^-(aq) + Cl^-(aq) \quad E°_r = 0.90\text{ V}$$

$$N_2H_4(aq) + 2\,H_2O(l) + 2\,e^- \rightarrow 2\,NH_3(g) + 2\,OH^-(aq) \quad E°_r = -0.10\text{ V}$$

62. Mercury(I) and mercury(II) ions are toxic. Elemental mercury metal, however, is relatively unreactive and safe. The Canadian Dental Association has determined that dental fillings containing elemental mercury **(Figure 2)** pose minimal health risks, even if the filling is swallowed. Evaluate the Canadian Dental Association's position, using evidence from a redox table to assess whether there is any danger from mercury if swallowed fillings were to mix with stomach acid. (10.2) K/U T/I A

Figure 2 The amalgam commonly used for dental fillings contains a mixture of metals, including mercury.

63. The scientific meaning of the word "battery" is quite different from its everyday use. In everyday language, for example, most people refer to both the AA alkaline dry cell and the 9 V alkaline battery as batteries. Do you think that the scientific definition of battery should be changed? Defend your answer. (10.3) T/I A

64. Evaluate the accuracy of the following statements concerning the corrosion of steel. Correct any inaccurate statements. (10.6) K/U T/I
    (a) Corrosion is an example of an electrolytic process.
    (b) The corrosion of steel involves the reduction of iron coupled with the oxidation of oxygen.
    (c) Steel rusts more easily in humid climates than in dry ones.
    (d) Salting roads in the winter has the added benefit of hindering the corrosion of steel.
    (e) The key to cathodic protection is to connect a metal more easily oxidized than iron to the surface to be protected.

65. Three methods that protect iron from corrosion are impressed current, use of a sacrificial metal, and coating the iron with an inert substance. Design an experiment to evaluate the effectiveness of each of these methods. Include a list of materials, a detailed procedure, and predictions of the observations you would expect to make if the method is effective and if it is ineffective. Also, predict which method you think will be most effective, giving reasons. (10.6) T/I A

66. Although aluminum is one of the most abundant elements on Earth, production of pure aluminum proved to be extremely difficult until the late 1800s. At this time, the Hall–Héroult process made it relatively easy to produce the pure metal. (10.7) K/U T/I A
    (a) Why was pure aluminum so difficult to produce and what was the key discovery behind the Hall–Héroult process?
    (b) How did this process affect the price and use of aluminum?

Reflect on Your Learning

67. In Chapter 10 you learned about the use of a standard hydrogen electrode as a reference electrode. Is the use of an arbitrary standard a difficult concept for you? What are its benefits? What other examples of measured quantities can you think of that have an arbitrary “zero”? T/I A

68. Before you began studying this chapter, what was your concept of the processes inside a commercial cell or battery? Did you know what happens when a battery goes “dead”? Were you aware that recharging a battery reverses the chemical reactions that normally release energy? How has your understanding of the operation of cells and batteries changed? T/I A

69. In this chapter you learned about the spontaneous electrochemical reactions that release energy and about non-spontaneous electrochemical reactions that consume electrical energy. How do these types of reactions relate to each other? How do they affect your life? T/I A

70. In Section 10.5 (Chemistry Journal: Cold Fusion) you read about a potential scientific discovery that was publicized before it was properly checked and confirmed by other scientists. Were you surprised to learn that scientists often keep quiet about their discoveries for months or even years, while their results are replicated by their peers? Do you think this is a good process, or is there a better way to confirm scientific discoveries? Discuss. T/I

Research

WEB LINK

71. For the holidays, you would like to create decorative ornaments for family members and friends. To create a unique gift, research a metal-plating procedure that can be safely completed at home. Create a plan for creating a holiday ornament that describes how to plate a metal on the ornament. Refer to the MSDS for all materials in order to include safety precautions and a waste disposal method with your procedure. C A

72. Commercial galvanic cells are used in many products today. Choose one type of galvanic cell or battery and research how it is made, its uses, its disposal, and any drawbacks associated with it. Include an example of its use. Present your findings as a poster to be displayed where these cells or batteries are sold, or as an “expert advice” web page. T/I C A

73. Research the advantages and limitations of lithium-ion batteries. Summarize your findings in some form of graphic organizer. T/I C A

74. Research the process used to recycle lead storage batteries (car batteries) in your part of Ontario, including any environmental benefits or drawbacks of this process. Draw a flow chart to summarize the steps involved. T/I C A

75. Compare and contrast lithium-ion batteries and lead storage batteries for use in vehicles. Conclude with a statement outlining the pros and cons of each. T/I A

76. Old batteries that corrode in land-fill sites are a major source of toxic metal ions in groundwater. To prevent future contamination, many scientists argue that a “cradle to grave” analysis of new batteries should be conducted before they are introduced to consumers. What does a “cradle to grave” analysis involve? Do you agree that it is necessary? Present your case in a format of your choice. T/I A C

77. Electrochemical processes can have serious environmental consequences. Recycling aluminum has many benefits. Research the benefits and consequences of recycling aluminum, and find out the percentage of aluminum that is recycled in Canada. Make a t-chart of your findings and provide two suggestions for increasing the percentage of recycled aluminum. T/I C A

78. In electrochemistry, an electrical energy source is often used to drive a non-spontaneous redox reaction. One of the problems with industrial redox reactions is that there is often a harmful by-product generated by the reaction. Research “greener” electrolytic reactions that do not produce harmful by-products. Briefly report on at least two such reactions in a format of your choice. T/I C A

UNIT 5 UNIT TASK

The Energy Pack

Batteries are sources of portable electrical energy in our mobile lives. Cellphones, automobiles, and medical equipment are just a few examples of devices that use batteries to provide electrical energy. Batteries contain galvanic cells that convert chemical energy to electrical energy. In order to be functional, batteries must deliver a required quantity of electrical energy for a certain length of time. Batteries must also be practical and safe.

In this Unit Task, you will use materials that are readily available at home or at school to construct a battery. Your teacher may give you a list of materials to choose from, and will supply the necessary equipment and materials for you to test. Your aim is to design a battery that allows an electrical device to work efficiently for 1 min. Then, you will describe how your battery works, and how it compares to commercial batteries. Finally, you will evaluate your battery's effectiveness, safety, and environmental impact, and suggest steps to improve your battery. WEB LINK

Purpose

To design and construct galvanic cells from various available materials, compare their cell potentials (voltages), and test their effectiveness as batteries to allow a small electrical device to operate

Prediction

Predict, using your previous knowledge and a table of standard reduction potentials, which cell design, electrodes, and electrolytes will make the most successful cell.

Equipment and Materials

- chemical safety goggles
- lab apron
- protective gloves
- several low voltage electrical devices (for example, small digital clock, LED, small motor)
- voltmeter
- variety of materials to be used to construct a battery, including
  - glass jars or beakers
  - U-tube with cotton batting for plugs
  - a variety of electrolytic solutions
  - a variety of solid materials to use as electrodes
  - paper towels

The electrolytes used in this task may be corrosive, irritating, or toxic. Any spills on the skin, splashes in the eyes, or on clothing should be washed immediately with plenty of cool water. Report any spills to your teacher. Wash your hands before leaving the laboratory.

Do not bring materials from home without your teacher's approval. Do not do any preliminary tests at home. All necessary equipment and materials will be supplied to you by your teacher.

Procedure

SKILLS HANDBOOK A1, A2.2

1. Outline a plan, using a flow chart or a series of steps, that will enable you to safely explore the effectiveness of various cells and/or batteries. List the equipment for a suitable cell design, and plan to test different electrode materials and different solutions to determine which combination produces the highest cell potential (voltage). Be sure to include safety precautions and disposal methods.
2. Once you have received your teacher's approval for your investigation, assemble the necessary equipment and materials and proceed with your tests. Continue testing, recording all modifications, until you have identified the optimum combination for your cell. Record your observations.
3. Test your cell's ability to make a small electrical device operate for at least a minute.
4. Obtain permission from your teacher to connect your cell with another group's cell. Test the resulting battery with the voltmeter and a variety of electrical devices.

Observations

Create a data table in which to record voltages as you test electrodes and electrolytes.

Analyze and Evaluate

(a) What variables were measured, recorded, and/or manipulated in this investigation? Which were the independent variables and which were dependent? K/U

(b) Which was the cell design and combination of electrodes and electrolyte(s) that produced the highest voltage? T/I

(c) If the cell reactions are known, write half-reaction equations for the reduction and oxidation reactions involved in your "best" cell. T/I

(d) Compare your observations with your prediction. Does your evidence support your prediction? If not, why not? T/I

(e) Justify the choice of materials used in your battery. T/I

(f) Justify the way in which the cells in your battery were assembled, if more than one cell was used. Include a diagram of how the cells were connected. T/I

(g) Research commercially produced cells and batteries that are designed for use in small, portable devices such as those you used in this task. Explore their physical design, their materials, their environmental impact, whether they are rechargeable, and any other relevant characteristics. T/I A

(h) Evaluate your "battery" by carefully considering its design, the materials used, and how it was tested. Is it effective? Is it safe? Is it environmentally benign? Is it rechargeable? How could it be made better? T/I A

(i) Compare your battery to a commercially available battery. What are the pros and cons of each? T/I A

(j) Present your findings as a report. Include in the report the purpose of the investigation; your prediction, procedure, and data; and a final paragraph describing what electrical device your battery was able to operate, and how your cell compares to commercially developed cells. T/I C

Apply and Extend

(k) What specific design modifications would you make to your battery to make it more usable as a source of portable electrical energy? T/I A

ASSESSMENT **CHECKLIST**

Your completed Unit Task will be assessed according to the following criteria:

Knowledge/Understanding

✓ Demonstrate an understanding of the components of a galvanic cell and their roles in converting chemical energy into electrical energy.

Thinking/Investigation

✓ Plan and safely conduct an investigation to determine the best design and materials for making a galvanic cell.

✓ Research commercially made batteries.

✓ Evaluate the design of your constructed cell or battery.

✓ Compare the design and operation of your constructed battery to a commercially made battery.

Communication

✓ Synthesize your findings clearly and concisely in a written report.

Application

✓ Justify the use of certain materials in the design of a cell.

✓ Provide a rationale for suggested improvements to the battery.

UNIT 5 SELF-QUIZ

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

For each question, select the best answer from the four alternatives.

1. Which of the following entities has an oxidation number of 0? (9.1) K/U
   (a) an atom in an element
   (b) a monatomic ion
   (c) hydrogen in its covalent compounds
   (d) oxygen in its compounds
2. What is the oxidation number of hydrogen in ammonia, $NH_3(g)$? (9.1) K/U
   (a) -1 (c) $+1$
   (b) 0 (d) -3
3. What is the oxidation number of phosphorus in the phosphate ion, PO_4^{3-}? (9.1) K/U
   (a) -5 (c) 0
   (b) -3 (d) $+5$
4. What happens to an atom that experiences an increase in oxidation number? (9.1) K/U
   (a) It is reduced.
   (b) It is an oxidizing agent.
   (c) It loses electrons.
   (d) It gains mass.
5. Which of the following statements is true about the nitrogen atom in the reaction represented by the following equation? (9.1) K/U
   $HNO_3(aq) + H_2S(g) \rightarrow NO(g) + S(s) + H_2O(l)$
   (a) Its oxidation number changes from +5 to +2.
   (b) It loses 3 electrons.
   (c) It is oxidized by gaining 3 electrons.
   (d) It is the reducing agent.
6. Which of the following half-reaction equations represents the reduction half-reaction for the equation $2\ AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2\ Ag(s)$? (9.1) K/U
   (a) $2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)$
   (b) $2\ Ag^+(aq) \rightarrow 2\ Ag(s) + 2\ e^-$
   (c) $Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$
   (d) $Cu(s) + 2\ e^- \rightarrow Cu^{2+}(aq)$
7. Which of the following chemical equations represents a redox reaction? (9.1) K/U
   (a) $H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$
   (b) $CaCO_3(s) + 2\ HCl(aq) \rightarrow$
   $CaCl_2(aq) + H_2O(l) + CO_2(g)$
   (c) $2\ KClO_3(aq) \rightarrow 2\ KCl(aq) + 3\ O_2(g)$
   (d) none of the above
8. Which of the following statements best describes a reducing agent? (9.1) K/U
   (a) A reducing agent gains electrons and causes oxidation.
   (b) A reducing agent gains electrons and causes reduction.
   (c) A reducing agent loses electrons and causes oxidation.
   (d) A reducing agent loses electrons and causes reduction.
9. Metals are typically
   (a) good oxidizing agents
   (b) easily reduced
   (c) easily oxidized
   (d) good electron acceptors (9.1) K/U
10. Which of the following is the correct balanced equation for the reaction of potassium dichromate with water and sulfur to produce a solution of potassium hydroxide and chromium oxide plus sulfur dioxide gas?
    $K_2Cr_2O_7(aq) + H_2O(l) + S(s) \rightarrow$
    $KOH(aq) + Cr_2O_3(aq) + SO_2(g)$ (9.2) K/U
    (a) $K_2Cr_2O_7(aq) + H_2O(l) + S(s) \rightarrow$
    $KOH(aq) + Cr_2O_3(aq) + SO_2(g)$
    (b) $2\ K_2Cr_2O_7(aq) + 2\ H_2O(l) + 3\ S(s) \rightarrow$
    $4\ KOH(aq) + 2\ Cr_2O_3(aq) + 3\ SO_2(g)$
    (c) $4\ K_2Cr_2O_7(aq) + H_2O(l) + S(s) \rightarrow$
    $4\ KOH(aq) + Cr_2O_3(aq) + SO_2(g)$
    (d) $2\ K_2Cr_2O_7(aq) + H_2O(l) + S(s) \rightarrow$
    $4\ KOH(aq) + Cr_2O_3(aq) + SO_2(g)$
11. Copper is a stronger oxidizing agent than zinc. What happens when a zinc rod is placed into a solution of copper(II) sulfate? (9.3) K/U
    (a) Electrons are transferred from copper atoms to zinc ions.
    (b) The copper metal slowly dissolves.
    (c) No reaction occurs.
    (d) The zinc rod becomes copper plated.
12. What is a half-cell? (10.1) K/U
    (a) a U-shaped tube that allows the passage of electrons from one electrode to another
    (b) two electrodes connected by a wire along which electrons travel and a salt bridge through which ions transfer
    (c) an electrode in a solution of its ions
    (d) a solution in which both reduction and oxidation occur simultaneously

13. Which of the following statements is true for a galvanic cell? (10.1) K/U
    (a) Electrons flow from cathode to anode.
    (b) Oxidation takes place at the anode.
    (c) The reducing agent is at the cathode.
    (d) none of the above
14. A galvanic cell
    (a) produces current from a non-spontaneous reaction
    (b) uses electrical energy from an outside source to produce chemical change
    (c) is used in electroplating
    (d) uses current produced by the oxidation of a substance to cause the reduction of another substance (10.1) K/U
15. What is the cell potential of the cell that can be described with the following line notation? (Refer to Table 1 in Appendix B7.) (10.2) K/U T/I

    $Cu(NO_3)_2(aq) \mid Cu(s) \parallel Ag(s) \mid AgNO_3(aq)$

    (a) 1.99 V
    (b) 0.46 V
    (c) 1.65 V
    (d) −1.65 V
16. What is a battery? (10.3) K/U
    (a) a group of galvanic cells connected in series
    (b) a device that uses electrical energy to produce a chemical change
    (c) a group of half-cells connected in parallel
    (d) none of the above
17. Which of the following metals could be used to galvanize iron? (10.6) K/U
    (a) zinc
    (b) magnesium
    (c) copper
    (d) Any of the above could be used for galvanizing iron.
18. What is electroplating? (10.7) K/U
    (a) the use of electrolysis to coat a material with a layer of metal
    (b) the use of electrolysis to produce important metals such as aluminum and sodium
    (c) the use of a redox reaction to separate a compound into its ions
    (d) the use of a galvanic cell to coat a metal with electrons
19. During electrolysis, which of the following processes occurs? (10.7) K/U
    (a) Oxidation takes place at the cathode.
    (b) Reduction takes place at the anode.
    (c) Oxidation takes place at the anode.
    (d) none of the above

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

20. Oxidation is the process in which one or more electrons are gained. (9.1) K/U
21. The oxidation number of oxygen in hydrogen peroxide, $H_2O_2(aq)$, is -2. (9.1) K/U
22. In redox reactions, elements undergo changes in oxidation number. (9.1) K/U
23. The oxidizing agent is the reactant that gains electrons during a redox reaction. (9.1) K/U
24. The oxidation number of a monatomic ion is the same as the charge on the ion. (9.1) K/U
25. In the synthesis reaction that produces ammonia, $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$, nitrogen is reduced. (9.1) K/U
26. In the reaction between magnesium and sulfur to produce magnesium sulfate, $MgS(s)$, magnesium is the oxidizing agent. (9.1) K/U
27. The oxidation number of manganese in the permanganate ion, $MnO_4^{\,2-}$, is $+6$. (9.1) K/U
28. It is sometimes necessary to add the formulas for water and hydrogen ions or hydroxide ions to redox half-reaction equations in order to balance the equation. (9.2) K/U
29. Strong oxidizing agents easily give up electrons. (9.3) K/U
30. A galvanic cell is an arrangement of two half-cells that spontaneously produces electric current. (10.1) K/U
31. In a galvanic cell, a salt bridge is a connection between two half-cells designed so that ions cannot travel between the two half-reactions. (10.1) K/U
32. A battery is a group of galvanic cells connected in parallel. (10.3) K/U
33. Corrosion results from a spontaneous redox reaction. (10.6) K/U
34. Magnesium can be used as a sacrificial anode to protect iron because it undergoes oxidation more easily than iron. (10.6) K/U
35. Impressed current prevents steel from corroding by applying a current that gives the steel a positive charge. (10.6) K/U
36. In an electrolytic cell, chemical energy is converted to electrical energy. (10.7) K/U
37. An electrolytic cell can generate electricity only if the oxidation and reduction half-cells are completely separate from each other. (10.7) K/U
38. Electrolytic cells are similar to galvanic cells in that reduction always occurs at the anode. (10.7) K/U

UNIT 5 REVIEW

K/U Knowledge/Understanding T/I Thinking/Investigation C Communication A Application

Knowledge

For each question, select the best answer from the four alternatives.

1. Which of the following equations does not represent a redox reaction? (9.1) K/U
   (a) $2\ HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$
   (b) $2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$
   (c) $2\ Na(s) + Cl_2(g) \rightarrow 2\ NaCl(s)$
   (d) $Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$
2. In which of the following compounds does chlorine have the largest oxidation number? (9.1) K/U
   (a) $KClO_4$
   (b) $CaCl_2$
   (c) CCl_4
   (d) ClO_2
3. What is the oxidation number of oxygen in dinitrogen monoxide, $N_2O(g)$? (9.1) T/I
   (a) -2
   (b) 0
   (c) $+1$
   (d) $+2$
4. What is the oxidation number of chromium in potassium dichromate, $K_2Cr_2O_7(aq)$? (9.1) T/I
   (a) -7
   (b) -6
   (c) $+6$
   (d) $+7$
5. What is the role of copper in the reaction represented by the following equation? (9.1) K/U
   $2\ Ag^+(aq) + Cu(s) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$
   (a) It is being oxidized.
   (b) It gains 2 electrons.
   (c) It is the oxidizing agent.
   (d) It loses 1 electron.
6. Which of the following events can happen during a reduction half-reaction? (9.1) K/U
   (a) loss of electrons
   (b) loss of hydrogen from a molecule
   (c) the shift of electrons away from an atom in a covalent bond
   (d) gain of electrons
7. Which of the following equations represents a redox reaction? (9.1) K/U
   (a) $Zn(s) + 2\ HCl(g) \rightarrow ZnCl_2(s) + H_2(g)$
   (b) $C_2H_4(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 2\ H_2O(g)$
   (c) $6\ CO_2(aq) + 6\ H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6\ O_2(g)$
   (d) all of the above
8. Which of the following statements is a step used in balancing redox equations? (9.2) K/U
   (a) If the reaction takes place in a basic solution, add $H_2O(l)$ and $H^+(aq)$.
   (b) If the reaction takes place in a basic solution, add $OH^-(aq)$ and $H_2O(l)$.
   (c) If the reaction takes place in an acidic solution, add $OH^-(aq)$ and $H_2O(l)$.
   (d) If the reaction takes place in an acidic solution, add $H^+(aq)$ and $OH^-(aq)$.
9. Consider the unbalanced equation
   $$H_2O(l) + MnO_4^{\ -}(aq) + C_2O_4^{\ 2-}(aq) \rightarrow MnO_2(s) + CO_2(g) + OH^-(aq)$$
   When the equation is balanced, what is the coefficient of carbon dioxide? (9.2) K/U
   (a) 2
   (b) 4
   (c) 6
   (d) 8
10. Which of the following redox equations is balanced? (9.2) K/U
    (a) $2\ Na(s) + Br_2(l) \rightarrow NaBr(s)$
    (b) $H_2O(l) + SO_2(g) \rightarrow H_2SO_4(aq)$
    (c) $C_2H_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$
    (d) $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(l)$
11. For a magnesium–copper cell, which of the following half-reactions would occur as written? (9.3) K/U
    (a) $Mg \rightarrow Mg^{2+}(aq) + 2\ e^-$
    (b) $Cu^{2+}(aq) \rightarrow Cu(s) + 2\ e^-$
    (c) $Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$
    (d) none of the above
12. Which of the following combinations of reactants will result in a spontaneous reaction? (9.3) K/U
    (a) zinc metal in sodium chloride solution
    (b) copper metal in zinc nitrate solution
    (c) magnesium metal in nickel(II) nitrate solution
    (d) silver metal in potassium chloride solution
13. Which of the following statements best describes a galvanic cell? (10.1) K/U
    (a) a cell in which either oxidation or reduction occurs
    (b) a cell that uses an external source of electrical energy to produce a chemical change
    (c) a metal in a solution of its ions
    (d) two electrodes in electrolytes, connected by a wire and a salt bridge
14. Which of the following statements correctly describes the cathode in a galvanic cell? (10.1) K/U
    (a) It is the negative electrode.
    (b) It is where oxidation takes place.
    (c) It is where the reducing agent is found.
    (d) none of the above

15. What is the function of the salt bridge in a galvanic cell? (10.1) K/U
    (a) It separates two electrolytes, but allows ions to travel between the two half-cells.
    (b) It produces current from the oxidation of a metal.
    (c) It prevents ions from travelling between the two half-cells.
    (d) It prevents the electrodes from corroding.
16. The ability of a half-cell to attract electrons under standard conditions is called the
    (a) standard cell potential
    (b) standard oxidation potential
    (c) standard reduction potential
    (d) spontaneity potential (10.2)
17. A battery is best described as
    (a) a rechargeable cell
    (b) several cells connected in series
    (c) a device for converting thermal energy to chemical energy
    (d) an apparatus consisting of two connected electrodes in solutions of electrolytes (10.3)
18. Methods that can be used to prevent corrosion include
    (a) anodic protection
    (b) use of a sacrificial cathode
    (c) galvanizing
    (d) all of the above (10.6) K/U
19. Which phrase best describes electrolysis? (10.7) K/U
    (a) delivering chemical energy as a result of a spontaneous reaction
    (b) using chemical energy to cause a non-spontaneous reaction to occur
    (c) producing current when an oxidation–reduction reaction proceeds spontaneously
    (d) forcing a current through a cell to produce a chemical change
20. What is the difference between a galvanic cell and an electrolytic cell? (10.1, 10.7) K/U
    (a) A galvanic cell uses electrical energy to bring about a chemical reaction. An electrolytic cell uses a chemical reaction to produce electrical energy.
    (b) A galvanic cell uses a chemical reaction to produce electrical energy. An electrolytic cell uses electrical energy to bring about a chemical reaction.
    (c) In a galvanic cell, oxidation takes place at the anode. In an electrolytic cell, oxidation takes place at the cathode.
    (d) In a galvanic cell, oxidation takes place at the cathode. In an electrolytic cell, oxidation takes place at the anode.
21. What are the products of the electrolysis of water? (10.7) K/U
    (a) hydrogen ions and hydroxide ions
    (b) water vapour and liquid hydrogen
    (c) hydrogen gas and oxygen gas
    (d) an acid and a base

Indicate whether each statement is true or false. If you think the statement is false, rewrite it to make it true.

22. Reduction is the process in which one or more electrons are gained. (9.1) K/U
23. In a redox reaction, electrons are lost in the reduction half-reaction. (9.1) K/U
24. Oxidation causes a decrease in oxidation number. (9.1) K/U
25. Substances in their elemental form have oxidation numbers of 1. (9.1) K/U
26. The sum of the oxidation numbers in a polyatomic ion must equal 0. (9.1) K/U
27. The oxidation number of phosphorus in the dihydrogen phosphate ion, $H_2PO_4^-$, is +5. (9.1) K/U
28. In the synthesis reaction that produces sulfur dioxide from elemental sulfur and oxygen gas, sulfur is reduced. (9.1) K/U
29. A change in the oxidation number of an element indicates that a redox reaction has occurred. (9.1) K/U
30. Iodine, $I_2(s)$, is not able to oxidize zinc metal to Zn^{2+} ions. (9.3) K/U
31. When elemental iron is processed from iron ore, the iron in iron(III) oxide, Fe_2O_3, is reduced when it gains 3 electrons. (9.3) K/U
32. The more reactive a metal, the greater its tendency to lose electrons. (9.3) K/U
33. In a galvanic cell, oxidation takes place at the anode. (10.1) K/U
34. A galvanic cell is a device in which electrical energy is converted to another form of energy. (10.1) K/U
35. The voltage of a cell depends on the concentrations of the reactants present in the solution. (10.2) K/U
36. A primary cell is designed with a redox reaction that can be reversed by running a current through the cell. (10.3) K/U
37. A fuel cell is a galvanic cell for which the reactants are continuously supplied. (10.3) K/U
38. Corrosion is the oxidation of metal. (10.6) K/U
39. Electrolysis is the application of current through a cell to produce a chemical change. (10.7) K/U
40. Electric current must be supplied to carry out the synthesis of water. (10.7) K/U

Match each term on the left with the most appropriate description on the right.

41. (a) $E°_r$
    (b) line notation
    (c) electrolysis
    (d) half-reaction equation
    (e) primary cell
    (f) $\Delta E°_{r\,(cell)}$
    (g) redox table
    (h) sacrificial anode

    (i) standard cell potential
    (ii) a method of cathodic protection
    (iii) standard reduction potential
    (iv) a description of either the oxidation or reduction process
    (v) a ranking of half-reactions according to their reduction potentials
    (vi) the use of electricity to force a non-spontaneous reaction to occur
    (vii) a brief way of describing a cell
    (viii) involving a reaction that cannot easily be reversed (9.1, 9.3, 10.1, 10.2, 10.3, 10.6, 10.7) K/U

Write a short answer to each question.

42. What is the oxidation number of each element in each of the following compounds? (9.1) K/U T/I
    (a) P_2O_5
    (b) NO_2
    (c) Na_2SO_4
    (d) $Cu(NO_3)_2$
    (e) $KMnO_4$
    (f) $Na_3Fe(OH)_6$
    (g) $XeOF_4$
43. What is the oxidation number of sulfur in each of the following compounds or ions? (9.1) T/I
    (a) Na_2SO_4
    (b) $K_2S_2O_8$
    (c) $S_2O_3^{2-}$
    (d) SO_2
44. What are the roles of oxidizing agents and reducing agents in redox reactions? (9.1) T/I
45. Why must oxidation always occur with reduction? (9.1) T/I
46. Identify the entity that is reduced in each of the following reactions: (9.1) T/I
    (a) $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$
    (b) $H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$
    (c) $S(s) + Cl_2(g) \rightarrow SCl_2(l)$
    (d) $2\ Li(s) + F_2(g) \rightarrow 2\ LiF(s)$
47. For each of the following equations, identify the element that is oxidized, the element that is reduced, the oxidizing agent, and the reducing agent: (9.1) T/I
    (a) $PbO_2(aq) + 4\ HI(aq) \rightarrow I_2(aq) + PbI_2(s) + 2\ H_2O(I)$
    (b) $Mg(s) + Cu(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + Cu(s)$
    (c) $As_2O_3(s) + Cl_2(g) + H_2O(l) \rightarrow H_3AsO_4(aq) + HCl(aq)$
    (d) $I_2O_5(s) + CO(g) \rightarrow I_2(s) + CO_2(g)$
48. Write equations for the following half-reactions: (9.1) T/I
    (a) reduction of chlorine, Cl_2
    (b) reduction of sulfur, S_8
    (c) oxidation of zinc
    (d) oxidation of sodium
49. Write equations for the half-reactions that occur when magnesium ribbon is placed into a solution of copper(II) sulfate. Identify the oxidation half-reaction and the reduction half-reaction. (9.1) T/I
50. Consider the reaction between sodium metal and fluorine gas to form solid sodium fluoride. (9.2) K/U
    (a) Using oxidation numbers, how many electrons would each sodium atom lose, and how many electrons would each fluorine atom gain?
    (b) How many sodium atoms are needed to react with one fluorine molecule? Explain.
    (c) Write a balanced chemical equation for this reaction.
51. Refer to Table 1 in Appendix B7 to determine whether or not each of the following reactions will occur spontaneously: (9.3) T/I
    (a) $Ca(s) + Fe^{2+}(aq) \rightarrow Ca^{2+}(aq) + Fe(s)$
    (b) $Ca^{2+}(aq) + Fe(s) \rightarrow Ca(s) + Fe^{2+}(aq)$
    (c) $3\ Ca(s) + 2\ Au^{3+}(aq) \rightarrow 3\ Ca^{2+}(aq) + Au(s)$
    (d) $Au^{3+}(aq) + 3\ Fe(s) \rightarrow 2\ Au(s) + 3\ Fe^{2+}(aq)$
    (e) $Fe(s) + 2\ H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$
    (f) $3\ Mg(s) + 2\ Cr^{3+}(aq) \rightarrow 3\ Mg^{+2}(aq) + Cr(s)$
    (g) $3\ Cu(s) + 2\ NO_3^-(aq) + 8\ H^+(aq) \rightarrow 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O(l)$
52. **Figure 1** shows a magnesium–iron galvanic cell. (9.3, 10.1) K/U C
    (a) Determine which metal will be the cathode and which the anode.
    (b) Copy Figure 1 into your notebook and add labels to indicate all parts of the cell, including the ions in the solutions.

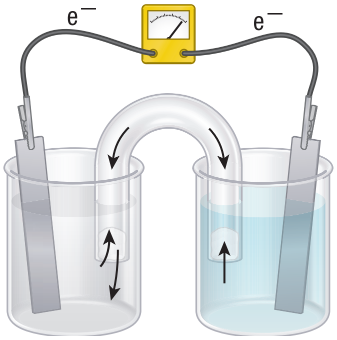


Figure 1

53. Describe the structure and purpose of a salt bridge. (10.1) K/U

54. What is the difference between a cathode and an anode? (10.1) T/I

55. A cell is constructed for which the line notation is $Mg(s)|Mg^{2+}(aq) \,||\, Fe^{2+}(aq)|Fe$ (10.1) K/U T/I
    (a) Write the half-reaction equations and the net ionic equation.
    (b) Determine the cell potential.

56. A student constructs a nickel–zinc galvanic cell. (10.1) K/U T/I C
    (a) Write the net ionic equation.
    (b) Determine the cell potential.
    (c) Represent the cell using line notation.

57. Write the line notation for the galvanic cell that uses the reaction
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ (10.1) T/I

58. Refer to Table 1 in Appendix B7 to identify the standard reduction potential for each of the following half-reactions, then rank the substances on the right side of each equation in order of increasing strength as reducing agents: (9.3, 10.2) K/U
$2\ H_2O(l) + 2\ e^- \rightleftharpoons H_2(g) + 2\ OH^-(aq)$
$Ni^{2+}(aq) + 2\ e^- \rightleftharpoons Ni(s)$
$Au^{3+}(aq) + 3\ e^- \rightleftharpoons Au(s)$
$IO_3^-(aq) + 6\ H^+(aq) + 5\ e^- \rightleftharpoons \frac{1}{2}\ I_2(s) + 3\ H_2O(l)$
$Li^+(aq) + e^- \rightleftharpoons Li(s)$

59. What is the relationship between cells and batteries? (10.3) K/U

60. What is a dry cell battery? (10.3) T/I

61. Compare and contrast corrosion and rusting. (10.6) K/I

62. Write the balanced chemical equation representing the overall cell reaction for the corrosion of iron. (10.6) K/I

63. In an electrolytic cell used for plating chromium onto an object, should the chromium be present as ions or as the metallic element? Explain your answer. (10.7) T/I A

64. Write the half-reaction equations that take place at the cathode and the anode when each of the following ionic compounds is electrolyzed: (10.7) T/I
    (a) molten nickel bromide, $NiBr_2(l)$
    (b) molten aluminum fluoride, $AlF_3(l)$
    (c) molten magnesium iodide, $MgI_2(l)$

65. List three commercial processes that use electrolytic cells. (10.7) K/I

66. What is the function of an electrolyte such as sodium sulfate, $Na_2SO_4(aq)$, during the electrolysis of water? (10.7) K/I

Understanding

67. What is the relationship between the ionic charge and the oxidation number of a monatomic ion? (9.1) T/I

68. What is the relationship between oxidation and reduction? (9.1) T/I

69. Given its position on the reduction potentials table, is chlorine gas, $Cl_2(g)$, more likely to be oxidized or reduced in chemical reactions? Why? (9.1) T/I C

70. What is the purpose of writing half-reactions for redox reactions? (9.1) T/I

71. Create a table in which to communicate which of the following equations represent redox reactions, and the identity of the element that is oxidized, the element that is reduced, the oxidizing agent, and the reducing agent (if relevant): (9.1) T/I C
    (a) $Cu(s) + 2\ Ag^+(aq) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$
    (b) $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
    (c) $SiCl_4(l) + 2\ H_2O(l) \rightarrow 4\ HCl(aq) + SiO_2(s)$
    (d) $SiCl_4(l) + 2\ Mg(s) \rightarrow 2\ MgCl_2(s) + Si(s)$

72. Balance each of the following redox equations using the oxidation numbers method: (9.2) T/I
    (a) $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$
    (b) $Mg(s) + HCl(aq) \rightarrow Mg^{2+}(aq) + Cl^-(aq) + H_2(g)$
    (c) $KIO_4(aq) + KI(aq) + HCl(aq) \rightarrow KCl(q) + I_2(s) + H_2O(l)$
    (d) $Cl_2(g) + KOH(aq) \rightarrow KClO_3(aq) + KCl(aq) + H_2O(l)$
    (e) $K_2Cr_2O_7(aq) + HCl(aq) \rightarrow CrCl_3(aq) + KCl(aq) + Cl_2(g) + H_2O(l)$
    (f) $MnO_2(s) + H_2C_2O_4(aq) + H_2SO_4(aq) \rightarrow MnSO_4(aq) + CO_2(g) + H_2O(l)$

73. Why is it possible to add hydrogen ions or hydroxide ions to half-reactions when balancing redox equations in acidic or basic solutions? (9.2) T/I

74. Balance the following equations for redox reactions that occur in acidic solution: (9.2) T/I
    (a) $MnO(s) + PbO_2(s) \rightarrow MnO_4^-(aq) + Pb^{2+}(aq)$
    (b) $I^-(aq) + ClO^-(aq) \rightarrow I_3^-(aq) + Cl^-(aq)$
    (c) $As_2O_3(s) + NO_3^-(aq) \rightarrow H_3AsO_4(aq) + NO(g)$
    (d) $Br^-(aq) + MnO_4^-(aq) \rightarrow Br_2(l) + Mn^{2+}(aq)$
    (e) $CH_3OH(aq) + Cr_2O_7^{2-}(aq) \rightarrow CH_2O(aq) + Cr^{3+}(aq)$

75. Consider the reaction that occurs between manganese metal and a solution of gold(III) ions. (9.2) T/I
    (a) Write the unbalanced net ionic equation for the reaction.
    (b) Identify the oxidizing agent in the reaction.
    (c) Identify the reducing agent.
    (d) Write the half-reaction equations.
    (e) Write the balanced equation.

76. Balance the following equation for a redox reaction that occurs in basic solution: (9.2) T/I

$MnO_4^-(aq) + CN^-(aq) \rightarrow MnO_2(aq) + CNO^-(aq)$

77. What reaction occurs spontaneously, if any, when each of the following operations is performed at SATP? For the reactions that do occur, write a balanced chemical equation. (9.3) K/U T/I
    (a) Crystals of iodine are added to a solution of sodium chloride.
    (b) Chlorine gas is bubbled into a solution of sodium iodide.
    (c) A silver wire is placed in a solution of copper(II) chloride.
    (d) An acidic solution of iron(II) sulfate, $FeSO_4(aq)$, is exposed to air.

78. Write the half-reaction equations and the overall balanced chemical equation for the reactions that would occur spontaneously in the following situations. If no reaction would occur spontaneously, write "no reaction." (9.3) T/I
    (a) Aqueous potassium permanganate is used to titrate an acidic solution of iron(II) sulfate.
    (b) A strip of copper is placed in a beaker of hydrochloric acid.
    (c) An iron pipe is exposed to the wind and the rain.

79. Describe what you expect to happen if you poured a solution of copper(II) nitrate into an empty steel can. Explain your prediction. (9.3) K/U T/I

80. When magnesium metal is added to a beaker of hydrochloric acid, HCl(aq), a gas is produced. (9.1, 9.2, 10.1) T/I
    (a) Identify the oxidizing agent and the reducing agent.
    (b) Write the balanced chemical equation for the reaction.
    (c) How many electrons are transferred per magnesium atom reacting?
    (d) Does the reaction produce useful electrical energy when magnesium is added directly to the beaker of hydrochloric acid? Explain.
    (e) How can you harness this reaction to produce an electric current?

81. Draw a labelled diagram of a galvanic cell constructed using magnesium metal and 1.0 mol/L magnesium nitrate solution along with copper metal and 1.0 mol/L copper(II) nitrate solution. Include the half-reactions and the net ionic equation. (10.1) K/U C

82. Explain the electrochemical process that occurs in a galvanic cell. (10.1) T/I

83. Draw a labelled diagram of a galvanic cell constructed using magnesium metal and 1.0 mol/L magnesium nitrate solution along with copper metal and 1.0 mol/L copper(II) nitrate solution. Label the anode, cathode, reducing agent, and oxidizing agent, and draw arrows indicating the direction of electron transfer and ion transfer. Include the half-reactions and the net ionic equation. (10.1) K/U C

84. What do the double vertical lines represent in the line notation used to describe galvanic cells? (10.1) T/I

85. What mass changes are expected as a galvanic cell operates? Explain. (10.1) T/I

86. A zinc electrode and a 1.0 mol/L solution of zinc nitrate are used to make a half-cell. Another half-cell is constructed using a nickel electrode and a 1.0 mol/L solution of nickel(II) nitrate. (10.1) T/I C
    (a) Draw the galvanic cell that could be constructed from these half-cells. Label the anode, the cathode, the salt bridge, and the direction of the electron and ion flow.
    (b) Write equations for the half-reactions that occur at each electrode.
    (c) Write the net ionic equation.
    (d) Use cell notation to summarize this cell.

87. Use Table 1 in Appendix B7 to determine whether aluminum foil immersed in an electrolyte solution can be used to restore the lustre to silverware. Show the balanced equation and the cell potential for the overall reaction. Assume 1.0 mol/L solutions for all reactants. (10.2) T/I A

88. When silver metal is placed in 1.0 mol/L hydrochloric acid, HCl(aq), under standard conditions, there is no observable reaction. However, when magnesium metal is placed in the same acid solution, the metal oxidizes and hydrogen gas is produced. Explain these two observations. (10.2) T/I

89. The term "battery" is commonly used to refer to a portable source of electrical energy. Explain why this usage is not always correct. (10.3) K/U A

90. Create an illustration showing how four cells should be connected in series to provide energy to light an electric bulb. (10.3) T/I C A

91. How does a fuel cell differ from a conventional galvanic cell? (10.3) T/I

92. List two advantages of lithium-ion batteries over hydrogen fuel cells, and two advantages of hydrogen fuel cells over lithium-ion batteries. (10.4) T/I A

93. (a) Use the standard reduction potentials table to predict whether gold can be oxidized by oxygen.
    (b) Suggest one reason why most metals are found in nature in oxidized form rather than as pure elements. (10.6) T/I

94. In order to prevent corrosion of steel hulls of ships, blocks of metals such as magnesium, aluminum, or zinc are placed in contact with the steel hull. How would these sacrificial anodes prevent or reduce the rusting of steel hulls? (10.6) T/I

95. Producing 1 kg of silver from its ions by electrolysis requires much less electrical energy than producing 1 kg of aluminum from its ions. Explain why this is so, referring to standard reduction potentials. (9.3, 10.7) T/I

96. Construct a Venn diagram comparing and contrasting galvanic and electrolytic cells. (10.1, 10.7) T/I C

97. Name three practical applications of electrolysis. (10.7) T/I

98. A molten solution of tin(II) chloride is placed in an electrolytic cell. (10.7) T/I
    (a) Predict the product formed at the anode.
    (b) Predict the reactant formed at the cathode.
    (c) What visible evidence would confirm your predictions in (a) and (b)?
    (d) Write the net ionic equation for this cell.
    (e) Predict the minimum voltage that must be supplied to the cell.

99. Describe electroplating in a short paragraph. Draw a diagram summarizing the process. (10.7) K/U C

100. Predict what happens to the pH of the solution near the cathode and near the anode when aqueous sodium chloride undergoes electrolysis. (10.7) T/I

Analysis and Application

101. Fluorine gas cannot be prepared from by the chemical oxidation of sodium fluoride. Explain. (9.1) T/I

102. In disproportionation, an element is simultaneously reduced and oxidized to form two different products. (9.1) T/I
    (a) Write the chemical equation for the disproportionation of hydrogen peroxide into water and oxygen.
    (b) Which element is both oxidized and reduced?
    (c) How many electrons are lost in the oxidation reaction?
    (d) How many electrons are gained in reduction?

103. Oxidizing agents have important industrial applications. They are used to dissolve metals, as disinfectants, and in photography, etching, and dyeing. (9.1) T/I A
    (a) Explain why oxidizing agents are stored separately from other substances.
    (b) What type of safety equipment should be worn when working with strong oxidizing agents?
    (c) Why should strong oxidizing agents be stored in a cool, dry place?

104. A police officer might use a breathalyzer to determine whether a person has been drinking beverages containing ethanol, $CH_3CH_2OH(aq)$. One type of breathalyzer relies on a reaction involving yellowish-orange dichromate ions, $Cr_2O_7^{2-}(aq)$ and green chromium (III) ions, $Cr^{3+}(aq)$. The equation for this reaction is

$$CH_3CH_2OH(g) + Cr_2O_7^{2-}(aq) + H^+(aq) \rightarrow CH_3CO_2H(aq) + Cr^{3+}(aq) + H_2O(l)$$

(9.1, 9.2) K/U A
    (a) Determine the oxidation number for each of the elements in this reaction.
    (b) Balance the equation.
    (c) Predict what colour change would occur if a person exhales air containing alcohol into this solution.

105. Predict whether silver metal in a solution of chloride ions will produce silver ions and chlorine gas. Explain your prediction. (9.3) T/I A

106. Predict what will happen if you use an iron spoon to stir a solution of copper(II) chloride, $CuCl_2(aq)$. (9.3) T/I A

107. How can you determine experimentally which electrode in a galvanic cell is the anode and which is the cathode? (10.1) T/I A

108. A redox reaction is represented by the following net ionic equation:

$$Ni^{2+}(aq) + Fe(s) \rightarrow Ni(s) + Fe^{2+}(aq)$$

(10.1, 10.2) T/I C
    (a) Sketch a galvanic cell in which this reaction takes place. On your diagram, label the cathode and anode. Indicate the charges on the electrodes, the direction of electron flow, and the direction of flow of cations and anions.
    (b) If the concentrations of the ions are each 1.0 mol/L, what is the potential of the cell?

109. An electrochemical cell is constructed using zinc and silver metals. Solutions of zinc nitrate and silver nitrate (both 0.1 mol/L) are also used. (10.1, 10.2) T/I C
    (a) Draw the cell, labelling all parts and indicating the direction of electron flow and the direction of ion flow.
    (b) Describe this cell using line notation.
    (c) Predict the reaction occurring at the anode.
    (d) Predict the reaction occurring at the cathode.
    (e) Predict the cell potential, assuming standard conditions.
    (f) Would the cell potential be more or less than your prediction in (e)? Explain your answer.

110. A silver battery is smaller than an alkaline battery and is used to provide energy for devices such as hearing aids, watches, and cameras. The silver battery uses the same anode half-reaction as the alkaline battery with the following cathode half-reaction:

$$Ag_2O(s) + H_2O(l) + 2\ e^- \rightarrow 2\ Ag(s) + 2\ OH^-(aq)$$

Use this information to determine the chemical reaction that takes place in the battery. Write a balanced chemical equation for the reaction. (10.3) T/I A

111. Fuel cells can be used to generate electricity. List at least two advantages of using fuel cells over generating electricity from fossil fuels. (10.3, 10.4) A

112. Steel screws and bolts can be plated with cadmium to minimize rusting. (10.6) T/I A
    (a) From the following balanced equation, determine the half-cell potential for the reduction of cadmium:

$$Cd^{2+}(aq) + Ni(s) \rightarrow Cd(s) + Ni^{2+}(aq)$$
$$\Delta E°_r = -0.17\ V$$

    (b) What is the significance of the negative sign in the value of $\Delta E°_r$?

113. What is cathodic protection? Would copper metal make a good cathodic protector to prevent iron from rusting? Explain. (10.6) T/I A

114. Zinc is often found as sphalerite, a zinc sulfide ore. A geochemist combines the ore with sulfuric acid and oxygen gas. The resulting reaction is represented by the following unbalanced equation:

$$ZnS(s) + H_2SO_4(aq) + O_2(g) \rightarrow ZnSO_4(aq) + S(s) + H_2O(l)$$

(9.1, 9.2, 10.2, 10.7) K/U T/I
    (a) Determine the oxidation number of each of the elements in the unbalanced equation.
    (b) Write the balanced equation.
    (c) The geochemist then subjects the solution to electrolysis. Predict the products of electrolysis.
    (d) What is the minimum potential difference that must be supplied to the cell?

115. For each application below, state whether it involves a chemical process that produces electricity or involves the use of electrical energy to drive a chemical process. (10.3, 10.6, 10.7) T/I
    (a) using a flashlight
    (b) producing aluminum from its ore
    (c) electroplating jewellery
    (d) galvanizing metal

116. An electrolytic cell is constructed using graphite electrodes in an aqueous copper(II) iodide solution. (10.7) T/I
    (a) Predict the products at the anode and cathode. Show your reasoning.
    (b) What evidence would you expect to see of the product at each electrode?

117. One method of obtaining copper metal is to let a solution containing copper(II) ions trickle over scrap iron. Is this an efficient process? Explain. (10.7) A

118. Alkaline AA and the larger C cells have the same voltage: 1.5 V. Why are C cells better suited than AA cells for use in remote-controlled cars? (10.7) T/I A

119. When jump-starting a car with a dead battery, the ground jumper should be attached to a remote part of the engine block. Why? (10.7) T/I A

120. If you wished to plate a steel spoon with a layer of silver using an electrolytic cell, should the spoon be the anode or the cathode? What would you use as the other electrode? Use half-cell reaction equations in your explanation. (10.7) T/I C A

121. An electrolytic cell is constructed using inert electrodes. During electrolysis, the cell releases bromine vapour and hydrogen gas. After electrolysis, the cell is found to contain a concentrated solution of potassium hydroxide, KOH(aq). (10.7) T/I A
    (a) Write a balanced chemical equation to show the redox reaction taking place.
    (b) What was the composition of the cell before electrolysis began?

Evaluation

122. Consider the statement, "Oxidation numbers were developed simply for bookkeeping. Except for simple ions like Na^+ or F^-, the charges are fictitious." Discuss the truth of this statement and its impact on predicting oxidation–reduction reactions. (9.1) T/I A

123. Traditionally, oxidation has been defined as the loss of electrons while reduction was defined as the gain of electrons. Recently, it has been suggested that these definitions be updated to:
    - oxidation is an increase in oxidation number of an element
    - reduction is the decrease of oxidation number of an element

    What are the advantages or disadvantages of the proposed definitions? In your opinion, should the definitions be changed? (9.1) T/I

124. All of the following phosphorus compounds are stable. What can you infer about the oxidation number of phosphorus in its compounds?

PH_3, PCl_3, P_2H_4, PCl_5, H_3PO_4, Na_3PO_3 (9.1, 9.3)
T/I A

125. What are the similarities and differences between primary and secondary cells? Which do you think is the best? Why? (10.3) T/I A

126. What advantages and disadvantages do hydrogen fuel cells offer over other common sources of energy for transportation? Should the use of fuel cells in vehicles be extended? (10.3, 10.4) T/I A

127. Compare the different methods used to halt iron corrosion. Discuss when each would be an appropriate method to use to protect a large steel bridge. (10.6) T/I A

128. One way of preventing the corrosion of iron is to prevent oxygen and water from coming into contact with the iron. Is this a practical approach to preventing corrosion on a large scale? What are the drawbacks? Explain. (10.6) T/I A

129. Sodium metal can be produced from the electrolysis of molten sodium chloride. (10.2, 10.7) T/I A
   (a) What is the other product of this electrolysis?
   (b) Solid sodium chloride must be heated to very high temperature to produce the molten salt. Aqueous sodium chloride is much easier to produce. Would it be possible to produce sodium by the electrolysis of a sodium chloride solution? Explain.

130. Some people consider aluminum to be an "infinitely recyclable" manufactured material. Do you think they are right? Explain your reasoning. (10.7) T/I A

Reflect on Your Learning

WEB LINK

131. Construct a concept map using electrochemical processes as the central concept and include all of the key terms from this unit. T/I C

132. Were there any concepts in this unit that you felt were particularly confusing or hard to understand? If so, how could you improve your grasp of these concepts? Make a plan for learning and put it into action. A

Research

WEB LINK

133. Use Internet resources to research the contributions to our knowledge of redox reactions of one of the following scientists: Robert Boyle, Joseph Black, Joseph Priestley, Henry Cavendish, or Antoine Lavoisier. Present your findings as a paper, a comic strip, or in some other format. T/I C A

134. Find out why coating iron or steel with a layer of zinc is called galvanizing. Prepare a poster or cartoon to communicate your discovery. T/I

135. Many of the biological processes that take place in the human body involve redox reactions. Choose one such process, research it, and create a drawing or computer graphic that illustrates the process. Include complete, balanced chemical equations and a written explanation. T/I C A

136. There are many applications of electrochemical processes in the world around us. Write a paper describing how electrochemical processes affect living organisms and the environment, researching additional information as necessary. Focus on three specific examples and include the complete chemical equations for all reactions. Describe the social and economic implications of each reaction. T/I C A

137. Research and evaluate the cost and environmental impact of several types of single-use and rechargeable batteries. Include the advantages and disadvantages of each type. Summarize your findings into a web page, poster, or brochure designed to make consumers better informed. C A

138. There are many chemical reactions involved in photography. Use Internet resources to research and write a paper on this topic geared to a specific audience. T/I C

139. Iron is often protected from rust by contact with a more active metal. Research, compare, and evaluate the effectiveness of different metals used by automobile manufacturers to prevent the corrosion of body panels. Present your findings in a format that is accessible and interesting to potential car buyers. C A

140. Canada is the third-largest copper producer in the world. Research the various methods used in this country to produce copper. Also research the financial costs and environmental impacts of each method. Prepare a report, in the medium of your choice, comparing and evaluating at least two different methods. C A

Appendices

CONTENTS

SKILLS HANDBOOK LINKS

Throughout this textbook you will see links to the Skills Handbook, where appropriate, in each activity. These links identify supporting material in the Skills Handbook that will help you with that activity.

APPENDIX A SKILLS HANDBOOK

A1 Safety

A1.1 Safety Conventions and Symbols

Although we make every effort to make the science experience a safe one, there are some inherent risks. These risks are generally associated with the materials and equipment used, and with disregard of safety instructions when conducting investigations. Most of these risks pose no more danger than we normally experience in everyday life. We can reduce these risks by doing the following: being aware of the possible hazards, knowing the rules, behaving appropriately, and using common sense.

Remember, you share the responsibility not only for your own safety, but also for the safety of those around you (**Figure 1**). Always alert your teacher in case of an accident. In this textbook, chemicals, equipment, and procedures that are hazardous are indicated by the appropriate Workplace Hazardous Materials Information System (WHMIS) symbol or by ✋.

Figure 1 Taking the proper safety precautions will ensure a safe environment for you and your classmates.

WHMIS SYMBOLS AND HHPS

The Workplace Hazardous Materials Information System (WHMIS) provides workers and students with complete and accurate information about hazardous products. All chemical products supplied to schools, businesses, and industries must contain standardized labels and be accompanied by a Material Safety Data Sheet (MSDS). The MSDS provides detailed information about the product. Clear and standardized symbols are an important component of WHMIS (**Table 1**, p. 698). These symbols must be present on the product's original container and shown on other containers if the product is transferred.

The *Canadian Hazardous Products Act* requires manufacturers of consumer products containing chemicals to include a symbol that specifies the nature of the hazard and whether it is the contents or the container that is dangerous. In addition, the label must state any secondary hazards, first-aid treatment, and storage and disposal instructions. Household Hazardous Product Symbols (HHPS) are used to show the type of hazard. The shape of the frame around the symbol indicates whether the hazard is due to the contents or the container (**Figure 2**).

Symbol	Danger
	**Explosive** This container can explode if it is heated or punctured.
	**Corrosive** This product will burn skin or eyes on contact, or throat and stomach if swallowed.
	**Flammable** This product, or its fumes, will catch fire easily if exposed to heat, flames, or sparks.
	**Poisonous** Licking, eating, drinking, or sometimes smelling, this product is likely to cause illness or death.

Figure 2 Household Hazardous Products Symbols (HHPS) appear on many products. A triangular frame indicates that the container is potentially dangerous. An octagonal frame indicates that the contents pose a hazard.

Table 1 The Workplace Hazardous Materials Information System (WHMIS)

Class and type of compounds	WHMIS symbol	Risks	Precautions
Class A: *Compressed Gas* Material that is normally gaseous and kept in a pressurized container		• could explode due to pressure • could explode if heated or dropped • possible hazard from both the force of explosion and the release of contents	• ensure container is always secured • store in designated areas • do not drop or allow to fall
Class B: *Flammable and Combustible Materials* Materials that will continue to burn after being exposed to a flame or other ignition source		• may ignite spontaneously • may release flammable products if allowed to degrade or when exposed to water	• store in designated areas • work in well-ventilated areas • avoid heating • avoid sparks and flames • ensure that electrical sources are safe
Class C: *Oxidizing Materials* Materials that can cause other materials to burn or support combustion		• can cause skin or eye burns • increases fire and explosion hazards • may cause combustibles to explode or react violently	• store away from combustibles • wear body, hand, face, and eye protection • store in container that will not rust or oxidize
Class D: *Toxic Materials Immediate and Severe* Poisons and potentially fatal materials that cause immediate and severe harm		• may be fatal if ingested or inhaled • may be absorbed through the skin • small volumes have a toxic effect	• avoid breathing dust or vapours • avoid contact with skin or eyes • wear protective clothing, and face and eye protection • work in well-ventilated areas and wear breathing protection
Class D: *Toxic Materials Long-Term Concealed* Materials that have a harmful effect after repeated exposures or over a long period		• may cause death or permanent injury • may cause birth defects or sterility • may cause cancer • may be sensitizers causing allergies	• wear appropriate personal protection • work in well-ventilated areas • store in appropriate designated areas • avoid direct contact • use hand, body, face, and eye protection • ensure respiratory and body protection is appropriate for the specific hazard
Class D: *Biohazardous Infectious Materials* Infectious agents or a biological toxin causing a serious disease or death		• may cause anaphylactic shock • includes viruses, yeasts, moulds, bacteria, and parasites that affect humans • includes fluids containing toxic products • includes cellular components	• special training is required to handle materials • work in designated biological areas with appropriate engineering controls • avoid forming aerosols • avoid breathing vapours • avoid contamination of people and/or area • store in special designated areas
Class E: *Corrosive Materials* Materials that react with metals and living tissue		• eye and skin irritation on exposure • severe burns/tissue damage on longer exposure • lung damage if inhaled • may cause blindness if contacts eyes • environmental damage from fumes	• wear body, hand, face, and eye protection • use breathing apparatus • ensure protective equipment is appropriate • work in well-ventilated areas • avoid all direct body contact • use appropriate storage containers and ensure non-venting closures
Class F: *Dangerously Reactive Materials* Materials that may have unexpected reactions		• may react with water • may be chemically unstable • may explode if exposed to shock or heat • may release toxic or flammable vapours • may vigorously polymerize • may burn unexpectedly	• handle with care, avoiding vibration, shocks, and sudden temperature changes • store in appropriate containers • ensure storage containers are sealed • store and work in designated areas

A1.2 Safety in the Laboratory

Safety in the laboratory is an attitude and a habit more than it is a set of rules. It is easier to prevent accidents than to deal with the consequences of an accident. Most of the following rules are common sense:

- Do not enter a laboratory unless a teacher or other supervisor is present, or you have permission to do so.
- Know your school's safety regulations.
- Tell your teacher about any allergies or medical problems you may have.
- Wear eye protection, a lab apron, and safety gloves when instructed by your teacher. Wear closed shoes.
- Tie back long hair and wear a protective lab coat over loose clothing. Remove any loose jewellery and finger rings.
- Keep yourself and your work area tidy and clean. Keep aisles clear.
- Never eat, drink, or chew gum in the laboratory.
- Do not taste any substance in a laboratory or remove substances from the laboratory to consume elsewhere.
- Know the location of MSDS information, exits, and all safety equipment, such as the first-aid kit, fire blanket, fire extinguisher, and eyewash station, and be familiar with their contents and operation.
- Avoid moving suddenly or rapidly in the laboratory, especially near chemicals or sharp instruments.
- If you are not sure what to do, ask your teacher for directions.
- Never change anything, or start an investigation on your own, without your teacher's approval.
- Before you start an investigation that you have designed yourself, get your teacher's approval.
- Never attempt unauthorized experiments.
- Never work in a crowded area or alone in the laboratory.
- Always stand up when doing laboratory practical work. Do not sit down.
- Use stands, clamps, and holders to secure any potentially dangerous or fragile equipment that could be tipped over.
- Never smell chemicals unless specifically instructed to do so by your teacher. Do not inhale the vapours, or gas, directly from the container. Take a deep breath to fill your lungs with air, then waft or fan the vapours toward your nose.
- Report all accidents.
- Inform your teacher of any spills and follow your teacher's instructions on how to clean up the spill. Clean up all spills, even water spills, immediately.
- Wash your hands with soap and warm water when you finish an investigation, and before you leave the laboratory.
- Remember safety procedures when you leave the laboratory. Accidents can also occur outdoors, at home, and at work.

EYE, EAR, AND FACE SAFETY

- Always wear approved eye protection in a laboratory. Keep the safety glasses or goggles over your eyes, not on top of your head. For certain experiments, full face protection may be necessary.
- If you must wear contact lenses in the laboratory, be extra careful; whether or not you wear contact lenses, do not touch your eyes without first washing your hands. If you do wear contact lenses, make sure that your teacher is aware of it. Carry your lens case and a pair of glasses with you.
- If you wear prescription eyeglasses, you must still wear the appropriate eye protection on top of them.
- Do not stare directly at any bright source of light (for example, burning magnesium ribbon). You will not feel any pain if your retina is being damaged by intense radiation. You cannot rely on the sensation of pain to protect you.
- If a piece of glass or other foreign object enters your eye, seek immediate medical attention.

HANDLING GLASSWARE SAFELY

- Never use glassware that is broken, cracked, or chipped. Give such glassware to your teacher or dispose of it as directed. Do not put the item back into circulation.
- Never pick up broken glassware with your fingers. Use a broom and dustpan.
- Dispose of glass fragments in special containers marked "Broken Glass."
- Check with your teacher before heating any glassware. Heat glassware only if it is approved for heating.
- Be very careful when cleaning glassware. There is an increased risk of breakage from dropping when the glassware is wet and slippery.
- If you cut yourself, inform your teacher immediately and get appropriate first aid. Embedded glass or continued bleeding requires medical attention.

USING SHARP INSTRUMENTS SAFELY

- Make sure that your instruments are sharp. Dull cutting instruments require more pressure than sharp instruments and are, therefore, much more likely to slip.
- Select the appropriate instrument for the task. Never use a knife when scissors would work best.
- Always cut away from yourself and others.
- If you cut yourself, inform your teacher immediately and get appropriate first aid.

HEAT SAFETY

- Make sure that heating equipment, such as the burner, hot plate, or electric heater, is secure on the bench and clamped in place when necessary.
- Do not use a laboratory burner near wooden shelves, flammable liquids, or any other item that is combustible.
- Do not allow overheating if you are performing an experiment in a closed area.
- Always assume that hot plates and electric heaters are hot and use protective gloves when handling.
- In a laboratory where burners or hot plates are being used, never pick up a glass or metal object without first checking the temperature by placing your hand near but not touching it. It may be hot enough to burn you.
- Do not touch a light source that has been on for some time. It may be hot and cause burns.
- If you burn yourself, *immediately* run cold water gently over the burned area or immerse the burned area in cold water and inform your teacher.
- Never look down the barrel of a laboratory burner.
- Always pick up a burner by its base, never by its barrel.
- Never leave a lighted burner unattended.
- Any metal powder can be explosive. Do not put these in a flame.
- When heating a test tube over a laboratory burner, use a test-tube holder or a utility clamp. Holding the test tube at an angle, with the open end pointed away from you and others, gently move the test tube back and forth through the flame.
- To heat a beaker, put it on the hot plate and secure with a ring support attached to a utility stand. (Placing a wire gauze under the beaker is optional.)
- Remember to include a cooling time in your experiment plan; do not put away hot equipment.

FIRE SAFETY

To use a burner:

- Tie back long hair and tie back or roll up long sleeves or other loose clothing.
- Secure the burner to a stand using a metal clamp.
- Check that the rubber hose is properly connected to the gas valve.
- Close the air vents on the burner. Use a sparker to light the burner.
- Open the air vents just enough to get a blue flame.
- Control the size of the flame using the gas valve.
- Immediately inform your teacher of any fires. A very small fire in a container may be extinguished by covering the container with a wet paper towel or a ceramic square to cut off the supply of air. Alternatively, sand may be used to smother small fires. A bucket of sand with a scoop should be available in the laboratory.
- If anyone's clothes or hair catch fire, tell the person to drop to the floor and roll. Then use a fire blanket to smother the flames. Never wrap the blanket around a standing person on fire.
- For larger fires, immediately evacuate the area. Call the office or sound the fire alarm. Do not try to extinguish larger fires. As you leave the classroom, make sure that the windows and doors are closed.
- If you use a fire extinguisher, direct the extinguisher at the base of the fire and use a sweeping motion, moving the extinguisher nozzle back and forth across the front of the fire's base.
- Different extinguishers are effective for different classes of fires. The fire classes are outlined in **Table 2**. Fire extinguishers in the laboratory are 2A10BC. They extinguish class A, B, and C fires.

Table 2 Classes of Fires

Class	Description	Firefighting strategy
Class A	• ordinary combustible materials that leave coals or ashes (e.g., wood, paper, cloth)	• water or dry chemical extinguishers
Class B	• flammable liquids (e.g., gasoline or solvents)	• carbon dioxide or dry chemical extinguishers
Class C	• live electrical equipment (e.g., appliances, photocopiers, computers, laboratory equipment)	• carbon dioxide or dry chemical extinguishers • do not use water
Class D	• burning metals (e.g., sodium, potassium, magnesium, aluminum)	• sand, salt, or graphite • do not use water
Class E	• radioactive substances	• requires special consideration at each site

ELECTRICAL SAFETY

- Do not operate electrical equipment near running water or a large container of water. Water or wet hands should never be near electrical equipment such as a hot plate, a light source, or a microscope.
- Check the condition of electrical equipment. Do not use it if wires or plugs are damaged, or if the ground pin has been removed.
- Make sure that electrical cords are not placed where someone could trip over them.
- When unplugging equipment, remove the plug gently from the socket. Do not pull on the cord.

WASTE DISPOSAL

Waste disposal at school, at home, and at work is a societal issue. It is your responsibility to follow procedures and to dispose of waste in the safest possible manner according to your teacher's instructions.

FIRST AID

The following guidelines apply in case of an injury, such as a burn, cut, chemical spill, ingestion, inhalation, or splash in the eyes:

- Always inform your teacher immediately of any injury.
- If the injury is a minor cut or abrasion, wash the area thoroughly. Using a compress (for example, clean paper towels), apply pressure to the cut to stop the bleeding. When bleeding has stopped, replace the compress with a sterile bandage. If the cut is serious, apply pressure and seek medical attention immediately.
- If you get a chemical in your eye, quickly use the eyewash or nearest running water. Continue to rinse the eye with water for at least 15 min. Unless you have a plumbed eyewash system, you will also need assistance in refilling the eyewash container. Have another student inform your teacher of the accident. The injured eye should be examined by a doctor.
- If the injury is a burn, immediately immerse the affected area in cold water, or run cold water gently over the burned area. This will reduce the temperature and prevent further tissue damage.
- In case of electric shock, unplug the appliance and do not touch it or the victim. Inform your teacher immediately.
- If a classmate's injury has rendered him/her unconscious, notify your teacher immediately. Your teacher will perform CPR if necessary. Do not administer CPR unless under specific instructions from your teacher. Call the school office and request emergency medical help.

A2 Scientific Inquiry

As we observe the natural world, we encounter questions, mysteries, or events that are not readily explainable. To develop explanations, we investigate using inquiry investigations. An important aspect of inquiry investigations is that science is only one of many ways in which people explore, explain, and come to understand the world around them. Inquiry investigations generally involve the following:

- formulating questions that can be answered through investigation
- using appropriate tools and techniques to gather, analyze, and interpret data
- developing descriptions, explanations, predictions, and models using evidence
- thinking critically and logically to see the relationships between evidence and explanations
- recognizing and analyzing alternative explanations and predictions
- communicating scientific procedures and explanations

The methods used in inquiry investigations depend, to a large degree, on the purpose of the inquiry. There are three types of inquiry investigations used in this textbook: (1) the controlled experiment, (2) the observational study, and (3) the activity. These types of inquiry investigations require specific skills. The skills are discussed below, followed by a detailed description of how they relate to each type of inquiry investigation.

A2.1 Skills of Scientific Inquiry

Certain skills are important in the process of conducting a scientific investigation. These skills can be organized into four categories: initiating and planning, performing and recording, analyzing and interpreting, and communicating.

INITIATING AND PLANNING

1. Questioning: Most inquiry investigations begin with a question. It is important to ask the right questions. In certain types of inquiry investigations, the question must be testable. This means that it must ask about a possible cause-and-effect relationship. A cause-and-effect relationship is one in which a change in one variable (see point 3 below) causes a change in another variable. A testable question might start in one of the following ways: What is the relationship between . . . and . . . ? How does . . . affect . . . ? If . . . , what happens to . . . ?
2. Researching: This is a skill that occurs across all four categories of scientific investigation and includes preparing for research, accessing resources, processing information, and transferring learning. The process involves identifying the type of information that is required, using strategies to locate and access the information, recording the information, synthesizing findings, and formulating conclusions.
3. Identifying variables: Considering the variables involved in an investigation is an important step in designing an effective investigation. Variables are any factors that could affect the outcome of an investigation. There are three kinds of variables in a controlled experiment: the manipulated variable, the responding variable, and the controlled variables.
    - The manipulated variable (also known as the independent variable or cause variable) is the variable that is deliberately changed by the investigator.
    - The responding variable (also known as the dependent variable or effect variable) is the variable that the investigator believes will be affected by a change in the manipulated variable.
    - The controlled variables are variables that may affect the responding variable, but that are held constant so that they cannot affect the responding variable. A controlled experiment is a test of whether (and how) a manipulated variable affects a responding variable. To make the test fair, all other variables that may affect the responding variable are kept constant (unchanging).
4. Hypothesizing: A hypothesis is a predicted answer to the testable question. It proposes a possible explanation based on an already known scientific theory, law, or other generalization.

   A hypothesis may be written in the form of an "If . . . , then . . . because . . ." statement. If the manipulated (independent) variable is changed in a particular way, then we predict that the responding (dependent) variable will change in a particular way, and we provide a theoretical explanation for the prediction. For example:

   > If an air-filled balloon is placed in a freezer and its temperature is decreased, then its volume will decrease because, according to the kinetic molecular theory, atoms and molecules slow down and occupy less space at lower temperatures.

   You may create more than one hypothesis from the same testable question.

   When you conduct an investigation, your observations do not always support the prediction in your hypothesis. When this happens, you may re-evaluate and modify your hypothesis and design a new experiment.
5. Planning: Planning an inquiry investigation involves developing an experimental design, identifying variables, selecting necessary equipment and materials, addressing safety concerns, and writing a step-by-step procedure.

PERFORMING AND RECORDING

1. Conducting the inquiry investigation: As you perform an investigation, follow the steps in the procedure carefully and thoroughly. Check with your teacher if you find that you need to make significant alterations to your procedure. Use all equipment and materials safely, appropriately, and with precision.
2. Making observations: When you conduct an inquiry investigation, you should make accurate observations at regular intervals and record them carefully and accurately. Record exactly what you observe. Observations from an experiment may not always be what you expect them to be. Qualitative (descriptive) and quantitative (measured) observations may be made during an investigation. Some observations may also be provided for you during an investigation.

   Quantitative observations are based on measured quantities, such as temperature, volume, and mass. They are usually recorded in data tables.

   Qualitative observations describe characteristics that cannot be expressed in numbers, such as texture, smell, and taste. They can be recorded using words, pictures, tables, or labelled diagrams.
3. Collecting, organizing, and recording data: During an investigation you should collect and record all data and observations, and organize these into formats that are easily interpreted (such as tables, charts, etc.).

ANALYZING AND INTERPRETING

1. Analyzing: Analyzing involves looking for patterns and relationships that will help explain your results and give new information about the question you are investigating. Your analysis will tell you whether your observations support your hypothesis.
2. Evaluating: It is very important to evaluate the evidence that is obtained through observations and analysis. When evaluating the results of an investigation, here are some aspects you should consider:
   - Experimental design: Were there any problems with the way you planned your experiment? Did you control all the variables except for the manipulated variable?
   - Equipment and materials: Was the equipment adequate? Would other equipment have been better? Was equipment used incorrectly? Did you have difficulty with a piece of equipment?
   - Skills: Did you have the appropriate skills for the investigation? Did you have to use a skill that you were just beginning to learn?
   - Observations: Did you accurately record all the relevant observations?

COMMUNICATING

1. It is important to share both your process and your results. Other people may want to repeat your investigation, or they may want to use or apply your results in another situation. Your write-up or report should reflect the process of scientific inquiry that you used in your investigation.
2. At this stage, you should be prepared to extend insights and opinions from your findings, suggest areas for further investigation, and relate research findings to the world around you.

In the following sections, we will detail the components of the three types of inquiry investigation: controlled experiments, observational studies, and activities.

A2.2 Controlled Experiments

A controlled experiment is an inquiry investigation in which a manipulated variable is intentionally changed to determine its effect on a responding variable. All other variables are controlled (kept constant). Controlled experiments are performed when the purpose of the inquiry is to create, test, or use a scientific concept.

The common components of controlled experiments are outlined below. Note that there are normally many cycles through the steps during an actual experiment.

TESTABLE QUESTION

A testable question forms the basis for your controlled experiment: the investigation is designed to answer the question. Controlled experiments are about relationships among variables, so your question could inquire about changes to variable A that may occur as a result of changes to variable B.

VARIABLES

The primary purpose of a controlled experiment is to determine whether a change in a manipulated variable causes a noticeable change in a responding variable while all other variables remain constant. Therefore, you must identify all major variables that you will measure and/or control in your investigation. What is the manipulated (independent) variable? What is the responding (dependent) variable? What are the controlled variables?

When conducting a controlled experiment, change only one manipulated variable at a time, holding all the others (except the responding variable) constant. This way, you can assume that the results are caused by the manipulated variable and not by any of the other variables.

HYPOTHESIS

When formulating a hypothesis, first read the testable question, the experimental design, and the procedure, if provided. Then, try to identify the manipulated variable, the responding variable, and the controlled variables. Your hypothesis will be a predicted answer to your testable question accompanied by a theoretical explanation for your prediction.

EXPERIMENTAL DESIGN

The design of a controlled experiment shows how you plan to answer your question. The design outlines how you will change the manipulated variable, measure any variations in the responding variable, and control all the other variables. It is a summary of your plan for the experiment.

EQUIPMENT AND MATERIALS

Make a detailed list of all equipment and materials used, including sizes and quantities where appropriate. Be sure to include safety equipment, such as eye protection, lab apron, protective gloves, and tongs, where needed. Draw a diagram to show any complicated setup of apparatus.

PROCEDURE

Write a step-by-step description of how you will perform your investigation. It must be clear enough for someone else to follow and it must explain how you will deal with each of the variables in your investigation. The first step in a procedure usually refers to any safety precautions that need to be addressed, and the last step relates to any cleanup that needs to be done.

OBSERVATIONS

There are many ways you can gather and record observations during your investigation. It is helpful to plan ahead and think about what data you will need to answer the question and how best to record them (for example, data tables, pictures, or labelled diagrams may be helpful). This helps to clarify your thinking about the question posed at the beginning, the variables, the number of trials, the procedure, the materials, and your skills. It will also help you organize your evidence for easier analysis.

ANALYZE AND EVALUATE

You will need to analyze and interpret your observations—this may include graphing your data and analyzing any patterns or trends that may be evident in your graphs. After thoroughly analyzing your observations, you may have sufficient and appropriate evidence to enable you to answer the testable question posed at the beginning of the investigation.

You must evaluate the processes that you followed to plan and perform the investigation. Identify and take into account any sources of error and uncertainty in your measurements. Note that experimental error does not include human error, such as careless measurements or spilled reactants or products. Rather, it includes contaminated chemicals, unwanted reactions, and the unavailability of ideal equipment.

You will also evaluate the outcome of the investigation, which involves evaluating your hypothesis/prediction. You must identify and take into account any sources of error and uncertainty in your measurements.

Finally, compare your hypothesis/prediction with the evidence. Is your hypothesis supported by the evidence?

APPLY AND EXTEND

Reflect on how your investigation relates to the world around you: how can you use your findings in everyday life?

REPORTING ON THE INVESTIGATION

Your lab report should describe your planning process and procedure clearly and in enough detail that the reader could duplicate your experiment. You should present your observations, your analysis, and your evaluation of your experiment clearly, accurately, and honestly.

A2.3 Observational Studies

Often, the purpose of an inquiry is simply to study a natural phenomenon with the intention of gaining scientifically significant information to answer a question. Observational studies involve observing a subject or phenomenon in an unobtrusive manner, usually with no specific hypothesis. The inquiry does not start off with a hypothesis, but a hypothesis may be generated as information is collected.

The stages and processes of observational studies are summarized below. Even though the sequence is presented as linear, there are normally many cycles through the steps during an actual study.

PURPOSE

In planning an observational study, it is important to pose a general question about the natural world. Choose a topic that interests you. Determine whether you are going to replicate or revise a previous study, or create a new one. Indicate your decision in a statement of the purpose.

EQUIPMENT AND MATERIALS

Make a detailed list of all equipment and materials used, including sizes and quantities where appropriate. Be sure to include safety equipment, such as eye protection, lab apron, protective gloves, and tongs, where needed. Draw a diagram to show any complicated setup of apparatus.

PROCEDURE

Write a step-by-step description of how you will make your observations. It must be clear enough for someone else to follow. The first step in a procedure usually refers to any safety precautions that need to be addressed, and the last step relates to any cleanup that needs to be done.

OBSERVATIONS

There are many ways you can gather and record observations—including quantitative observations—during an observational study. All observations should be objective and unambiguous. Organize your information for easier analysis.

ANALYZE AND EVALUATE

After thoroughly analyzing your observations, you may have sufficient and appropriate evidence to enable you to answer the question posed at the beginning of the investigation. You may also have enough observations and information to form a hypothesis for a controlled experiment.

At this stage of the investigation, you will evaluate the processes used to plan and perform the investigation. Evaluating the processes includes evaluating the materials, the design, the procedure, and your skills. The results of most such investigations will suggest further studies, perhaps controlled experiments or correlational studies, to explore tentative hypotheses you may have developed.

APPLY AND EXTEND

At this stage you should reflect on how your investigation relates to the world around you: how can you use what you have learned in your everyday life?

REPORTING ON THE INVESTIGATION

In your report, describe your design and procedure accurately, and report your observations accurately and honestly.

A2.4 Activities

An activity is a type of scientific inquiry that provides opportunities to demonstrate knowledge and understanding of specific concepts. In many cases, an activity might involve constructing a device, reasoning your way through a problem (thought experiment), or using given information to complete a task. You can also consider creative ways of presenting the concept, be it through performance, digital platforms, or print material. The materials required for an activity can vary greatly, so will need special planning and attention. Activities do not have structured stages and processes, but to demonstrate a thorough understanding of the concept being modelled, it is important to communicate key points. You will need to analyze and evaluate your presentation—this may include looking at how your understanding of the concept has grown and applying what you have learned in the chapter to other areas.

A2.5 Lab Reports

When carrying out inquiry investigations, it is important that scientists keep records of their plans and results, and share their findings. In order to have their investigations repeated (replicated) and accepted by the scientific community, scientists generally share their work by publishing reports in which details of their design, materials, procedure, evidence, analysis, and evaluation are provided.

Lab reports are prepared after an investigation is completed. To ensure that you can accurately describe the investigation, keep thorough and accurate records of your activities as you carry out the investigation. Your lab book or report should reflect the type of scientific inquiry that you used in the investigation (controlled experiment, observational study, or activity), and should be based on the following headings, *as appropriate*:

TITLE

At the beginning of your report, write the number and title of your investigation. If you are designing your own investigation, create a title that suggests what the investigation is about. Include the date the investigation was conducted and the names of all lab partners (if you worked as a team).

PURPOSE

State the purpose of the investigation. Why are you doing this investigation?

TESTABLE QUESTION

State the question that you attempted to answer in the investigation. Sometimes the question is provided for you; other times you are expected to formulate your own. If it is appropriate to do so, state the question in terms of manipulated and responding variables.

HYPOTHESIS/PREDICTION

For a controlled experiment you will usually have to compose a hypothesis or prediction. This will be a proposed answer to your testable question. When writing a hypothesis, include both a prediction and a reason for the prediction, based on scientific theory, law, or other generalization. You may use the "If . . . , then . . . because . . ." form. A simple prediction may be written in the "If . . . , then . . ." form.

VARIABLES

Identify all major variables that you measured and/or controlled in the investigation. What is the manipulated variable? What is the responding variable? What are the major controlled variables?

EXPERIMENTAL DESIGN

Provide a brief general overview (one to three sentences) of what you did in your investigation. If your investigation involved manipulated, responding, and controlled variables, list them and indicate how they were changed, measured, or held constant. Identify any control or control group that was used in the investigation.

EQUIPMENT AND MATERIALS

Include a detailed list of all equipment and materials used, including sizes and quantities where appropriate. Be sure to include safety equipment, such as eye protection, lab apron, protective gloves, and tongs, where needed. Draw a diagram to show any complicated setup of apparatus.

PROCEDURE

Describe, in detailed, numbered steps, the procedure you followed to carry out your investigation. Your teacher may specify which style you should use. Examples of three common writing styles are

1. third person past tense ("The test tubes were heated . . .")
2. first person plural past tense ("We heated the test tubes . . .")
3. second person imperative ("Heat the test tubes . . .")

Include steps to clean up and dispose of waste.

OBSERVATIONS

Present your observations in a form that is easily understood. This includes all the qualitative and quantitative observations that you made. Be as precise as possible when describing quantitative observations. Include any unexpected observations and present your information clearly. If you have only a few observations, this could be a list; for controlled experiments and for many observations, a data table, labelled diagram, or written descriptions would be more appropriate.

ANALYSIS

Complete the questions found in the Analyze and Evaluate section of the investigation outline. These questions will prompt you to analyze and interpret your observations, answer a testable question, draw conclusions, and evaluate both your experiment and your conclusions. You will also be prompted to graph your data and analyze these graphs where applicable.

If you are writing up an investigation for which there are no questions, write your own analysis. Interpret your observations and present the evidence in the form of titled tables, graphs, or illustrations, as appropriate. Include any calculations, the results of which can be shown in a table. Make statements about any patterns or trends you observed. Conclude the analysis with a statement based only on the evidence you have gathered, answering the question that initiated the investigation.

EVALUATION

The evaluation is your judgment about the quality of evidence obtained and about the validity of the prediction and hypothesis (if present). This section can be divided into two parts:

1. Evaluation of the procedure and/or experimental design: Did your procedure/design provide reliable and valid evidence to enable you to answer the question? Consider the experimental design, the procedure, and your laboratory skills. Were they all adequate? Are you confident enough in the evidence to use it to evaluate any prediction and/or hypothesis you made?
2. Evaluation of the prediction/hypothesis: Was your prediction or hypothesis supported or not supported by the evidence? Answer the question that you posed at the beginning of the investigation on the basis of your evaluation of your prediction or hypothesis.

APPLY AND EXTEND

Answer any Apply and Extend questions in the investigation outline. Number your answers as they appear in the Apply and Extend section in the textbook.

A3 Laboratory Skills and Techniques

A3.1 Lighting and Using a Laboratory Burner

Practise and memorize the procedure outlined below. Note the safety caution. You are responsible for your safety and the safety of others near you.

1. Turn the air and gas adjustments to the off position.
2. Connect the burner hose to the gas outlet on the bench.
3. Turn the bench gas valve to the fully on position.
4. If you suspect that there may be any gas leaks, replace the burner. (Give the leaky burner to your teacher.)
5. Holding a spark lighter ready above and to one side of the barrel, open the burner gas valve. Immediately strike a few sparks until a small yellow flame results (**Figure 1**).
6. Adjust the airflow and obtain a pale blue flame with a dual cone (**Figure 2**). In most common types of burners, rotating the barrel adjusts the air intake. Rotate the barrel slowly. If too much air is added, the flame may go out. If this happens, immediately turn the gas flow off. Relight the burner using the procedure outlined previously.

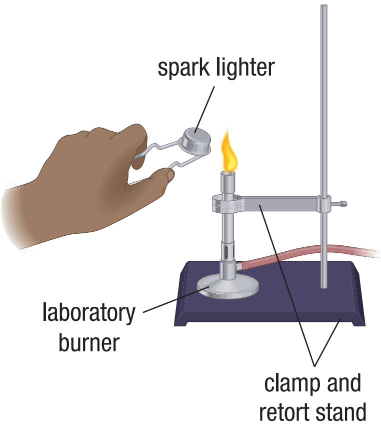


Figure 1 Lighting a laboratory burner

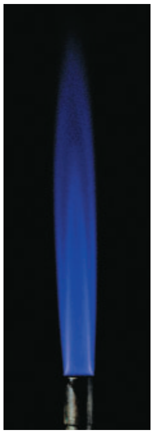


Figure 2 A blue flame indicates complete combustion.

7. Adjust the gas valve on the burner to increase or decrease the height of the blue flame. The hottest part of the flame is the tip of the inner blue cone. You will usually use a 5 to 10 cm flame that just about touches the object being heated. Never leave a lit burner unattended. If the burner is on but not being used, adjust the air and gas intakes to obtain a small yellow flame. This flame is more visible and, therefore, less likely to cause problems.

When lighting or using a laboratory burner, never position your head or fingers directly above the barrel. Tie back long hair and secure loose clothing.

A3.2 Using a Laboratory Balance

A balance is a sensitive instrument used to measure the mass of an object or substance. There are some general rules that you should follow when using a balance.

- All balances must be handled carefully and kept clean. The pan of an electronic balance should be removed for cleaning.
- To avoid error due to convection currents in the air, allow hot or cold samples to return to room temperature before placing them on the balance. Do not lean on the bench when using the balance.
- Always place chemicals into a container such as a beaker or plastic boat, or use a weighing paper, to avoid contamination and corrosion of the balance pan.
- Place the empty container or weighing paper on the pan and reset (tare) the balance so the mass of the container registers as zero.
- The last digit may not be constant, indicating uncertainty due to air currents or the high sensitivity of the balance.
- Always record masses showing the correct precision. On a centigram balance, mass is measured to the nearest hundredth of a gram (0.01 g).
- When it is necessary to move a balance, hold the instrument by the base and steady the beam. Never lift a balance by the beams or pans.
- To avoid contaminating a whole bottle of reagent, a scoop should not be placed in the original container of a chemical. A quantity of the chemical should be poured out of the original reagent bottle into a clean, dry beaker or bottle, from which samples can be taken. Another acceptable technique for dispensing a small quantity of chemical is to rotate or tap the chemical bottle.

A3.3 Using a Pipette

A pipette is a specially designed glass tube used to measure precise volumes of liquids. There are two types of pipettes and a variety of sizes for each type. A volumetric pipette

(**Figure 3(a)**) is used to measure a fixed volume, such as 10.00 mL or 25.00 mL, accurate to within 0.04 mL. A graduated pipette (**Figure 3(b)**) measures a range of volumes within the limit of the scale, just as a graduated cylinder does. A 10 mL graduated pipette measures volumes accurate to within 0.1 mL.

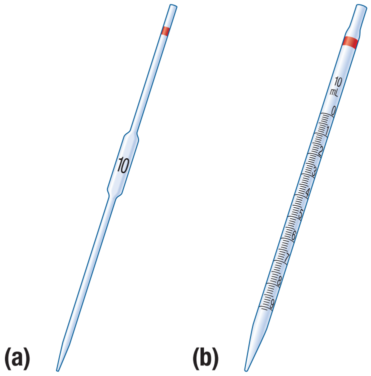


Figure 3 (a) A volumetric pipette measures the volume printed on the label if the temperature is near room temperature. (b) To use a graduated pipette you must be able to start and stop the flow of the liquid.

Never use your mouth to draw a liquid into a pipette. Always use a pipette bulb or pump.

To use a pipette:

1. Rinse the pipette with small volumes of distilled water using a wash bottle, then with the sample solution. A clean pipette has no visible residue or liquid drops clinging to the inside wall.
2. Hold the pipette with your thumb and fingers near the top. Leave your index finger free.
3. Place the pipette in the sample solution, resting the tip on the bottom of the container if possible. Be careful that the tip does not hit the sides of the container.
4. Squeeze the bulb into the palm of your hand and place the bulb firmly and squarely on the end of the pipette (**Figure 4**) with your thumb across the top of the bulb.

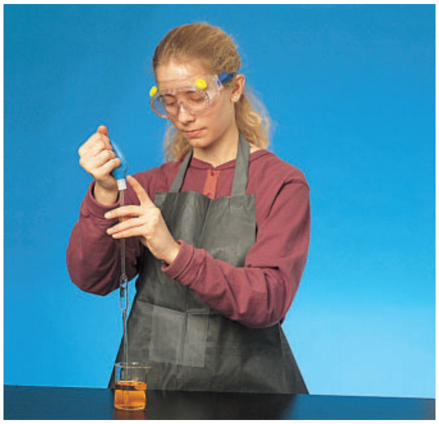


Figure 4 Release the bulb slowly. Pressing down with your thumb placed across the top of the bulb maintains a good seal. Setting the pipette tip on the bottom slows the rise or fall of the liquid.

5. Release your grip on the bulb until the liquid has risen above the calibration line. This may require bringing the level up in stages: remove the bulb, put your finger on the pipette, squeeze the air out of the bulb, replace the bulb, and continue the procedure.
6. Remove the bulb, placing your index finger over the top. If you are using a dispensing bulb (**Figure 5**) or a pipette pump (**Figure 6**), leave it attached to the pipette.

Figure 5 A dispensing bulb uses a small valve in the side stem to control the flow of liquid in a pipette.

Figure 6 A pipette pump has a small roller that can be turned to draw liquid in or to let liquid out of the pipette.

7. Wipe all solution from the outside of the pipette using a paper towel.
8. While touching the tip of the pipette to the inside of a waste beaker, gently roll your index finger (or squeeze the valve of the dispensing bulb) to allow the liquid level to drop until the bottom of the meniscus reaches the desired calibration line (**Figure 7**). To avoid errors, read the meniscus at eye level. Use the bulb to raise the level of the liquid again if necessary.

Figure 7 To allow the liquid to drop slowly to the calibration line, it is necessary for your finger and the pipette top to be dry. Also keep the tip on the bottom to slow down the flow.

9. While holding the pipette vertically, touch the pipette tip to the inside wall of a clean receiving container. Remove your finger or adjust the valve

and allow the liquid to drain freely until the solution stops flowing.

10. Finish by touching the pipette tip to the inside of the container held at about a 45° angle (**Figure 8**). Do not shake the pipette. The delivery pipette is calibrated to leave a small volume in the tip.

Figure 8 A vertical volumetric pipette is drained by gravity and then the tip is placed against the inside wall of the container. A small volume is expected to remain in the tip.

A3.4 Filtration

In filtration, solids are separated from a mixture using porous filter paper. The more porous papers are called qualitative filter papers. Quantitative filter papers allow only invisibly small particles through the pores of the paper.

1. Set up a filtration apparatus (**Figure 9**): stand with ring clamp, filter funnel, waste beaker, wash bottle, and a stirring rod with a flat plastic or rubber end for scraping.

Figure 9 The tip of the funnel should touch the inside wall of the collecting beaker.

2. Fold the filter paper along its diameter and then fold it again to form a cone. A better seal of the filter paper on the funnel is obtained if a small piece of the outside corner of the filter paper is torn off (**Figure 10**).

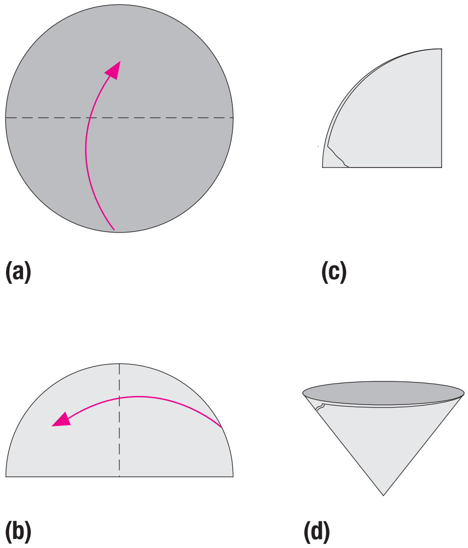


Figure 10 To prepare a filter paper, fold it in half twice and then remove the outside corner as shown.

3. Measure and record the mass of the filter paper after removing the corner.
4. While holding the open filter paper in the funnel, wet the entire paper and seal the top edge firmly against the funnel with the tip of the cone centred in the bottom of the funnel.
5. With the stirring rod touching the spout of the beaker, decant most of the solution into the funnel. Transferring the solid too soon clogs the pores of the filter paper. Keep the level of liquid about two-thirds up the height of the filter paper. The stirring rod should be rinsed each time it is removed.
6. When most of the solution has been filtered, pour the remaining solid and solution into the funnel. Use the wash bottle and the flat end of the stirring rod to clean any remaining solid from the beaker.
7. Use the wash bottle to rinse the stirring rod and the beaker.
8. Wash the solid two or three times to ensure that no solution is left in the filter paper. Direct a gentle stream of water around the top of the filter paper.
9. When the filtrate has stopped dripping from the funnel, remove the filter paper. Press your thumb against the thick (three-fold) side of the filter paper and slide the paper up the inside of the funnel.
10. Transfer the filter paper from the funnel onto a labelled watch glass and unfold the paper to let the precipitate dry.
11. Determine the mass of the filter paper and dry precipitate.

A3.5 Preparing Standard Solutions

Laboratory procedures often call for the use of a solution of specific, precise concentration.

A STANDARD SOLUTION FROM A SOLID

Sometimes you will have to prepare a solution of known concentration from a solid solute and water.

1. Calculate the required mass of solute from the volume and concentration of the solution.
2. Obtain the required mass of solute on a weighing paper or in a clean, dry beaker. (Refer to A3.2 Using a Laboratory Balance earlier in this section.)

If water is added directly to some solids or concentrated liquids, there may be boiling or splattering. Always add a solid solute or concentrated liquids to water.

3. Pour distilled water into a beaker to a volume that is less than half of the final volume of the solution. Transfer the solute to the water. Stir to dissolve.
4. Transfer the solution into a clean volumetric flask. Use a funnel to avoid spills. Rinse the beaker and any other equipment two or three times with distilled water, adding the rinse water to the volumetric flask. Add more distilled water to the flask until the level of the liquid is a few millilitres less than the desired volume.
5. Use a dropper bottle to add the final few millilitres of distilled water. Use a meniscus finder to set the bottom of the meniscus on the calibration line.
6. Place a stopper in the mouth of the flask. Swirl the flask to mix the solution.

A STANDARD SOLUTION FROM A CONCENTRATED SOLUTION

Sometimes you will have to prepare a solution of known concentration using an existing stock (concentrated) solution.

1. Calculate the volume of stock solution required.
2. Add approximately one-half of the final volume of distilled water to the volumetric flask.
3. Measure the required volume of stock solution using a pipette. (Refer to A3.3 Using a Pipette.)
4. Transfer the stock solution slowly into the volumetric flask, using a funnel. Rinse the container two or three times with distilled water, adding the rinse water to the volumetric flask. Add more distilled water to the flask until the level of the liquid is a few millilitres less than the desired volume.
5. Use a dropper bottle to add the final few millilitres of distilled water. Use a meniscus finder to set the bottom of the meniscus on the calibration line.
6. Place a stopper in the mouth of the flask. Swirl the flask to mix the solution.

A3.6 Titration

Titration is used in the volumetric analysis of an unknown concentration of a solution. Titration involves adding a solution (the titrant) from a burette to another solution (the sample) in an Erlenmeyer flask until a recognizable endpoint, such as a colour change, occurs.

1. Rinse the burette with small volumes of distilled water using a wash bottle. Using a burette funnel, rinse with small volumes of the titrant (**Figure 11**). (If liquid droplets remain on the sides of the burette after rinsing, scrub the burette with a burette brush. If the tip of the burette is chipped or broken, replace the tip or the whole burette.)

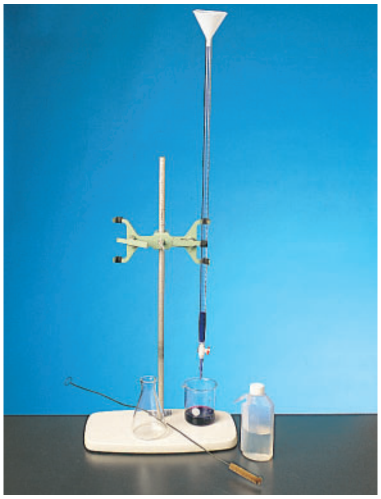


Figure 11 A burette should be rinsed with water and then the titrant before use. Use a burette brush only if necessary.

2. When filling a burette, always use a funnel. Work with the top of the burette below eye level to reduce the possibility of the solution splashing into your eyes. Pour the solution into the burette until the level is near the top. Open the valve for maximum flow to clear any air bubbles from the tip and to bring the liquid level down to the scale.
3. Record the initial burette reading to the nearest 0.1 mL. Avoid parallax errors by reading volumes at eye level with the aid of a meniscus finder.
4. Use a pipette to transfer a sample of the solution of unknown concentration into a clean Erlenmeyer flask. Place a piece of white paper beneath the Erlenmeyer flask to make it easier to detect colour changes.
5. Add an indicator if one is required. Add the smallest quantity necessary (usually 1 to 2 drops) to produce a noticeable colour change in your sample.
6. Add the solution from the burette quickly at first, and then slowly, drop-by-drop, near the endpoint (**Figure 12**). Stop as soon as a drop of the titrant produces a permanent colour change in the sample

Figure 12 Near the endpoint, continuous gentle swirling of the solution is particularly important.

solution. A permanent colour change is considered to be a noticeable change that lasts for 10 s after swirling.

7. Record the final burette reading to the nearest 0.1 mL.
8. The final burette reading for one trial becomes the initial burette reading for the next trial. Three trials with results within 0.2 mL are normally required for a reliable analysis of an unknown solution.
9. Drain and rinse the burette with pure water. Store the burette upside down with the valve open.

A3.7 Diagnostic Tests

The tests described in **Table 1** are commonly used to detect a specific substance. All diagnostic tests include a brief procedure, some expected evidence, and an interpretation of the evidence obtained. This is conveniently communicated using if-then statements.

Diagnostic tests can be constructed using any characteristic empirical property of a substance, like determining the pH of certain solutions. For specific chemical reactions, properties of the products that the reactants do not have, such as the insolubility of a precipitate or the production of a gas can be used to construct diagnostic tests.

If possible, you should use a control to illustrate that the test does not give the same results with other substances. For example, in the test for oxygen, you typically insert a glowing splint into a test tube that contains a gas suspected to be oxygen. You should also conduct the test on a test tube containing air, to compare the effects. This is the control test. If the splint reacts the same way in both test tubes, you could not conclude that the "oxygen" test tube contains any more oxygen than is present in air.

Table 1 Some Standard Diagnostic Tests

Substance tested	Diagnostic test
water	If cobalt(II) chloride paper is exposed to a liquid or vapour, and the paper turns from blue to pink, then water is likely present.
oxygen	If a glowing splint is inserted into the test tube, and the splint glows brighter or relights, then oxygen gas is likely present.
hydrogen	If a flame is inserted into the test tube, and a squeal or pop is heard, then hydrogen is likely present.
carbon dioxide	If the unknown gas is bubbled into a limewater solution, and the limewater turns cloudy, then carbon dioxide is likely present.
halogens	If a few millilitres of mineral oil is added, with shaking, to a solution in a test tube, and the colour of the oil appears to be • light yellow-green, then chlorine is likely present • orange, then bromine is likely present • purple, then iodine is likely present
acid	If strips of blue and red litmus paper are dipped into the solution, and the blue litmus turns red, then an acid is present.
base	If strips of blue and red litmus paper are dipped into the solution, and the red litmus turns blue, then a base is present.
neutral solution	If strips of blue and red litmus paper are dipped into the solution, and neither changes colour, then only neutral substances are likely present.
neutral ionic solution	If a neutral substance is tested for conductivity with a voltmeter or multimeter, and the solution conducts a current, then a neutral ionic substance is likely present.
neutral molecular solution	If a neutral solution is tested and does not conduct a current, then a neutral molecular substance is likely present.

A4 Scientific Publications

Communicating in Science

Advances in science and our understanding of the natural world are the result of scientists sharing ideas and information. Ernest Rutherford used alpha particles emitted by the radioactive element polonium to discover the nucleus. Rutherford's discovery was possible only because Marie Curie had recognized, a few years earlier, that polonium is radioactive.

It is important for scientists to share ideas and research with other scientists. New research findings are shared at conferences or in journal publications. Research scientists take pride in being published. Being published confirms that the research adds to the knowledge base of the scientific community. Sharing information helps to spread knowledge, solve problems, and inspire other scientists. For an example, please see the P.F. Frame paper cited in the "Further Reading" section.

The Scientific Journal

Scientific journals are publications that are used to report the results of new research. There are thousands of different science journals published worldwide, and in many languages. A scientific journal may be specific to a subject (for example, *Journal of Atmospheric Chemistry*) or contain articles that cover a variety of subjects within a field (for example, *Nature*). These publications may be electronic (online) or in print and may be published weekly, monthly, bimonthly or quarterly.

Peer Review

When an article is submitted to a journal the research findings are critically reviewed by experts in that discipline. This ensures that the research presents ideas that are supported by practices of good science. High-quality evidence and appropriate conclusions are necessary for the article to be accepted for publication. An article that is submitted to a reputable journal may take months to be approved for publication. The article may be returned to the author(s) for revision if necessary.

Scientists aim to be published in the most respected journals. The peer-review process contributes to the reputation of a journal. It helps to maintain standards and provide credibility. A scientific journal becomes reputable by ensuring that only articles of high quality are published. Very prestigious journals (such as *Nature, Science*, and *Pure and Applied Chemistry*) are known for publishing research backed by only the best practices of science. Reputable journals are widely read and considered reliable by the scientific community. Publication in a reputable journal brings immediate recognition for the author(s). Research that is not published in a peer-reviewed journal is often overlooked.

Format of Research Articles

Research articles have specific sections. Articles often include an abstract, introduction, methods, results, discussion, conclusions, and references. Go to the Nelson Science website to see an example of a real research article with a description of each section. WEB LINK

THE ABSTRACT

The abstract is a short summary of the article. It presents the purpose of the research, outlines the design of the methods used, and summarizes findings or conclusions. A well-written abstract is useful when looking for articles with specific information. Time may be saved by reading the abstract and then deciding if the article is going to be helpful in supporting research. The background material, methods used, results, main subject, and discussion are all summarized within the abstract.

CITING SOURCES AND GIVING CREDIT

Once a scientist has found useful sources and included them in an article or paper, information must be provided about the article so that someone else who is interested in learning more will be able to find it. This also shows the reader that information supporting the research is current.

More importantly, citing another scientist's work provides a measure of value of what he or she has published. It gives credit to the scientist. More citations often mean that the work is worthwhile and influential. For example, in 1939 Linus Pauling wrote a very influential book entitled *The Nature of the Chemical Bond*. By 1969, this book had been cited over 16 000 times by other scientists working the field! Similarly, Ronald Gillespie of McMaster University developed a simple yet powerful theory to explain the shapes of molecules. Soon after his work was published in 1957, citations started appearing in scholarly journals, and have continued to appear ever since.

Further Reading

Day, R.A., & Gastel, B. (2006). *How to write and publish a scientific paper* (6th ed.). Cambridge: Cambridge University Press.

Frame, P.F., Hik, D.S., Cluff, H.D., & Paquet, P.C. (June 2004). Long foraging movement of a denning tundra wolf. *Arctic*, 57 (2), 196–203.

WEB LINK

A5 Exploring Issues and Applications

Throughout this textbook you will have many opportunities to examine the connections between science, technology, society, and the environment (STSE) by exploring issues and applications.

An issue is a situation in which several points of view need to be considered in order to make a decision. There can be many positions, generally determined by the values that an individual or a society holds, on a single issue. Which solution is "best" is a matter of opinion; ideally, the solution that is implemented is the one that is most appropriate for society as a whole. Researching information about an issue will help you make an educated decision about it. All the skills listed in Section A5.1 may be useful in an activity that involves exploring an issue.

Scientific research produces knowledge or understanding of natural phenomena. Technologists and engineers look for ways to apply this knowledge in the development of practical products and processes. Technological inventions and innovations can have wide-ranging applications for, and impacts on, society and the environment. The purpose of exploring an application is to research a particular technological invention or innovation to determine how it works, how it is used, and how it may affect society and the environment. The skills of researching, communicating, and evaluating may be useful in an activity that involves exploring an application.

A5.1 Research Skills

The following skills are involved in many types of research. Some of these skills will help you research issues only, while some will help you research issues or applications. Refer to this section when you have questions about any of the following skills and processes.

DEFINING THE ISSUE

When exploring an issue, the first step in understanding the issue is to explain why it exists, the problems associated with it, and, if applicable, the individuals or groups, also known as stakeholders, that are involved in it. The issue includes information about the role a person takes when thinking about an issue as well as a description of who your audience will be. You could brainstorm questions involving who, what, where, when, why, and how. Develop background information on the issue by clarifying facts and concepts, and identifying relevant attributes, features, or characteristics of the problem.

RESEARCHING

When beginning your research for both issues and applications, you need to formulate a research question that helps to limit, narrow, or define the scope of your research. You then need to develop a plan to find reliable and relevant sources of information. This includes outlining the stages of your research: gathering, sorting, evaluating, selecting, and integrating relevant information. You should gather information from a variety of sources if possible (for example, print, web, and personal interviews).

As you collect information, do your best to ensure that the information is reliable, accurate, and current. Avoid biased opinions: those that are not supported by or that ignore credible evidence. It is important to ensure that the information you have gathered addresses all aspects of the issue or application you are researching.

IDENTIFYING ALTERNATIVES

When exploring an issue, examine the situation and think of as many alternative solutions as you can. Be creative about combining the solutions. At this point, it does not matter if the solutions seem unrealistic. To analyze the alternatives, you should examine the issue from a variety of perspectives. Stakeholders may bring different viewpoints to an issue and these may influence their position on the issue. Consider these viewpoints as you brainstorm or hypothesize how different stakeholders would feel about your alternatives.

ANALYZING THE ISSUE

An important part of exploring an issue is analyzing the issue. First, you should establish criteria for evaluating your information to determine its relevance and significance. You can then evaluate your sources, determine what assumptions may have been made, and assess whether you have enough information to make your decision.

To effectively analyze an issue you should

- establish criteria for determining the relevance and significance of the data you have gathered
- evaluate the sources of information
- identify and determine what assumptions have been made
- challenge unsupported evidence
- evaluate the alternative solutions, possibly by conducting a risk–benefit analysis

Once the issue has been analyzed, you may begin to consider possible solutions. You may decide to carry out a risk–benefit analysis—a tool that enables you to look at each possible result of a proposed action and helps you make a decision. (See Section A5.2 for more information.)

DEFENDING A DECISION

After analyzing your information on your issue, you can answer your research question and take an informed position or draw a conclusion on the issue. If you are working as a group, this is the stage where everyone gets a chance to share ideas and information gathered about the issue. Then the group needs to evaluate all the possible alternatives and decide on their preferred solution based on the criteria.

Your position on the issue, or conclusion, must be justified using supporting information that you have researched. You should be able to defend your position to people with different perspectives. Ask yourself the following questions:

- Do I have supporting evidence from a variety of sources?
- Can I state my position clearly?
- Can I show why this issue is relevant and important to society?
- Do I have solid arguments (with solid evidence) supporting my position?
- Have I considered arguments against my position, and identified their faults?
- Have I analyzed the strong and weak points of each perspective?

COMMUNICATING

When exploring an issue, there are several things to consider when communicating your decision. You need to state your position clearly and take into consideration who your audience is. You should always support your decision with objective data and a persuasive argument if possible. Be prepared to defend your position against any opposition.

You should be able to defend your solution in an appropriate format—debate, class discussion, speech, position paper, multimedia presentation, brochure, poster, video, etc.

When exploring an application you should communicate the "need or want" for the application (why the application was developed in the first place); the "how" (how the application/technology actually works); and the risks and benefits to society, individuals, and the environment. You should conclude with your "assessment" of the application.

EVALUATING

The final phase of your decision making when exploring an issue includes evaluating the decision itself and the process used to reach the decision. After you have made a decision, carefully examine the thinking that led to your decision.

Some questions to guide your evaluation are as follows:

- What was my initial perspective on the issue? How has my perspective changed since I first began to explore the issue?
- How did we make our decision? What process did we use? What steps did we follow?
- To what extent were my arguments factually accurate and persuasively made?
- In what ways does our decision resolve the issue?
- What are the likely short- and long-term effects of the decision?
- To what extent am I satisfied with the final decision?
- What reasons would I give to explain our decision?
- If we had to make this decision again, what would I do differently?

A5.2 Risk–Benefit Analysis Model

Risk–benefit analysis is a tool used to organize and analyze information gathered in research, especially when exploring a socio-scientific issue. A thorough analysis of the risks and benefits associated with each alternative solution can help you decide on the best alternative.

- Research as many aspects of the situation as possible. Look at it from different perspectives.
- Collect as much evidence as you can, including reasonable projections of likely outcomes if the proposal is adopted.
- Classify every individual potential result as being either a benefit or a risk.
- Quantify the size of the potential benefit or risk (perhaps as a dollar figure, or a number of lives affected, or on a scale of 1 to 5).
- Estimate the probability (percentage) of that event occurring.
- By multiplying the size of a benefit (or risk) by the probability of its happening, you can calculate a probability value for each potential result.
- Total the probability values of all the potential risks, and all the potential benefits.
- Compare the sums to help you decide whether to accept the proposed action.

A6 Math Skills

A6.1 Scientific Notation

It is difficult to work with very large or very small numbers when they are written in common decimal notation. Usually it is possible to accommodate such numbers by changing the SI prefix so that the number falls between 0.1 and 1000. For example, 237 000 000 mm can be expressed as 237 km, and 0.000 000 895 kg can be expressed as 0.895 mg. However, this prefix change is not always possible, either because an appropriate prefix does not exist or because it is essential to use a particular unit of measurement in a calculation. In these cases, the best method of dealing with very large and very small numbers is to write them using scientific notation. Scientific notation expresses a number by writing it in the form $a \times 10^n$, where $1 \leq |a| < 10$ and the digits in the coefficient a are all significant. **Table 1** shows situations where scientific notation would be used.

Table 1 Examples of Scientific Notation

Expression	Common decimal notation	Scientific notation
"124.5 million kilometres"	124 500 000 km	1.245×10^8 km
"154 thousand picometres"	154 000 pm	1.54×10^5 pm
"602 sextillion molecules"	602 000 000 000 000 000 000 000 molecules	6.02×10^{23} molecules

To multiply numbers in scientific notation, multiply the coefficients and add the exponents. To divide numbers in scientific notation, divide the coefficients and subtract the exponents. The answer is always expressed in scientific notation. Note that the coefficient should always be between 1 and 10. For example,

$$\begin{aligned}(4.73 \times 10^5 \text{ m})(5.82 \times 10^7 \text{ m}) &= 27.5 \times 10^{12} \text{ m}^2 \\ &= 2.75 \times 10^{13} \text{ m}^2\end{aligned}$$

$$\frac{(6.4 \times 10^6 \text{ m})}{(2.2 \times 10^3 \text{ s})} = 2.9 \times 10^3 \text{ m/s}$$

When evaluating exponents, the following rules apply:

$$x^a \cdot x^b = x^{a+b} \qquad (xy)^b = x^b y^b$$

$$\frac{x^a}{x^b} = x^{a-b} \qquad \left(\frac{x}{y}\right)^b = \frac{x^b}{y^b}$$

$$(x^a)^b = x^{ab}$$

SCIENTIFIC NOTATION WITH CALCULATORS

On many calculators, scientific notation is entered using a special key: EXP or EE. This key includes "× 10" from the scientific notation; you need to enter only the exponent. For example, to enter

7.5×10^4 press 7.5 EXP 4

3.6×10^{-3} press 3.6 EXP +/− 3

Depending on the type of calculator you have, +/− may need to be entered after the relevant number.

A6.2 Logarithms

Any positive number N can be expressed as a power of some base b where $b > 1$. Some obvious examples are:

$16 = 2^4$	base 2, exponent 4
$25 = 5^2$	base 5, exponent 2
$27 = 3^3$	base 3, exponent 3
$0.001 = 10^{-3}$	base 10, exponent −3

In each of these examples, the exponent is an integer; however, exponents may be any real number, not just an integer. If you use the x^y button on your calculator, you can experiment to obtain a better understanding of this concept.

The most common base is base 10. Some examples for base 10 are

$10^{0.5} = 3.162$

$10^{1.3} = 19.95$

$10^{-2.7} = 0.001\ 995$

By definition, the exponent to which a base b must be raised to produce a given number N is called the **logarithm** of N to base b (abbreviated as $\log_b$). When the value of the base is not written, it is assumed to be base 10. Logarithms to base 10 are called **common logarithms**. We can express the previous examples as logarithms:

$\log 3.162 = 0.5000$

$\log 19.95 = 1.299$

$\log 0.001\ 995 = -2.700$

Most measurement scales you have encountered are linear in nature. For example, a speed of 80 km/h is twice as fast as a speed of 40 km/h and four times as fast as a speed of 20 km/h. However, there are several examples in science where the range of values of the variable being measured is so great that it is more convenient to use a logarithmic scale to base 10. One example of this is the scale for measuring the acidity of a solution (the pH scale). For example, a solution with a pH of 3 is 10 times more acidic than a solution with a pH of 4 and 100 times (10^2) more acidic than a solution with a pH of 5. Other situations that use logarithmic scales are sound intensity (the dB scale) and the intensity of earthquakes (the Richter scale).

A6.3 Uncertainty in Measurements

There are two types of quantities that are used in science: exact values and measurements. Exact values include defined quantities (1 m = 100 cm) and counted values

(5 beakers or 10 trials). Measurements, however, are not exact because there is some uncertainty or error associated with every measurement.

PRECISION AND ACCURACY

"Precision" and "accuracy" are terms used to describe how close a measurement is to a true value. The precision of a measurement depends upon the gradations of the measuring device. Precision is the place value of the last measurable digit. For example, a measurement of 12.74 cm is more precise than a measurement of 127.4 cm because the first value was measured to hundredths of a centimetre, whereas the latter was measured only to tenths of a centimetre.

No matter how precise a measurement is, it still may not be accurate. Accuracy refers to how close a value is to its true, or accepted, value. An accurate measurement has a low uncertainty. **Figure 1** shows an analogy between precision and accuracy: the positions of darts on a dartboard.

How certain you are about a measurement depends on two factors: the precision of the instrument used and the size of the measured quantity. More precise instruments give more certain values. For example, a mass measurement of 13 g is less precise than a measurement of 13.12 g; you are more certain about the second measurement than the first. Certainty also depends on the size of the measurement. For example, consider the measurements 0.4 cm and 15.9 cm; both have the same precision. However, if the measuring instrument is precise to ± 0.1 cm, the first measurement is 0.4 ± 0.1 cm (0.3 cm or 0.5 cm) for an error of 25 %, whereas the second measurement could be 15.9 ± 0.1 cm (15.8 cm or 16.0 cm) for an error of 0.6 %. For both factors—the precision of the instrument used and the value of the measured quantity—the more digits there are in a measurement, the more certain you are about the measurement.

ROUNDING

When adding or subtracting measurements of different precisions, the answer is rounded to the same precision as the least precise measurement. For example, using a calculator,

$$11.7\ \text{cm} + 3.29\ \text{cm} + 0.542\ \text{cm} = 15.532\ \text{cm}$$

The answer must be rounded to 15.5 cm because the first measurement limits the precision to a tenth of a centimetre.

Follow these rules to round answers to calculations:

1. When the first digit to be dropped is 4 or less, the last digit retained should not be changed.
   3.141 326 rounded to 4 digits is 3.141
2. When the first digit to be dropped is greater than 5, or if it is a 5 followed by at least one digit other than zero, the last digit retained is increased by 1 unit.
   2.221 682 rounded to 5 digits is 2.2217
   4.168 501 rounded to 4 digits is 4.169
3. When the first digit discarded is 5 followed by only zeros, the last digit retained is increased by 1 if it is odd, but not changed if it is even.
   2.35 rounded to 2 digits is 2.4
   2.45 rounded to 2 digits is 2.4
   −6.35 rounded to 2 digits is −6.4

SIGNIFICANT DIGITS

The certainty of any measurement is communicated by the number of significant digits in the measurement. In a measured or calculated value, significant digits are the digits that are known reliably, or for certain, and include the last digit that is estimated or uncertain. Significant digits include all digits correctly reported from a measurement.

Follow these rules to decide if a digit is significant:

1. All non-zero digits are significant.
2. If a decimal point is present, zeros to the left of other digits (leading zeros) are not significant.
3. If a decimal point is not present, zeros to the right of the last non-zero digit (trailing zeros) are not significant.
4. Zeros placed between other digits are always significant.
5. Zeros placed after other digits to the right of a decimal point are significant.
6. When a measurement is written in scientific notation, all digits in the coefficient are significant.
7. Counted and defined values have infinite significant digits.

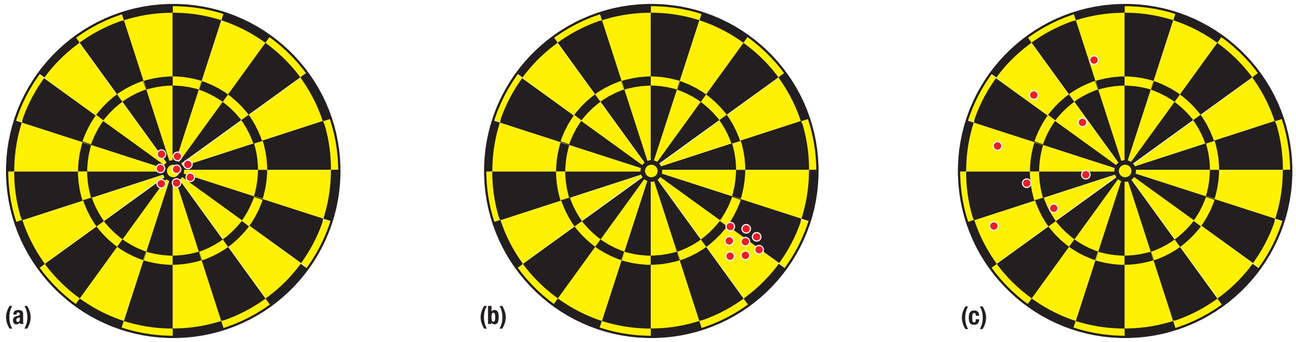


Figure 1 The positions of the darts in these diagrams represent measured or calculated results in a laboratory setting. In (a) the results are precise and accurate, in (b) they are precise but not accurate, and in (c) they are neither precise nor accurate.

Table 2 shows examples of significant digits.

Table 2 Certainty in Significant Digits

Measurement	Number of significant digits
32.07 m	4
0.0041 g	2
5.23×10^5 kg	3
7002 N•m	4
6400 s	2
6.0000 A	5
204.0 cm	4
10.0 kJ	3
100 people (counted)	infinite

MULTIPLICATION AND DIVISION

An answer obtained by multiplying and dividing measurements is rounded to the same number of significant digits as the measurement with the fewest significant digits. For example, using a calculator to solve the following equation, you obtain

$$77.8 \text{ km/h} \times 0.8967 \text{ h} = 69.76326 \text{ km}$$

However, the certainty of the answer is limited to three significant digits because the value with the fewest significant digits is 77.8 km/h. So, the answer is rounded up to 69.8 km.

SCIENTIFIC NOTATION

The same rule applies to adding, subtracting, multiplying, and dividing numbers written in scientific notation. For example, the answer obtained when adding two numbers written in scientific notation is

$$(5.5 \times 10^4) + (4.236 \times 10^4) = 9.736 \times 10^4$$

The answer is rounded to two significant digits, or 9.7×10^4, because the number with the fewest significant digits, 5.5×10^4, has only two significant digits.

Similarly, in the calculation

$$(7.23 \times 10^2)(3.2 \times 10^8) = 2.3136 \times 10^{11}$$

the answer is rounded to 2.3×10^{11} because the number with the fewest significant digits is 3.2×10^8, which has two significant digits.

Note that only the real number to the left of the multiplication sign is considered when determining the number of significant digits in scientific notation.

LOGARITHMS

When using logarithms, for instance in the calculations of pH, the number of decimal places in the log value must equal the number of significant digits in the original value. For example, consider this calculation:

$$\text{pH} = -\log (8.82 \times 10^{-5})$$

The significant digits are 3, giving an answer of 4.055.

MEASUREMENT ERROR

There are two types of measurement error: random error and systematic error. Random error results when an estimate is made to obtain the last significant digit for any measurement. The size of the random error is determined by the precision of the measuring instrument. For example, when measuring length with a measuring tape, it is necessary to estimate between the marks on the measuring tape. If these marks are 1 cm apart, the random error will be greater and the precision will be less than if the marks are 1 mm apart. Such errors can be reduced by taking the average of several readings.

Systematic error is associated with an inherent problem with the measuring system, such as the presence of an interfering substance, incorrect calibration, or room conditions. For example, if a balance is not zeroed at the beginning, all measurements will have a systematic error; using a slightly worn metre stick will also introduce a systematic error.

REPORTING DATA INVOLVING MEASUREMENTS

A formal report of an experiment involving measurements should include an analysis of uncertainty, percentage uncertainty, and percentage error or percentage difference. Uncertainty is often assumed to be plus or minus half of the smallest division of the scale on the instrument; for example, the estimated uncertainty of 15.8 cm is ± 0.05 cm or ± 0.5 mm.

Whenever calculations involving addition or subtraction are performed, the uncertainties accumulate. Thus, to find the total uncertainty, the individual uncertainties must be added. For example,

$$(34.7 \text{ cm} \pm 0.05 \text{ cm}) - (18.4 \text{ cm} \pm 0.05 \text{ cm}) = 16.3 \text{ cm} \pm 0.10 \text{ cm}$$

Percentage uncertainty is calculated by dividing the uncertainty by the measured quantity and multiplying by 100. Use your calculator to prove that 28.0 cm ± 0.05 cm has a percentage uncertainty of ± 0.18 %.

Whenever calculations involving multiplication or division are performed, the percentage uncertainties must be added. If desired, the total percentage uncertainty can be converted back to uncertainty. For example, consider the area of a certain rectangle:

$$\begin{aligned} A &= lw \\ &= (28.0 \text{ cm} \pm 0.18 \%)(21.5 \text{ cm} \pm 0.23 \%) \\ &= 602 \text{ cm}^2 \pm 0.41 \% \\ A &= 602 \text{ cm}^2 \pm 2.5 \text{ cm}^2 \end{aligned}$$

Percentage error can be determined only if it is possible to compare a measured value with that of the most commonly accepted value. The equation is

$$\% \text{ error} = \frac{\text{measured value} - \text{accepted value}}{\text{accepted value}} \times 100$$

Percentage difference is useful for comparing two measurements when the true measurement is not known or for comparing a measured value to a predicted value. The percentage difference is calculated as

$$\% \text{ difference} = \frac{\text{measured value} - \text{predicted value}}{\text{predicted value}} \times 100$$

A6.4 Use of Units

When solving problems in science it is important to denote the units that go with a numerical value. The measurement 170 is unacceptable since there are no units. The measurement 170 g/mL denotes a density, 170 °C denotes a temperature, 170 K denotes a temperature in kelvins, and 170 kPa denotes a pressure. Understanding and placing units with a value gives the proper context of the value.

You can also identify a formula by looking at the units. For instance, if a density of 9.01 g/cm^3 is given, you can note that the density units have grams (mass) divided by cm^3 (volume), so the formula for density is mass divided by volume or $d = \frac{m}{V}$.

A6.5 Graphing

There are many types of graphs that you can use to organize your data. You need to identify which type of graph is best for your data before you begin graphing. Three of the most useful kinds are bar graphs, circle (pie) graphs, and point-and-line graphs. When both variables are quantitative, use a point-and-line graph. The following guidelines show how to construct a point-and-line graph from the data in **Table 3**.

Table 3 Experimental Data for a Sample of Argon

Temperature (°C)	Volume (mL)
11	95.6
25	100.0
47	107.4
73	116.1
159	145.0
233	169.8
258	178.1

1. Use graph paper and construct your graph on a grid. The horizontal edge on the bottom of this grid is the x-axis and the vertical edge on the left is the y-axis. Do not be too thrifty with graph paper—a larger graph is easier to interpret.
2. Decide which variable goes on which axis and label each axis, including the units of measurement. The manipulated (independent) variable is generally plotted along the x-axis and the responding (dependent) variable along the y-axis.
3. Title your graph. The title should be a concise description of the data contained in the graph.
4. Determine the range of values for each variable. The range is the difference between the largest and smallest values. Graphs often include extra length on each axis, to make them appear less cramped.
5. Choose a scale for each axis. This will depend on how much space you have and the range of values for each axis. Each line on the grid usually increases steadily in value by a convenient number, such as 1, 2, 5, 10, 50, or 100.
6. Plot the points. Start with the first pair of values, which may or may not be at the origin of the graph.
7. After you have plotted and checked all the points, draw a line through them to show the relationship between the variables, if possible. Not all points may lie exactly on a line; small errors in each measurement may have occurred, causing the data points to move away from the perfect line. Draw a line that comes closest to most of the points. This is called the line of best fit—a smooth line that passes through or between the points so that there are about the same number of points on each side of the line. The line of best fit may be straight or curved (**Figure 2**). Graphs often use different colours or symbols to indicate the different sets, and include a legend. In some cases, it might be more appropriate to "join the dots" when graphing values that are counted rather than measured (for example, when plotting the counted number of bubbles produced rather than the measured volume of gas produced).

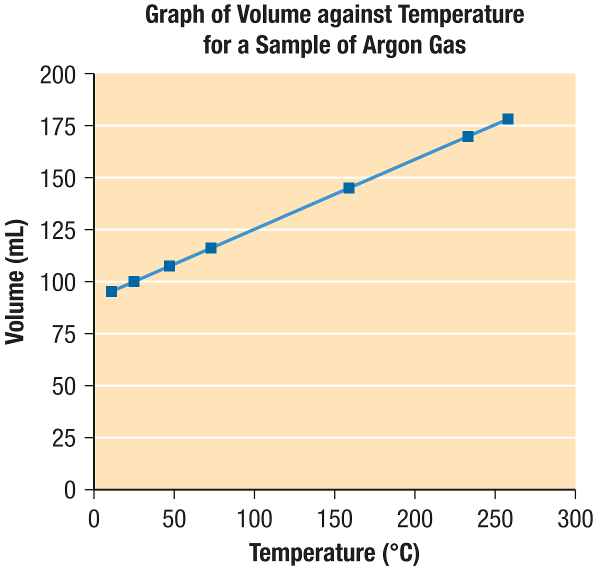


Figure 2 A point-and-line graph

A7 Choosing Appropriate Career Pathways

Often, one of the most difficult tasks in high school is deciding what career path to follow after graduation. The science skills and concepts presented in this book will be of benefit to many careers, whether you are planning a career in scientific research (such as research geneticist or astrophysicist) or in areas related to science (such as environmental lawyer, pharmaceutical sales rep, or electrician). The strong critical-thinking and problem-solving skills that are emphasized in science programs are a valuable asset for any career.

Career Links and Pathways

Throughout this textbook you will have many opportunities to explore careers related to your studies in chemistry. The Career Links icons found at the ends of some paragraphs indicate that you can learn more about these careers on the Nelson Science website. At the end of each chapter you will also find a Career Pathways feature that illustrates sample educational pathways for some of the careers mentioned.

It is wise to begin researching academic requirements as early as possible. Understanding the options available to pursue a particular career will help you make decisions on whether to attend university or college, and which program of study you should take. In addition, understanding the terminology used by universities and colleges will play an integral role in planning your future.

University and College Programs

Undergraduate university programs generally lead to a three-year general bachelor degree or a four-year honours bachelor degree. These degree designations begin with a "B" followed by the area of specialization; for example, a B.Sc. (Hons.) indicates an Honours Bachelor of Science degree. These degrees can lead to employment or to further education in postgraduate programs at the masters or doctoral level. The length of postgraduate degrees generally varies from one to four years.

College programs typically fall into three categories: one-year certificates, two-year diplomas, and three-year advanced diplomas. Certificates and diplomas can lead directly to employment opportunities or to graduate certificate programs. In some programs, there are transfer agreements with universities, which allow college graduates to enter university programs with advanced standing toward a university degree.

Pathways in Chemistry

The Career Pathways graphic organizer illustrates possible pathways to follow after high school. Certain pathways lead to careers via university while others may lead to careers via college. Look at **Figure 1** below. The pathways of three students are shown. Student A wishes to become a research scientist and must complete the Grade 11 and 12 University Chemistry courses (along with other prerequisites) and enter an undergraduate university program. Student A must obtain a Bachelor of Science degree, and then continue on to further education in masters and doctorate programs before becoming a research scientist.

Student B wishes to become a food scientist and must complete the Grade 11 University Chemistry course (along with other prerequisites) and enter an undergraduate university program. Student B must obtain a Bachelor of Science degree in food science or a related degree such as biochemistry before becoming a food scientist.

Student C wishes to become a dental hygienist, and must complete Grade 12 University or College Preparation Chemistry followed by a diploma course in dental hygiene.

Planning for Your Future

Planning ahead for your educational and career paths will provide a rewarding future. You should consult your guidance counsellors for specific advice on career planning and which courses you should take in high school. Take the time to research university and college websites for specific program information, as these sites will provide the prerequisite information and, most often, career-planning advice. While it may seem overwhelming at times, utilizing as many resources as possible will help alleviate some of the stress in planning your future.

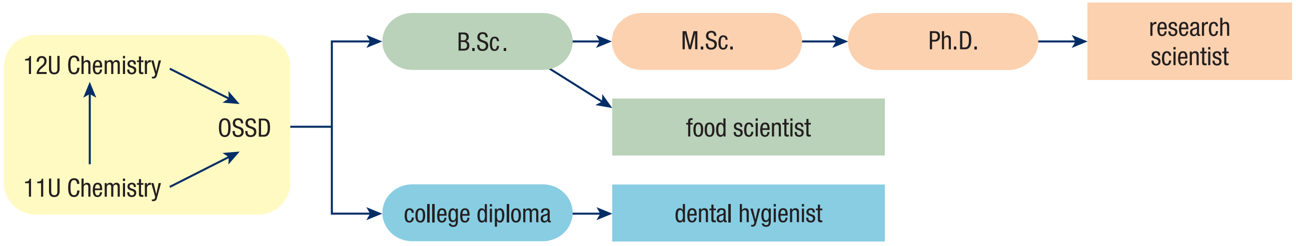
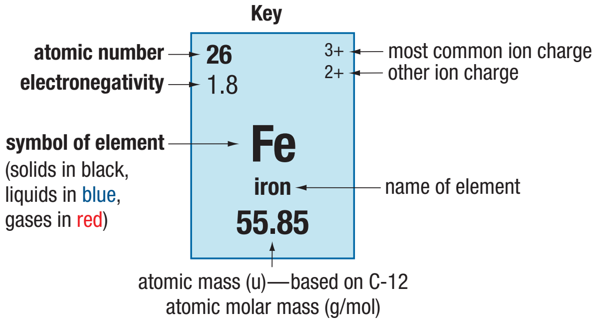


Figure 1 This graphic organizer shows pathways to several careers that involve chemistry. The blue pathway indicates a career that requires a college diploma. The green pathway shows a career path following an undergraduate degree. The orange career pathway involves one or more postgraduate university degrees.

B1 The Periodic Table

Nelson Chemistry 12



	1	2	3	4	5	6	7	8	9
1	1 1+ 1– 2.1 **H** hydrogen 1.01								
2	3 1+ 1.0 **Li** lithium 6.94	4 2+ 1.5 **Be** beryllium 9.01							
3	11 1+ 0.9 **Na** sodium 22.99	12 2+ 1.2 **Mg** magnesium 24.31							
4	19 1+ 0.8 **K** potassium 39.10	20 2+ 1.0 **Ca** calcium 40.08	21 3+ 1.3 **Sc** scandium 44.96	22 4+ 3+ 1.5 **Ti** titanium 47.87	23 5+ 4+ 1.6 **V** vanadium 50.94	24 3+ 2+ 1.6 **Cr** chromium 52.00	25 2+ 4+ 1.5 **Mn** manganese 54.94	26 3+ 2+ 1.8 **Fe** iron 55.85	27 2+ 3+ 1.9 **Co** cobalt 58.93
5	37 1+ 0.8 **Rb** rubidium 85.47	38 2+ 1.0 **Sr** strontium 87.62	39 3+ 1.2 **Y** yttrium 88.91	40 4+ 1.4 **Zr** zirconium 91.22	41 5+ 3+ 1.6 **Nb** niobium 92.91	42 6+ 1.8 **Mo** molybdenum 95.96	43 7+ 1.9 **Tc** technetium (98)	44 3+ 4+ 2.2 **Ru** ruthenium 101.07	45 3+ 2.2 **Rh** rhodium 102.91
6	55 1+ 0.7 **Cs** cesium 132.91	56 2+ 0.9 **Ba** barium 137.33	57 3+ 2+ 1.1 **La** lanthanum 138.91	72 4+ 1.3 **Hf** hafnium 178.49	73 5+ 1.5 **Ta** tantalum 180.95	74 6+ 1.7 **W** tungsten 183.84	75 7+ 1.9 **Re** rhenium 186.21	76 4+ 2.2 **Os** osmium 190.23	77 4+ 2.2 **Ir** iridium 192.22
7	87 1+ 0.7 **Fr** francium (223)	88 2+ 0.9 **Ra** radium (226)	89 3+ 2+ 1.1 **Ac** actinium (227)	104 — **Rf** rutherfordium (261)	105 — **Db** dubnium (262)	106 — **Sg** seaborgium (266)	107 — **Bh** bohrium (264)	108 — **Hs** hassium (277)	109 — **Mt** meitnerium (268)
	Alkali metals	Alkaline earth metals							

6	58 3+ 1.1 **Ce** cerium 140.12	59 3+ 1.1 **Pr** praseodymium 140.91	60 3+ 1.1 **Nd** neodymium 144.24	61 3+ — **Pm** promethium (145)	62 3+ 2+ 1.1 **Sm** samarium 150.36
7	90 4+ 1.3 **Th** thorium 232.04	91 5+ 4+ 1.4 **Pa** protactinium 231.04	92 6+ 4+ 1.4 **U** uranium 238.03	93 5+ 1.4 **Np** neptunium (237)	94 4+ 6+ 1.3 **Pu** plutonium (244)

🟦	Metals
🟩	Metalloids
🟥	Non-metals
🟨	Hydrogen

Periodic Table of the Elements

Measured values are subject to change as experimental techniques improve. Atomic molar mass values in this table are based on IUPAC website values (2011).

10	11	12	13	14	15	16	17	18	
								2 — — **He** helium 4.00	1
			5 — 2.0 **B** boron 10.81	**6** — 2.5 **C** carbon 12.01	**7** 3− 3.0 **N** nitrogen 14.01	**8** 2− 3.5 **O** oxygen 16.00	**9** 1− 4.0 **F** fluorine 19.00	**10** — — **Ne** neon 20.18	2
			13 3+ 1.5 **Al** aluminum 26.98	**14** — 1.8 **Si** silicon 28.09	**15** 3− 2.1 **P** phosphorus 30.97	**16** 2− 2.5 **S** sulfur 32.07	**17** 1− 3.0 **Cl** chlorine 35.45	**18** — — **Ar** argon 39.95	3
28 2+ 3+ 1.9 **Ni** nickel 58.69	**29** 2+ 1+ 1.9 **Cu** copper 63.55	**30** 2+ 1.6 **Zn** zinc 65.38	**31** 3+ 1.6 **Ga** gallium 69.72	**32** 4+ 1.8 **Ge** germanium 72.64	**33** 3− 2.0 **As** arsenic 74.92	**34** 2− 2.4 **Se** selenium 78.96	**35** 1− 2.8 **Br** bromine 79.90	**36** — 3.0 **Kr** krypton 83.80	4
46 2+ 3+ 2.2 **Pd** palladium 106.42	**47** 1+ 1.9 **Ag** silver 107.87	**48** 2+ 1.7 **Cd** cadmium 112.41	**49** 3+ 1.7 **In** indium 114.82	**50** 4+ 2+ 1.8 **Sn** tin 118.71	**51** 3+ 5+ 1.9 **Sb** antimony 121.76	**52** 2− 2.1 **Te** tellurium 127.60	**53** 1− 2.5 **I** iodine 126.90	**54** — 2.6 **Xe** xenon 131.29	5
78 4+ 2+ 2.2 **Pt** platinum 195.08	**79** 3+ 1+ 2.4 **Au** gold 196.97	**80** 2+ 1+ 1.9 **Hg** mercury 200.59	**81** 1+ 3+ 1.8 **Tl** thallium 204.38	**82** 2+ 4+ 1.9 **Pb** lead 207.2	**83** 3+ 5+ 1.9 **Bi** bismuth 208.98	**84** 2+ 4+ 2.0 **Po** polonium (209)	**85** 1− 2.2 **At** astatine (210)	**86** — — **Rn** radon (222)	6
110 — **Ds** darmstadtium (281)	**111** — **Rg** roentgenium (272)	**112** — **Cn** copernicium (285)	**113** — **Uut** ununtrium (284)	**114** — **Uuq** ununquadium (289)	**115** — **Uup** ununpentium (288)	**116** — **Uuh** ununhexium (291)	**117** — **Uus** ununseptium (294)	**118** — **Uuo** ununoctium (294)	7
							Halogens	Noble gases	

63 3+ 2+ — **Eu** europium 151.96	**64** 3+ 1.2 **Gd** gadolinium 157.25	**65** 3+ — **Tb** terbium 158.93	**66** 3+ 1.2 **Dy** dysprosium 162.50	**67** 3+ 1.2 **Ho** holmium 164.93	**68** 3+ 1.2 **Er** erbium 167.26	**69** 3+ 1.3 **Tm** thulium 168.93	**70** 3+ 2+ — **Yb** ytterbium 173.05	**71** 2+ 1.3 **Lu** lutetium 174.97	6
95 3+ 4+ 1.3 **Am** americium (243)	**96** 3+ 1.3 **Cm** curium (247)	**97** 3+ 4+ 1.3 **Bk** berkelium (247)	**98** 3+ 1.3 **Cf** californium (251)	**99** 3+ 1.3 **Es** einsteinium (252)	**100** 3+ 1.3 **Fm** fermium (257)	**101** 2+ 3+ 1.3 **Md** mendelevium (258)	**102** 2+ 3+ 1.3 **No** nobelium (259)	**103** 3+ — **Lr** lawrencium (262)	7

B2 Units, Symbols, Quantities, and Prefixes

Throughout *Nelson Chemistry 12* and in this reference section, we have attempted to be consistent in the presentation and usage of units. As far as possible, the text uses the International System of Units (SI). However, some other units have been included because of their practical importance, wide usage, or use in specialized fields. *Nelson Chemistry 12* has followed the most recent Canadian Metric Practice Guide (CAN/CSA-Z234.1-00), published in 2000 and updated in 2003 by the Canadian Standards Association.

Table 1 SI Base Units

Quantity	Symbol	Unit	Symbol
amount of substance	n	mole	mol
electric current	I	ampere	A
length	L, l, h, d, w	metre	m
luminous intensity	I_v	candela	cd
mass	m	kilogram	kg
temperature	T	kelvin	K
time	t	second	s

Table 2 Some SI-Derived Units

Quantity	Symbol	Unit	Symbol	SI base unit
pressure	P	newton per square metre	N/m^2	$kg/m{\cdot}s^2$
amount concentration	c	mole per litre	mol/L	$kmol/m^3$
volume	V	cubic metre	m^3	m^3

Table 3 Defined and Measured Quantities

Defined (exact) quantities	Measured (uncertain) quantities
1 t = 1000 kg = 1Mg STP = 0 °C and 101.325 kPa (use 0 °C and 101 kPa) SATP = 25 °C and 100 kPa 0 °C = 273.15 K (use 273 K) 1 atm = 101.325 kPa (use 101 kPa) 1 atm = 760 mm Hg 1 bar = 100 kPa	$R = 8.314$ kPa·L/(mol·K) $V_{STP} = 22.4$ L/mol $V_{SATP} = 24.8$ L/mol $N_A = 6.02 \times 10^{23}$ entities/mol

Table 4 Stoichiometry Symbols and Units

Quantity	Quantity symbol	Unit(s)
amount of substance	n	mol
mass of substance	m	g or kg
amount concentration of solution	c	mol/L
volume of solution or gas	V	mL or L
molar mass of substance	M	—
molar volume of gas	—	L

Table 5 Numerical Prefixes

Powers and subpowers of ten		
Prefix	**Power**	**Symbol**
deca	10^1	da
hecto	10^2	h
kilo	10^3	k
mega	10^6	M
giga	10^9	G
tera	10^{12}	T
peta	10^{15}	P
deci	10^{-1}	d
centi	10^{-2}	c
milli	10^{-3}	m
micro	10^{-6}	μ
nano	10^{-9}	n
pico	10^{-12}	p
femto	10^{-15}	f
atto	10^{-18}	a

Some Examples of Prefix Use

0.00350 L $= 3.50 \times 10^{-3}$ L = 3.50 mL
0.27 m $= 27 \times 10^{-2}$ m = 27 cm
3 000 000 000 Hz $= 3 \times 10^9$ Hz = 3 GHz

Table 6 Greek Letters Used in Chemistry

A	α	alpha
B	β	beta
Γ	γ	gamma
Δ	δ	delta

Table 7 Physical Constants

Quantity	Symbol	Approximate value
atomic mass unit	u	1.661×10^{-27} kg
Avogadro's constant	N_A	$6.022\ 141\ 99 \times 10^{23}$ (use 6.02×10^{23})

LEARNING **TIP**

SI Prefixes

Sometimes it is difficult to remember the metric prefixes. A mnemonic is a saying that helps you remember something. "King Henry Doesn't Mind Drinking Chocolate Milk" is a mnemonic for kilo, hecto, deca, metre, deci, centi, and milli. Another helpful hint is that mega (M) represents a million ($\times 10^6$) and tera (T) represents a trillion ($\times 10^{12}$). The first letter of each prefix and of what it represents are the same.

B3 Elements and Compounds

Table 1 Common Chemicals

Common name	Recommended name	Formula	Common use/source
acetic acid	ethanoic acid	$CH_3COOH(aq)$	vinegar
acetone	propanone	$(CH_3)_2CO(l)$	nail polish remover
acetylene	ethyne	$C_2H_2(g)$	cutting/welding torch
ASA (Aspirin)	acetylsalicylic acid	$C_6H_4COOCH_3COOH(s)$	for pain relief medication
baking soda	sodium hydrogen carbonate	$NaHCO_3(s)$	leavening agent
battery acid	sulfuric acid	$H_2SO_4(aq)$	car batteries
bleach	sodium hypochlorite	$NaClO(s)$	bleach for clothing
bluestone	copper(II) sulfate pentahydrate	$CuSO_4 \cdot 5\ H_2O(s)$	algicide/fungicide
brine	aqueous sodium chloride	$NaCl(aq)$	water-softening agent
carbon monoxide	carbon monoxide	$CO(g)$	toxic product of incomplete combustion
citric acid	2-hydroxy-1,2,3-propanetricarboxylic acid	$C_3H_4OH(COOH)_3$	in fruit and beverages
CFC	chlorofluorocarbon	$C_xCl_yF_z(l)$; e.g., $C_2Cl_2F_4(l)$	refrigerant
charcoal/graphite	carbon	$C(s)$	fuel/lead pencils
dry ice	carbon dioxide	$CO_2(g)$	"fizz" in carbonated beverages
ethylene	ethene	$C_2H_4(g)$	for polymerization
ethylene glycol	1,2-ethandiol	$C_2H_4(OH)_2(l)$	radiator antifreeze
formaldehyde	methanal	$CH_2O(g)$	preservative, solvent
Freon-12	dichlorodifluoromethane	$CCl_2F_2(l)$	refrigerant

Table 1 Common Chemicals (continued)

Common name	Recommended name	Formula	Common use/source
Glauber's salt	sodium sulfate decahydrate	$Na_2SO_4 \cdot 10H_2O(s)$	solar heat storage
glucose	D-glucose; dextrose	$C_6H_{12}O_6(s)$	in plants and blood
grain alcohol	ethanol (ethyl alcohol)	$C_2H_5OH(l)$	beverage alcohol
gypsum	calcium sulfate dihydrate	$CaSO_4 \cdot 2H_2O(s)$	wallboard
lime (quicklime)	calcium oxide	$CaO(s)$	masonry
limestone	calcium carbonate	$CaCO_3(s)$	chalk and building materials
lye (caustic soda)	sodium hydroxide	$NaOH(s)$	oven/drain cleaner
malachite	copper(II) hydroxide carbonate	$Cu(OH)_2 \cdot CuCO_3(s)$	copper mineral
methyl hydrate	methanol (methyl alcohol)	$CH_3OH(l)$	gas-line antifreeze
milk of magnesia	magnesium hydroxide	$Mg(OH)_2(s)$	antacid (for indigestion)
MSG	monosodium glutamate	$NaC_5H_8NO_4(s)$	flavour enhancer
muriatic acid	hydrochloric acid	$HCl(aq)$	in concrete etching
natural gas	methane	$CH_4(g)$	fuel
nitrogen dioxide	nitrogen dioxide	$NO_2(g)$	air pollutant
ozone	ozone	$O_3(g)$	atmospheric gas; ground-level pollutant
PCBs	polychlorinated biphenyls	$(C_6H_xCl_y)_2$; e.g., $(C_6H_4Cl_2)_2(l)$	in transformers
potash	potassium chloride	$KCl(s)$	fertilizer
radon	radon	$Rn(g)$	radioactive indoor air pollutant
road salt	calcium chloride or sodium chloride	$CaCl_2(s)$ or $NaCl_2(s)$	melts ice
rotten-egg gas	hydrogen sulfide	$H_2S(g)$	in natural gas
rubbing alcohol	2-propanol	$CH_3CHOHCH_3(l)$	for massage
sand (silica)	silicon dioxide	$SiO_2(s)$	in glass making
slaked lime	calcium hydroxide	$Ca(OH)_2(s)$	limewater
soda ash	sodium carbonate	$Na_2CO_3(s)$	in laundry detergents
sugar	sucrose	$C_{12}H_{22}O_{11}(s)$	sweetener
sulfur dioxide	sulfur dioxide	$SO_2(g)$	industrial air pollutant; major cause of acid precipitation
table salt	sodium chloride	$NaCl(s)$	seasoning
washing soda	sodium carbonate decahydrate	$Na_2CO_3 \cdot 10\ H_2O(s)$	water softener
vitamin C	ascorbic acid	$H_2C_6H_6O_6(s)$	vitamin
VOCs	mixture of volatile organic compounds	—	air pollutant

B4 Solubility Product Constants (K_{sp})

Table 1 Solubility Product Constants at 25 °C

Name	**Formula**	K_{sp}
barium carbonate	$BaCO_3(s)$	2.6×10^{-9}
barium chromate	$BaCrO_4(s)$	1.2×10^{-10}
barium sulfate	$BaSO_4(s)$	1.1×10^{-10}
calcium carbonate	$CaCO_3(s)$	5.0×10^{-9}
calcium hydroxide	$Ca(OH)_2$	5.5×10^{-6}
calcium oxalate	$CaC_2O_4(s)$; $CaOOCCOO(s)$	2.3×10^{-9}
calcium phosphate	$Ca_3(PO_4)_2(s)$	2.1×10^{-33}
calcium sulfate	$CaSO_4(s)$	7.1×10^{-5}
copper(I) chloride	$CuCl(s)$	1.7×10^{-7}
copper(I) iodide	$CuI(s)$	1.3×10^{-12}
copper(II) iodate	$Cu(IO_3)_2(s)$	6.9×10^{-8}
copper(II) sulfide	$CuS(s)$	6.0×10^{-37}
iron(II) hydroxide	$Fe(OH)_2(s)$	4.9×10^{-17}
iron(II) sulfide	$FeS(s)$	6.0×10^{-19}
iron(III) hydroxide	$Fe(OH)_3(s)$	2.6×10^{-39}
lead(II) bromide	$PbBr_2(s)$	6.6×10^{-6}
lead(II) chloride	$PbCl_2(s)$	1.2×10^{-5}
lead(II) iodate	$Pb(IO_3)_2(s)$	3.7×10^{-13}
lead(II) iodide	$PbI_2(s)$	8.5×10^{-9}
lead(II) sulfate	$PbSO_4(s)$	1.8×10^{-8}
magnesium carbonate	$MgCO_3(s)$	6.8×10^{-6}
magnesium fluoride	$MgF_2(s)$	6.4×10^{-9}
magnesium hydroxide	$Mg(OH)_2(s)$	5.6×10^{-12}
mercury(I) chloride	$Hg_2Cl_2(s)$	1.5×10^{-18}
silver bromate	$AgBrO_3(s)$	5.3×10^{-5}
silver bromide	$AgBr(s)$	5.4×10^{-13}
silver carbonate	$Ag_2CO_3(s)$	8.5×10^{-12}
silver chloride	$AgCl(s)$	1.8×10^{-10}
silver chromate	$Ag_2CrO_4(s)$	1.1×10^{-12}
silver iodate	$AgIO_3(s)$	3.2×10^{-8}
silver iodide	$AgI(s)$	8.5×10^{-17}
strontium carbonate	$SrCO_3(s)$	5.6×10^{-10}

Table 1 Solubility Product Constants at 25 °C (continued)

Name	Formula	K_{sp}
strontium fluoride	$SrF_2(s)$	4.3×10^{-9}
strontium sulfate	$SrSO_4(s)$	3.4×10^{-7}
zinc hydroxide	$Zn(OH)_2(s)$	7.7×10^{-17}
zinc sulfide	$ZnS(s)$	2.0×10^{-25}

- Values in this table are taken from *The CRC Handbook of Chemistry and Physics*, 85th Edition.

B5 K_a and K_b for Common Acids and Weak Bases

Table 1 Monoprotic Acids

Name	Formula of Acid	Formula of Conjugate Base	Equilibrium Constant, K_a
perchloric acid	$HClO_4(aq)$	$ClO_4^-(aq)$	very large
hydroiodic acid	$HI(aq)$	$I^-(aq)$	very large
hydrobromic acid	$HBr(aq)$	$Br^-(aq)$	very large
hydrochloric acid	$HCl(aq)$	$Cl^-(aq)$	very large
nitric acid	$HNO_3(aq)$	$NO_3^-(aq)$	very large
hydronium ion	$H_3O^+(aq)$	$H_2O(l)$	1.0
hydrogen sulfate ion	$HSO_4^-(aq)$	$SO_4^{2-}(aq)$	1.2×10^{-2}
chlorous acid	$HClO_2(aq)$	$ClO_2^-(aq)$	1.2×10^{-2}
iron(III) ion	$Fe(H_2O)_6^{3+}(aq)$	$Fe(H_2O)_5(OH)^{2+}(aq)$	1.5×10^{-3}
citric acid	$H_3C_6H_5O_7(aq)$	$H_2C_6H_5O_7^-(aq)$	7.4×10^{-4}
hydrofluoric acid	$HF(aq)$	$F^-(aq)$	6.6×10^{-4}
nitrous acid	$HNO_2(aq)$	$NO_2^-(aq)$	4.6×10^{-4}
hydrogen cyanate	$HOCN$	$OCN^-(aq)$	3.5×10^{-4}
methanoic acid	$HCHO_2$; $HCOOH(aq)$	$CHO_2^-(aq)$	1.8×10^{-4}
chromium(III) ion	$Cr(H_2O)_6^{3+}(aq)$	$Cr(H_2O)_5(OH)^{2+}(aq)$	1.0×10^{-4}
methyl orange	$HMo(aq)$	$Mo^-(aq)$	$\sim 10^{-4}$
benzoic acid	$HC_7H_5O_2(aq)$; $C_6H_5COOH(aq)$	$C_7H_5O_2^-(aq)$; $C_6H_5COO^-(aq)$	6.3×10^{-5}
ethanoic (acetic) acid	$HC_2H_3O_2(aq)$; $CH_3COOH(aq)$	$C_2H_3O_2^-(aq)$	1.8×10^{-5}
aluminum ion	$Al(H_2O)_6^{3+}(aq)$	$Al(H_2O)_5(OH)^{2+}(aq)$	9.8×10^{-6}
bromothymol blue	$HBb(aq)$	$Bb^-(aq)$	$\sim 10^{-7}$
hypochlorous acid	$HClO(aq)$	$ClO^-(aq)$	3.5×10^{-8}
phenolphthalein	$HPh(aq)$	$Ph^-(aq)$	$\sim 10^{-10}$
hydrocyanic acid	$HCN(aq)$	$CN^-(aq)$	6.2×10^{-10}

Table 1 Monoprotic Acids (continued)

Name	Formula of Acid	Formula of Conjugate Base	Equilibrium Constant, K_a
ammonium ion	$NH_4^+(aq)$	$NH_3(aq)$	5.8×10^{-10}
boric acid	$H_3BO_3(aq)$	$H_2BO_3^-(aq)$	5.8×10^{-10}
phenol	$C_6H_5OH(aq)$	$C_6H_5O^-(aq)$	1.0×10^{-10}
hydrogen peroxide	$H_2O_2(aq)$	$HO_2^-(aq)$	2.2×10^{-12}
water	$H_2O(l)$	$OH^-(aq)$	1.0×10^{-14}
hydroxide ion	$OH^-(aq)$	O^{2-} (aq)	very small

- Values in this table are taken from *Lange's Handbook of Chemistry,* 13th Edition for 25 °C.

Table 2 Polyprotic Acids

Name	Formula of Acid	Formula of Conjugate Base	Equilibrium Constant K_{a_1}	K_{a_2}	K_{a_3}
sulfuric acid	$H_2SO_4(aq)$	$HSO_4^-(aq)$	very large	1.0×10^{-2}	—
oxalic acid	$H_2C_2O_4(aq)$; HOOCCOOH(aq)	$HC_2O_4^-(aq)$	5.4×10^{-2}	5.4×10^{-5}	—
sulfurous acid ($SO_2 + H_2O$)	$H_2SO_3(aq)$	$HSO_3^-(aq)$	1.3×10^{-2}	6.2×10^{-8}	—
phosphoric acid	$H_3PO_4(aq)$	$H_2PO_4^-(aq)$	7.1×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
carbonic acid ($CO_2 + H_2O$)	$H_2CO_3(aq)$	$HCO_3^-(aq)$	4.4×10^{-7}	4.7×10^{-11}	—
hydrosulfuric acid	$H_2S(aq)$	$HS^-(aq)$	1.1×10^{-7}	1.3×10^{-13}	—

- Values in this table are taken from *Lange's Handbook of Chemistry,* 13th Edition for 25 °C.

Table 3 Weak Bases

Name	Formula	Equilibrium Constant, K_b
dimethylamine	$CH_3CH_3NH(aq)$	9.6×10^{-4}
methylamine	$CH_3NH_2(aq)$	4.4×10^{-4}
ethylamine	$CH_3CH_2NH_2(aq)$	4.3×10^{-4}
butylamine	$C_4H_9NH_2(aq)$	5.9×10^{-4}
trimethylamine	$CH_3CH_3CH_3N(aq)$	7.4×10^{-5}
ammonia	$NH_3(aq)$	1.8×10^{-5}
hydrazine	$N_2H_4(aq)$	1.7×10^{-6}
morphine	$C_{17}H_{19}NO_3(aq)$	7.5×10^{-7}
hypochlorite ion	$ClO^-(aq)$	3.45×10^{-7}
hydroxylamine	$NH_2OH(aq)$	1.1×10^{-8}
pyridine	$C_5H_5N(aq)$	1.7×10^{-9}
aniline	$C_5H_5NH_2(aq)$	4.1×10^{-10}
ethanoate ion	$C_2H_3O_2^-(aq)$	5.6×10^{-10}
urea	$NH_2CONH_2(aq)$	1.5×10^{-14}

B6 Acid–Base Indicators

Table 1 Acid–Base Indicators

Common Name	Colour of HIn(aq)	pH range	Colour of In^-(aq)	Common name	Colour of HIn (aq)	pH range	Colour of In^-(aq)
methyl violet	yellow	0.0–1.6	blue	chlorophenol red	yellow	5.4–6.8	red
cresol red (acid range)	red	0.2–1.8	yellow	litmus	red	6.0–8.0	blue
cresol purple (acid range)	red	1.2–2.8	yellow	bromothymol blue	yellow	6.2–7.6	blue
thymol blue (acid range)	red	1.2–2.8	yellow	phenol red	yellow	6.4–8.0	red
tropeolin oo	red	1.3–3.2	yellow	*m*-nitrophenol	colourless	6.4–8.8	yellow
orange iv	red	1.4–2.8	yellow	neutral red	red	6.8–8.0	yellow
benzopurpurine-4B	violet	2.2–4.2	red	cresol red	yellow	7.2–8.8	red
2,6-dinotrophenol	colourless	2.4–4.0	yellow	*m*-cresol purple	yellow	7.6–9.2	purple
2,4-dinotrophenol	colourless	2.5–4.3	yellow	thymol blue	yellow	8.0–9.6	blue
methyl yellow	red	2.9–4.0	yellow	phenolphthalein	colourless	8.0–10.0	red
congo red	blue	3.0–5.0	red	α-naphtholbenzein	yellow	9.0–11.0	blue
bromophenol blue	yellow	3.0–4.6	blue-violet	thymolphthalein	colourless	9.4–10.6	blue
methyl orange	red	3.1–4.4	yellow	alizarin yellow r	yellow	10.0–12.0	violet
bromocresol green	yellow	4.0–5.6	blue	nitramine	colourless	10.8–13.0	orange-brown
methyl red	red	4.4–6.2	yellow	tropeolin o	yellow	11.0–13.0	orange-brown
bromocresol purple	yellow	5.2–6.8	purple	indigo carmine	blue	11.4–13.0	yellow
bromophenol red	yellow	5.2–6.8	red	1,3,5-trinitrobenzene	colourless	12.0–14.0	orange
p-nitrophenol	colourless	5.3–7.6	yellow	—	—	—	—

B7 Standard Reduction Potentials

Table 1 Standard Reduction Potentials (or Redox) at 25 °C (298 K) for Many Common Half-Reactions

Decreasing Strength of Oxidizing Agents

Decreasing Strength of Reducing Agents

Half-reaction	**$E°_r$ (V)**
Strongest Oxidizing Agent; Weakest Reducing Agent	
$F_2(g) + 2\ e^- \rightleftharpoons 2\ F^-(aq)$	2.87
$Ag^{2+}(aq) + e^- \rightleftharpoons Ag^+(aq)$	1.99
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	1.82
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons 2\ H_2O(l)$	1.78
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	1.70
$PbO_2(s) + 4\ H^+ + SO_4^{2-}(aq) + 2\ e^- \rightleftharpoons PbSO_4(s) + 2\ H_2O(l)$	1.69
$MnO_4^-(aq) + 4\ H^+(aq) + 3\ e^- \rightleftharpoons MnO_2(s) + 2\ H_2O(l)$	1.68
$IO_4^-(aq) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons IO_3^-(aq) + H_2O(l)$	1.60
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightleftharpoons Mn^{2+}(aq) + 4\ H_2O(l)$	1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	1.50
$PbO_2(s) + 4\ H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2\ H_2O(l)$	1.46
$Cl_2(g) + 2\ e^- \rightleftharpoons 2\ Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightleftharpoons 2\ Cr^{3+}(aq) + 7\ H_2O(l)$	1.33
$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightleftharpoons 2\ H_2O(l)$	1.23
$MnO_2(s) + 4\ H^+(aq) + 2\ e^- \rightleftharpoons Mn^{2+}(aq) + 2\ H_2O(l)$	1.21
$IO_3^-(aq) + 6\ H^+(aq) + 5\ e^- \rightleftharpoons \frac{1}{2}\ I_2(s) + 3\ H_2O(l)$	1.20
$ClO_4^-(aq) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons ClO_3^-(aq) + H_2O(l)$	1.19
$Br_2(l) + 2\ e^- \rightleftharpoons 2\ Br^-(aq)$	1.09
$VO_2^+(aq) + 2\ H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	1.00
$AuCl_4^-(aq) + 3\ e^- \rightleftharpoons Au(s) + 4\ Cl^-(aq)$	0.99
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightleftharpoons NO(g) + 2\ H_2O(l)$	0.96
$ClO_2(g) + e^- \rightleftharpoons ClO_2^-(aq)$	0.954
$2\ Hg^{2+}(aq) + 2\ e^- \rightleftharpoons Hg_2^{2+}(aq)$	0.91
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	0.80
$Hg_2^{2+}(aq) + 2\ e^- \rightleftharpoons 2\ Hg(l)$	0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	0.77
$O_2(g) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons H_2O_2(aq)$	0.68
$MnO_4^-(aq) + e^- \rightleftharpoons MnO_4^{2-}(aq)$	0.56
$I_2(s) + 2e^- \rightleftharpoons 2\ I^-(aq)$	0.54

(*continued*)

Table 1 Standard Reduction Potentials (or Redox) at 25 °C (298 K) for Many Common Half-Reactions (continued)

Half-reaction	E°_r **(V)**
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	0.52
$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightleftharpoons 4\ OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2\ e^- \rightleftharpoons Cu(s)$	0.34
$Hg_2Cl_2(aq) + 2\ e^- \rightleftharpoons 2\ Hg(l) + 2\ Cl^-(aq)$	0.34
$AgCl(aq) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	0.22
$SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	0.20
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	0.16
$2\ H^+(aq) + 2\ e^- \rightleftharpoons H_2(g)$	0
$Fe^{3+}(aq) + 3\ e^- \rightleftharpoons Fe(s)$	−0.036
$Pb^{2+}(aq) + 2\ e^- \rightleftharpoons Pb(s)$	−0.13
$Sn^{2+}(aq) + 2\ e^- \rightleftharpoons Sn(s)$	−0.14
$Ni^{2+}(aq) + 2\ e^- \rightleftharpoons Ni(s)$	−0.23
$Co^{2+}(aq) + 2\ e^- \rightleftharpoons Co(s)$	−0.28
$PbSO_4(aq) + 2\ e^- \rightleftharpoons Pb + SO_4^{2-}(aq)$	−0.35
$Cd^{2+}(aq) + 2\ e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\ e^- \rightleftharpoons Fe(s)$	−0.44
$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$	−0.50
$Cr^{3+}(aq) + 3\ e^- \rightleftharpoons Cr(s)$	−0.73
$Zn^{2+}(aq) + 2\ e^- \rightleftharpoons Zn(s)$	−0.76
$2\ H_2O(l) + 2\ e^- \rightleftharpoons H_2(g) + 2\ OH^-(aq)$	−0.83
$Cr^{2+}(aq) + 2\ e^- \rightleftharpoons Cr(s)$	−0.91
$Mn^{2+}(aq) + 2\ e^- \rightleftharpoons Mn(s)$	−1.18
$Al^{3+}(aq) + 3\ e^- \rightleftharpoons Al(s)$	−1.66
$H_2(g) + 2\ e^- \rightleftharpoons 2\ H^-(aq)$	−2.23
$Mg^{2+}(aq) + 2\ e^- \rightleftharpoons Mg(s)$	−2.37
$La^{3+}(aq) + 3\ e^- \rightleftharpoons La(s)$	−2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2\ e^- \rightleftharpoons Ca(s)$	−2.76
$Ba^{2+}(aq) + 2\ e^- \rightleftharpoons Ba(s)$	−2.90
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05
Weakest Oxidizing Agent; Strongest Reducing Agent	

Decreasing Strength of Oxidizing Agents

Decreasing Strength of Reducing Agents

B8 Cations and Anions

Table 1 Common Cations

Ion	Name
H^+	hydrogen
Li^+	lithium
Na^+	sodium
K^+	potassium
Cs^+	cesium
Be^{2+}	beryllium
Mg^{2+}	magnesium
Ca^{2+}	calcium
Ba^{2+}	barium
Al^{3+}	aluminum
Ag^+	silver

Table 2 Common Anions

Ion	Name
H^-	hydride
F^-	fluoride
Cl^-	chloride
Br^-	bromide
I^-	iodide
O^{2-}	oxide
S^{2-}	sulfide
N^{3-}	nitride
P^{3-}	phosphide

Table 3 Selected Multivalent Cations

Metal	Ions	Classical names	IUPAC names
copper, Cu	Cu^+ Cu^{2+}	cuprous cupric	copper(I) copper(II)
iron, Fe	Fe^{2+} Fe^{3+}	ferrous ferric	iron(II) iron(III)
tin, Sn	Sn^{2+} Sn^{4+}	stannous stannic	tin(II) tin(IV)
lead, Pb	Pb^{2+} Pb^{4+}	plumbous plumbic	lead(II) lead(IV)
manganese, Mn	Mn^{2+} Mn^{3+} Mn^{4+} Mn^{6+} Mn^{7+}	—	manganese(II) manganese(III) manganese(IV) manganese(VI) manganese(VII)
chromium, Cr	Cr^{2+} Cr^{3+}	chromous chromic	chromium(II) chromium(III)
gold, Au	Au^+ Au^{3+}	—	gold(I) gold(III)
nickel, Ni	Ni^{2+} Ni^{3+}	—	nickel(II) nickel(III)

Table 4 Common Polyatomic Ions

Ion	Name
$C_2H_3O_2^-$	acetate
NH_4^+	ammonium
BO_3^{3-}	borate
BrO_3^-	bromate
CO_3^{2-}	carbonate
ClO_3^-	chlorate
ClO_2^-	chlorite
CrO_4^{2-}	chromate
CN^-	cyanide
$Cr_2O_7^{2-}$	dichromate
$H_2PO_4^-$	dihydrogen phosphate
$H_2PO_3^-$	dihydrogen phosphite
HCO_3^-	hydrogen carbonate (bicarbonate)
HPO_4^{2-}	hydrogen phosphate
HPO_3^{2-}	hydrogen phosphite
HSO_4^-	hydrogen sulfate (bisulfate)
HS^-	hydrogen sulfide (bisulfide)
HSO_3^-	hydrogen sulfite (bisulfite)
ClO^-, OCl^-	hypochlorite
H_3O^+	hydronium
OH^-	hydroxide
IO_3^-	iodate
NO_2^-	nitrite
NO_3^-	nitrate
$C_2O_4^{2-}$	oxalate
ClO_4^-	perchlorate
MnO_4^-	permanganate
SCN^-	thiocyanate
O_2^{2-}	peroxide
PO_4^{3-}	phosphate
SO_4^{2-}	sulfate
SO_3^{2-}	sulfite
$S_2O_3^{2-}$	thiosulfate

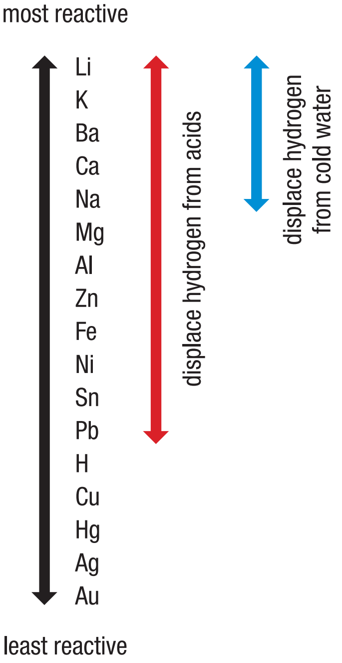
Table 5 Ion Colours

Ion in solution	Solution colour
Groups 1, 2, 17	colourless
Cr^{2+}	blue
Cr^{3+}	green
Co^{2+}	pink
Cu^{+}	green
Cu^{2+}	blue
Fe^{2+}	pale green
Fe^{3+}	yellow-brown
Mn^{2+}	pale pink
Ni^{2+}	green
CrO_4^{2-}	yellow
$Cr_2O_7^{2-}$	orange
MnO_4^{-}	purple
Ion	**Flame colour**
Li^{+}	bright red
Na^{+}	yellow
K^{+}	violet
Ca^{2+}	yellow-red
Sr^{2+}	bright red
Ba^{2+}	yellow-green
Cu^{2+}	green
Pb^{2+}	light blue-grey
Zn^{2+}	whitish green

Table 6 Solubility of Ionic Compounds at Room Temperature

Solubility	Ion	Exceptions
very soluble (aq) $\geq$ 0.1 mol/L	NO_3^{-}	none
	halides	except with Cu^{+}, Ag^{+}, Hg_2^{2+}, Pb^{2+}
	SO_4^{2-}	except with Ca^{2+}, Ba^{2+}, Sr^{2+}, Hg^{2+}, Pb^{2+}, Ag^{+}
	$C_2H_3O_2^{-}$	Ag^{+}
	Na^{+}, K^{+}	none
	NH_4^{+}	none
slightly soluble (s) < 0.1 mol/L	CO_3^{2-}	except with Group 1 ions and NH_4^{+}
	PO_4^{3-}	except with Group 1 ions and NH_4^{+}
	OH^{-}	except with Group 1 ions, Ca^{2+}, Ba^{2+}, Sr^{2+}
	S^{2-}	except with Groups 1 and 2 ions and NH_4^{+}

THE ACTIVITY SERIES OF METALS



B9 Naming Conventions

Table 1 Common Hydrates

	Name of hydrate	**Examples**
Traditional name	name of the ionic compound + Greek prefix + "hydrate"	• copper(II) sulfate pentahydrate • magnesium sulfate heptahydrate
Alternative names	name of the ionic compound + number of water molecules + "water"	• copper(II) sulfate-5-water • magnesium sulfate-7-water
	name of the ionic compound + "water" + ratio of formula units to water molecules	• copper(II) sulfate—water (1/5) • magnesium sulfate—water (1/7)

Table 2 Prefixes Used in the Names of Hydrates and Molecular Compounds

Number of atoms or water molecules in the chemical formula	**Prefix**
1	mono or mon
2	di
3	tri
4	tetra
5	penta
6	hexa
7	hepta
8	octa
9	nona
10	deca

Table 3 Binary Molecular Compounds

Name of compound	**Prefix**
prefix + name of first element + prefix + name of second element [exception: omit "mono" for first element]	• dinitrogen monoxide • carbon dioxide

Table 4 Oxyanions in Ionic Compounds

Name of parent oxyanion		**Examples**
stem of the non-metal name + -*ate*		• chlorate, ClO_3^- • nitrate, NO_3^- • sulfate, SO_4^{2-} • phosphate, PO_4^{3-} • carbonate, CO_3^{2-}
Names of related oxyanions		**Examples**
If oxyanion has one more oxygen atom than the parent oxyanion	*per* + stem of non-metal name + -*ate*	• perchlorate, ClO_4^-
If oxyanion has one fewer oxygen atom than the parent oxyanion	stem of non-metal name+ -*ite*	• nitrite, NO_2^- • sulfite, SO_3^{2-}
If oxyanion has two fewer oxygen atoms than the parent oxyanion	*hypo* + stem of non-metal name + -*ite*	• hypochlorite, ClO^-

Table 5 Binary Acids and Oxyacids

Name of binary acid	**Examples**
hydro + stem of anion name + -*ic acid*	• hydrochloric acid, HCl • hydrocyanic acid, HCN
Name of parent oxyacid	**Examples**
If the anion name ends in -*ate*, then the acid name ends in -*ic acid*.	• sulfate ion → sulfuric acid, H_2SO_4 • acetate ion → acetic acid, $C_2H_4O_2$
Names of related oxyacids	
If the anion name starts with *per*- and ends in -*ate*, then the acid name is *per*-____-*ic acid*	
If the anion name ends in -*ite*, then the acid name ends in -*ous acid*	
If the anion name starts with *hypo*_ and ends in -*ite*, then the acid name is *hypo*____-*ous acid*	

Table 6 Oxyacids

Acid name	Chemical formula	Parent oxyanion
acetic acid	$HC_2H_3O_2(aq)$	acetate, $C_2H_3O_2^-$
bromic acid	$HBrO_3(aq)$	bromate, BrO_3^-
carbonic acid	$H_2CO_3(aq)$	carbonate, CO_3^{2-}
chloric acid	$HClO_3(aq)$	chlorate, ClO_3^-
iodic acid	$HIO_3(aq)$	iodate, IO_3^-
nitric acid	$HNO_3(aq)$	nitrate, NO_3^-
phosphoric acid	$H_3PO_4(aq)$	phosphate, PO_4^{3-}
sulfuric acid	$H_2SO_4(aq)$	sulfate, SO_4^{2-}
perbromic acid	$HBrO_4(aq)$	perbromate, BrO_4^-
hypobromous acid	$HBrO(aq)$	hypobromite, BrO^-
perchloric acid	$HClO_4(aq)$	perchlorate, ClO_4^-
chlorous acid	$HClO_2(aq)$	chlorite, ClO_2^-
hypochlorous acid	$HClO(aq)$	hypochlorite, ClO^-
hypofluorous acid	$HFO(aq)$	hypofluorite, FO^-
periodic acid	$HIO_4(aq)$	periodate, IO_4^-
hypoiodous acid	$HIO(aq)$	hypoiodite, IO^-
nitrous acid	$HNO_2(aq)$	nitrite, NO_2^-

APPENDIX C ANSWERS

These pages include numerical and short answers to chapter section questions, selected Tutorial Practice questions, and Chapter Self-Quiz, Chapter Review, Unit Self-Quiz, and Unit Review questions.

Unit 1

Are You Ready?, pp. 4–5

4. HH, NH, BO, LiF
9. covalent, ionic, hydrogen, dipole–dipole, London dispersion
10. NH_3, H_2O, HF
25. (a) $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$, base
    (b) $HCl(aq) \rightarrow 2H^+(aq) + Cl^-(aq)$, acid
    (c) $H_2SO_4(aq) \rightarrow H^+(aq) + SO_4^{2-}(aq)$, acid
    (d) $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$, acid
    (e) $LiOH(aq) \rightarrow Li^+(aq) + OH^-(aq)$, base

1.1 Tutorial 1 Practice, p. 14

(a) octane
(b) 3-methylpentane
(c) 1,3-dichlorobutane
(d) 2,4-dimethylhexane

1.1 Questions, p. 17

2. (a) 2,2-dimethylbutane
   (b) 5-ethyl-2,3-dimethylheptane
   (c) 3,6-dimethyl-4-(propan-2-yl)octane
   (d) 2-bromo-4-chloropentane
   (e) 1,1-dimethylcyclohexane
   (f) propan-2-ylcyclopentane
   (g) 3-methylhexane
9. dodecane

1.2 Tutorial 1 Practice, p. 21

1. (a) but-1-ene
   (b) 4-methylhex-2-ene
   (c) 4-methylhex-2-yne
   (d) 4-bromo-3-methylcyclohex-1-ene

1.2 Tutorial 2 Practice, p. 23

2. (a) *trans*-pent-2-ene
   (b) *cis*-pent-2-ene

1.2 Questions, p. 27

2. (a) alkene
   (b) alkene
   (c) alkyne
5. (a) 1-bromo-2-butyne
   (b) 4-methyl-2-hexyne
7. (a) *cis*-2-hexene
   (b) *trans*-1-bromo-1-butene
9. (a) $CH_3CH{=}CHCH_3 + Cl_2 \rightarrow CH_3CHClCHClCH_3$
   (b) $CH_3CH{=}CHCH_2CH_2CH_3 + HBr \rightarrow CH_3CH_2CHBrCH_2CH_2CH_3$

1.3 Tutorial 1 Practice, p. 30

1. (a) 1-ethyl-3-methylbenzene
   (b) 3-methyl-2-phenylpentane

1.3 Questions, p. 31

1. (a) chlorobenzene
   (b) methylbenzene (toluene)
   (c) phenylethene
   (d) 1,3-dimethylbenzene
   (e) 1-bromo-2-pentylbenzene
5. (a) 1,4-dichlorobenzene
6. (a) (i) bromocyclohexane
       (ii) ethylbenzene + hydrogen chloride

1.4 Tutorial 1 Practice, p. 34

1. (a) pentane-1,4-diol
   (b) 4-ethyl-3-methyloctan-4-ol
   (c) benzene-1,3-diol

1.4 Tutorial 2 Practice, p. 37

2. $C_5H_{11}OH(l) \xrightarrow{H_2SO_4} C_5H_{10}(l) + H_2O(l)$

1.4 Tutorial 3 Practice, p. 38

1. (a) ethoxyethane
   (b) ethoxypropane

1.4 Questions, p. 39

1. (a) heptane-2,3-diol
   (b) 3-methylhexan-2-ol
   (c) 4-ethyl-5-methylheptan-3-ol
   (d) cyclopentane-1,3-diol
   (e) 1,2,4-trihydroxybenzene
   (f) 1-propoxybutane
   (g) 1-ethoxypentane
   (h) ethanethiol
4. (a) 2-heptanol
   (b) 1-butene + water
   (c) ethoxypropane + water
5. $2\ CH_3OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(g)$

1.5 Tutorial 1 Practice, p. 41

1. (a) pentanal
   (b) 4-ethylhexanal
   (c) 4-chloropentanal

1.5 Tutorial 2 Practice, p. 42

1. (a) butanone
   (b) 2-methyl-3-hexanone
   (c) cyclohexanone

1.5 Tutorial 3 Practice, p. 45

1. (a) pentan-2-ol, oxygen
   (b) pentan-1-ol, oxygen
2. (a) ethanol
   (b) butan-2-ol
3. (a) hexanal
   (b) hexanone
   (c) 2-methylpentanone

1.5 Questions, p. 46

2. (a) pentan-2-one
   (b) hexanal
3. (b) $CH_3COCH_3(l) + H_2(g) \rightarrow CH_3CHOHCH_3(l)$
4. (c) $CH_3CH_2OH(l) + [O] \rightarrow CH_3CHO(l) + H_2O(l)$

1.6 Tutorial 1 Practice, p. 48

1. (a) decanoic acid
   (b) butanoic acid
   (c) 3-methylheptanoic acid

1.6 Tutorial 2 Practice, p. 50

1. (a) ethyl pentanoate
   (b) methyl decanoate
   (c) butyl methanoate
   (d) propyl benzoate

1.6 Questions, p. 55

2. (a) methyl pentanoate
   (b) methyl butanoate

1.7 Tutorial 1 Practice, p. 58

1. (a) butan-2-amine
   (b) *N*,*N*-diethylbutan-1-amine
   (c) *N*-methyl-*N*-propylpropan-1-amine
   (d) octan-3-amine
   (e) *N*-ethylbutan-2-amine

1.7 Tutorial 2 Practice, p. 60

1. (a) butanamide
   (b) *N*-propylethanamide
   (c) *N*,*N*-dimethylbutanamide

1.7 Questions, p. 62

1. (a) propanamide
   (b) *N*,*N*-dimethylpropan-1-amine
   (c) *N*,*N*-diethylpropanamide
   (d) 2-chloroheptan-4-amine
   (e) hept-6-ene-2,4-diamine

Chapter 1 Self-Quiz, p. 71

1. (a)
2. (b)
3. (d)
4. (d)
5. (b)
6. (d)
7. (a)
8. (d)
9. F
10. F
11. T
12. F
13. F
14. T
15. T
16. T

Chapter 1 Review, pp. 72–77

1. (b)
2. (d)
3. (b)
4. (d)
5. (c)
6. (d)
7. (c)
8. (d)
9. (c)
10. (d)
11. (a)
12. T
13. T
14. F
15. F
16. F
17. F
18. T
19. F
20. F
21. (a) (vii)
    (b) (ii)
    (c) (iv)
    (d) (viii)
    (e) (iii)
    (f) (vi)
    (g) (i)
    (h) (v)
22. (a) $CH_3CHCHCH_2CH_3 + Br_2 \rightarrow CH_3CHBrCHBrCH_2CH_3$; addition reaction
    (b) $C_5H_8 + Br_2 \rightarrow C_5H_6Br_2$; addition reaction
    (c) $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$; substitution reaction
24. (a) $=O$, $C{=}C$, $-OH$
    (b) benzene ring, $-COOH$
    (c) benzene ring, $-NH_2$
25. (a) $-OH$, alcohol, propan-1-ol
    (b) $-COOH$, carboxylic acid, propanoic acid
    (c) $-CHO$, aldehyde, hexanal
    (d) $-O$, ether, 1-ethoxypropane
    (e) $-NH_2$, amine, methanamine
    (f) $-C{=}O$, ketone, pentan-2-one
    (g) $-COOC$, ester, propylethanoate
    (h) $-CON$, amide, *N*-methylpropanamide
    (i) $-C{=}O$, ketone, pentan-3-one
    (j) $-COOH$, carboxylic acid, methanoic acid
35. (a) $CH_3CH_2OH \xrightarrow{conc.H_2SO_4} CH_2CH_2 + H_2O$; dehydration
    (b) $2\ CH_3CH_2OH \xrightarrow{conc.H_2SO_4} CH_3CH_2OCH_2CH$; dehydration
    (c) $CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$; oxidation
    (d) $CH_2CHCH_2CH_2CH_3 + H_2O \rightarrow CH_3CHOHCH_2CH_2CH_3$; addition
    (e) $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$, oxidation; $CH_3CHO + [O] \rightarrow CH_3COOH$, oxidation
    (f) $HCOOH + CH_3CH_2OH \xrightarrow{conc.H_2SO_4} HCOOCH_2CH_3$; condensation

2.1 Questions, p. 83

1. (a) natural polymer
   (b) synthetic polymer
   (c) synthetic polymer
   (d) natural polymer
   (e) natural polymer
   (f) natural polymer
   (g) synthetic polymer
   (h) natural polymer

2.2 Questions, p. 93

1. chlorotrifluoroethene, $CFCl{=}CF_2$
2. (a) fluoroethene, $CFH{=}CH_2$
   (b) 1-bromo-2-chloroethene, $HBrC{=}CHCl$
   (c) phenylethene, $C_6H_5CH{=}CH_2$

2.4 Questions, p. 99

6. hexanediamine, $H_2NCH_2CH_2CH_2CH_2NH_2$
   hexanedioic acid, $HOOCCH_2CH_2CH_2CH_2COOH$

2.6 Questions, p. 105

5. (a) six: gly-ser-phe; gly-phe-ser; ser-gly-phe; ser-phe-gly; phe-gly-ser; phe-ser-gly
6. (a) hydrophobic
   (b) hydrophilic
   (c) hydrophobic
   (d) hydrophilic

Chapter 2 Self-Quiz, p. 109

1. (a)
2. (c)
3. (b)
4. (d)
5. (d)
6. (c)
7. (b)
8. (c)
9. (d)
10. (d)
11. F
12. T
13. T
14. F
15. F
16. F
17. F
18. T

Chapter 2 Review, pp. 110–115

1. (c)
2. (b)
3. (c)
4. (a)
5. (a)
6. (c)
7. (d)
8. (c)
9. (d)
10. (d)
11. (a)
12. (d)
13. (a)
14. (a)
15. (c)
16. (a)
17. (a)
18. F
19. T
20. T
21. F
22. F
23. T
24. F
25. F
26. (a) (iii)
   (b) (vi)
   (c) (xi)
   (d) (vii)
   (e) (i)
   (f) (ix)
   (g) (ii)
   (h) (x)
   (i) (v)
   (j) (viii)
   (k) (iv)
29. (a) 3-bromo-3-chloroprop-1-ene
34. (b) condensation polymerization
35. (a) condensation reaction
   (b) yes; HCl
37. water
38. amine and carboxylic acid
42. (a) glycogen
   (b) cellulose
   (c) DNA
60. (a) aldehyde
61. (a) 6
   (b) pentose
69. (b) ii
71. butan-1,4-diol

Unit 1 Self-Quiz, pp. 118–119

1. (c)
2. (d)
3. (c)
4. (b)
5. (c)
6. (d)
7. (b)
8. (c)
9. (c)
10. (c)
11. (b)
12. (d)
13. (b)
14. (c)
15. (a)
16. (d)
17. (a)
18. (b)
19. (c)
20. (d)
21. (b)
22. (b)
23. F
24. T
25. T
26. F
27. T
28. F
29. F
30. F
31. F
32. F
33. F
34. T
35. T
36. T
37. F
38. F
39. F
40. F
41. T
42. T
43. F
44. F
45. T
46. T

Unit 1 Review, pp. 120–127

1. (d)
2. (c)
3. (b)
4. (d)
5. (c)
6. (b)
7. (a)
8. (a)
9. (b)
10. (d)
11. (a)
12. (c)
13. (c)
14. (c)
15. (d)
16. T
17. F
18. F
19. F
20. T
21. F
22. F
23. F
24. F
25. T
26. T
27. F
28. F
29. T
30. T
31. T
32. T
33. F
34. T
35. T
36. F
37. (a) (iv)
   (b) (vii)
   (c) (x)
   (d) (v)
   (e) (iii)
   (f) (xi)
   (g) (viii)
   (h) (ii)
   (i) (ix)
   (j) (i)
   (k) (vi)
38. (a) (ii)
   (b) (iv)
   (c) (iii)
   (d) (i)
39. (a) 2,2,4-trimethylhexane
   (b) 5-methylnonane
   (c) 2,2,4,4-tetramethylpentane
   (d) 3-ethyl-3-methyloctane
   (e) 1,3-dichlorobutane
   (f) 1,1,1-trichlorobutane
   (g) 2,3-dichloro-2,4-dimethylhexane
   (h) 1,2-difluoroethane
42. decane
46. (a) 10
   (b) 14
   (c) 11
47. (a) C_nH_{2n+2}
   (b) C_nH_{2n}
48. (a) 5
   (b) 4
50. (a) but-1-ene
   (b) 4-methylhex-2-ene
   (c) 2,5-dimethylhept-3-ene
53. Markovnikov's rule
54. (a) 5-methylhex-2-ene
   (b) hexane-1,4-diene
   (c) 3,4-dimethylcyclohexene
58. (a) pentan-1-ol, primary
   (b) 3-chlorobutan-1-ol, primary
   (c) 3-methylhexan-3-ol, tertiary
   (d) 2-methylcyclopentanol, secondary
61. ketone
62. butan-1-ol, primary
   butan-2-ol, secondary
   2-methylpropan-1-ol, primary
   2-methylpropan-2-ol, tertiary
63. (a) ketone
   (b) primary alcohol
64. (a) pentanal
   (b) 3-ethylhexan-2-ol
   (c) 3-methylpentan-2-one
   (d) 2-methylcyclohexanol
   (e) hydroxybenzene
65. (a) cyclohexanone
66. (a) ketone: pentan-2-one
   (b) aldehyde: butanal
   (c) ketone: 4,5-dichlorohexan-3-one
   (d) aldehyde: 2,3-dimethylpentanal
70. (a) methanoic acid
   (b) 2-methylpropanoic acid
   (c) 3-ethyl-2-methylhexanoic acid
   (d) 4-chlorobenzoic acid
72. ethanol and butanoic acid
73. fatty acid
74. ethanol and benzoic acid
75. (a) aldehyde
   (b) ketone
   (c) amine
   (d) carboxylic acid
   (e) ketone
   (f) aldehyde
   (g) carboxylic acid
   (h) amine
83. (a) cross-links
85. no
89. (a) polyester
   (b) polyester
   (c) polyamide
   (d) polyamide
91. (a) rubber
   (b) nylon, a polyamide
   (c) carboxylic acid, amine
93. (a) carboxyl, amino
   (b) peptide, water
   (c) polyamide
95. no
99. no
102. ethanol
108. propane, propanamine, and propan-1-ol

Unit 2

Are You Ready?, pp. 130–131

1. (a) ionic
   (b) covalent
   (c) ionic
   (d) covalent
   (e) ionic
5. (a) 5 protons, 5 electrons, 6 neutrons
   (b) 25 protons, 25 electrons, 29 neutrons
   (c) 25 protons, 25 electrons, 30 neutrons
   (d) 17 protons, 18 electrons, 18 neutrons
8. (a) molecular
   (b) molecular
   (c) ionic
   (d) ionic
   (e) ionic
   (f) ionic
21. (a) carbon tetrabromide
   (b) chlorine dioxide
   (c) dinitrogen monoxide
   (d) sulfur hexafluoride
   (e) dinitrogen tetroxide

24. (a) calcium chloride
    (b) iron(II) nitrate
    (c) carbon monoxide
    (d) calcium sulfite
    (e) ammonium nitrate
    (f) ammonium sulfide
    (g) copper(II) chlorite
    (h) sodium hypochlorite
    (i) mercury(II) sulfide
    (j) calcium acetate

3.1 Questions, p. 142

1. (a) (i) 35 protons, 44 neutrons
        (ii) 35 protons, 46 neutrons
        (iii) 94 protons, 145 neutrons
        (iv) 55 protons, 78 neutrons
        (v) 1 proton, 2 neutrons
        (vi) 26 protons, 30 neutrons
   (b) (i) 35
        (ii) 35
        (iii) 94
        (iv) 55
        (v) 1
        (vi) 26
2. (a) $^{17}_{8}\text{O}$
   (b) $^{37}_{17}\text{Cl}$
   (c) $^{60}_{27}\text{Co}$
   (d) $^{57}_{26}\text{Fe}$
   (e) $^{131}_{53}\text{I}$
   (f) $^{7}_{3}\text{Li}$
3. (a) 56 protons, 54 electrons
   (b) 30 protons, 28 electrons
   (c) 7 protons, 10 electrons
   (d) 37 protons, 36 electrons
   (e) 27 protons, 24 electrons
   (f) 52 protons, 54 electrons
4. (a) $^{34}_{16}\text{S}^{2-}$
   (b) $^{32}_{16}\text{S}^{2-}$

3.4 Questions, p. 159

5. first shell: $n = 1, l = 0, m_l = 0$
   second shell: $n = 2, l = 0$ or 1, $m_l = 0, +1,$ or -1
   third shell: $n = 3, l = 0, 1,$ or 2, $m_l = -2, -1, 0, 1,$ or 2
6. (a) $n = 2, l = 0, m_l = 0,$ $m_s = \frac{1}{2}$ or $-\frac{1}{2}$
   (b) $n = 6, l = 0, m_l = 0,$ $m_s = \frac{1}{2}$ or $-\frac{1}{2}$
   (c) $n = 5, l = 0, 1, 2, 3$ or 4, $m_l = -4, -3, -2, -1, 0, 1, 2, 3,$ or 4, $m_s = \frac{1}{2}$ or $-\frac{1}{2}$
7. a, b, c, e
8. a, b, c, e
9. a, b, c, e
12. 2, 8

3.5 Questions, p. 172

3. (a) Cr: $[\text{Ar}]4s^{1}3d^{5}$, 6 unpaired electrons; Cu: $[\text{Ar}]4s^{1}3d^{10}$, 1 unpaired electron
6. (a) $3d$
   (b) $5p$
   (c) $6s$
7. (a) As: $[\text{Ar}]4s^{2}3d^{10}4p^{3}$
   (b) Uuh: $[\text{Rn}]7s^{2}5f^{14}6d^{10}7p^{4}$
   (c) Ta: $[\text{Xe}]6s^{2}4f^{14}5d^{3}$
   (d) At: $[\text{Xe}]6s^{2}4f^{14}5d^{10}6p^{5}$
8. (a) F: $1s^{2}2s^{2}2p^{5}$
   (b) K: $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{1}$
   (c) In: $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}5s^{2}4d^{10}5p^{1}$
   (d) C: $1s^{2}2s^{2}2p^{2}$;
       Si: $1s^{2}2s^{2}2p^{6}3s^{2}3p^{2}$;
       Ge: $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{2}$

Chapter 3 Self-Quiz, p. 185

1. (b)
2. (d)
3. (c)
4. (d)
5. (c)
6. (b)
7. (c)
8. (d)
9. (a)
10. T
11. T
12. F
13. T
14. T
15. F
16. F
17. F
18. T

Chapter 3 Review, pp. 186–191

1. (d)
2. (b)
3. (a)
4. (d)
5. (a)
6. (d)
7. (d)
8. F
9. T
10. F
11. T
12. F
13. T
14. T
15. T
27. (a) the first energy level ($n = 1$)
    (b) Groups 1A and 2A
    (c) metals
29. (a) 2
    (b) 8
    (c) 18
    (d) 36
33. helium: 2, 2, $1s^{2}$
    boron: 5, 5, $1s^{2}2s^{2}2p^{1}$
    chlorine: 17, 17, $1s^{2}2s^{2}2p^{6}3s^{2}3p^{5}$
    neon: 10, 10, $1s^{2}2s^{2}2p^{6}$
    phosphorus: 15, 15, $1s^{2}2s^{2}2p^{6}3s^{2}3p^{3}$
34. (a) $1s^{2}2s^{2}2p^{6}3s^{2}$
    (b) $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}$
    (c) $1s^{2}2s^{2}2p^{4}$
    (d) $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}5s^{1}$
    (e) $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}5s^{2}4d^{10}5p^{6}6s^{1}4f^{14}5d^{10}$
35. (a) $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}$
    (b) $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}$
36. (a) $[\text{Ne}]3s^{2}3p^{2}$
    (b) $[\text{Ar}]4s^{2}3d^{5}$
    (c) $[\text{Xe}]6s^{2}4f^{14}5d^{3}$
    (d) $[\text{Ar}]4s^{2}3d^{10}4p^{5}$
    (e) $[\text{Rn}]7s^{2}5f^{10}$
37. (a) -3, $[\text{Ne}]3s^{2}3p^{6}$
    (b) $+2$, [He]
    (c) $+3$, $[\text{Ar}]4s^{2}3d^{5}$
38. (a) $[\text{Kr}]5s^{2}4d^{1}$
    (b) $[\text{Kr}]5s^{2}4d^{10}5p^{3}$
    (c) [Xe]
41. (a) boron
    (b) beryllium
    (c) chlorine
    (d) sulfur
    (e) vanadium
42. $5p$
45. (a) As
    (b) Ho
    (c) Rb^{+}
    (d) I^{-}
48. (a) 2, $4s^{2}$
    (b) 6, $2s^{2}2p^{4}$
    (c) 7, $7s^{2}7p^{5}$
    (d) 3, $5s^{2}5p^{1}$
    (e) 8, $3s^{2}3p^{6}$
    (f) 5, $6s^{2}6p^{3}$
51. Li: 1 unpaired electron
    N: 3 unpaired electrons
    Ni: 2 unpaired electrons
    Te: 2 unpaired electrons
55. (a) $^{151}_{63}\text{Eu}^{3+}$
    (b) $^{118}_{50}\text{Sn}^{2+}$
56. (a) Br^{-}, Rb^{+}, Sr^{2+}
    (b) Br gains a $4p$ electron, Rb loses one $5s$ electron, Sr loses two $5s$ electrons
57. Ca
63. (a) Al: $1s^{2}2s^{2}2p^{6}3s^{2}3p^{1}$
65. (a) paramagnetic
    (b) not paramagnetic
    (c) paramagnetic
    (d) not paramagnetic
66. Fe^{2+}: $[\text{Ar}]3d^{6}$; Fe^{3+}: $[\text{Ar}]3d^{5}$
67. (a) Ca: $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}$
    (b) Ca: $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{1}4p^{1}$
    (c) Ca^{2+}: $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}$
69. (a) $Z = 42$
    (b) Mo: $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}5s^{2}4d^{4}$
    (c) Mo: $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}5s^{1}4d^{5}$
71. K_2O, Rb_2O, Cs_2O
72. $p^{+} = 26, n^{0} = 27, e^{-} = 24$

4.1 Questions, p. 205

2. (a) $(NH_4)_2SO_4$, $Ca_3(PO_4)_2$, K_2O, KCl
   (b) $(NH_4)_2SO_4$, $Ca_3(PO_4)_2$, P_2O_5
   (c) $(NH_4)_2SO_4$, $Ca_3(PO_4)_2$
6. (b) I in I_3^{-}; S in SF_4; P in PF_5; Xe in XeF_4

4.2 Questions, p. 216

2. (a) tetrahedral; 109.5°
   (b) trigonal pyramidal; 107°
   (c) bent or V-shaped; 104.5°
   (d) linear; 180°
   (e) trigonal pyramidal; 107°
   (f) bent or V-shaped; 104.5°
   (g) tetrahedral; 109.5°
3. (a) V-shaped; 120°
   (b) trigonal planar; 120°
   (c) linear; 180°
   (d) linear; 180°
4. linear
5. all four have a trigonal planar structure
6. all three have a tetrahedral arrangement
7. (a) linear
   (b) tetrahedral
   (c) trigonal planar
   (d) trigonal planar
   (e) trigonal planar around both C
8. (a) trigonal pyramidal
   (b) trigonal planar
   (c) linear
9. tetrahedral around first, fourth, and fifth carbons; trigonal planar around second and third carbons

4.3 Tutorial 1 Practice, p. 220

1. (a) polar covalent
   (b) polar covalent
   (c) ionic
2. (a) $H{-}H < C{-}H < B{-}H, Mg{-}H < Na{-}H < O{-}H < H{-}F$
   (b) $Cl{-}Cl < I{-}Cl < P{-}Cl < Al{-}Cl < Li{-}Cl < Rb{-}Cl$
   (c) $C{-}C = C{-}S < C{-}H < C{-}Cl < C{-}O < C{-}F$

4.3 Questions, p. 221

1. (a) C < N < O
   (b) Se < S < Cl
   (c) Si = Ge = Sn
   (d) Tl = Ge < S
3. (a) polar covalent
   (b) polar covalent
   (c) ionic
   (d) non-polar covalent
   (e) polar covalent
4. (a) Ge–F
   (b) P–Cl
   (c) S–F
   (d) Ca–Cl
6. (a) O: δ^{+}; F: δ^{-}
   (b) non-polar
   (c) C: δ^{+}; Br: δ^{-}
   (d) C: δ^{+}; O: δ^{-}
7. (a) correct
   (b) incorrect; $\delta^{+}I{-}Cl\delta^{-}$
   (c) correct
   (d) incorrect; non-polar
   (e) incorrect; $\delta^{+}P{-}O\delta^{-}$
8. (a) 1.5
   (b) polar covalent
9. (a) O, F
   (b) F
   (c) N, Cl, Br
10. (a) ionic
    (b) non-polar covalent
    (c) polar covalent
    (d) polar covalent
    (e) non-polar covalent
    (f) ionic

4.5 Questions, p. 229

4. (a) B: δ^{+}; F: δ^{-}
   (b) N: δ^{+}; Cl: δ^{-}
   (c) H: δ^{+}; C: δ^{-}
   (d) no partial charge

5. (a) polar
   (b) non-polar
   (c) non-polar
   (d) polar
   (e) non-polar
   (f) polar
   (g) polar
6. (a) polar
   (b) polar
   (c) polar

4.6 Questions, p. 238

4. (a) linear, trigonal planar, tetrahedral
   (b) sp and sp^2
8. (a) sp^3
   (b) sp^3
   (c) sp^3
   (d) sp
   (e) sp
   (f) sp^2
9. (b) 120°

4.7 Questions, p. 247

1. (a) HBr
   (b) NaCl
   (c) I_2
   (d) N_2
   (e) CH_4
   (f) HF
2. (a) CBr_4
   (b) F_2
   (c) CH_3CH_2OH
   (d) H_2O_2
   (e) H_2CO
4. (a) OCS
   (b) SeO_2
   (c) $H_2NCH_2CH_2NH_2$
   (d) H_2CO
   (e) CH_3OH
5. F_2
6. (a) 78.5 °C
   (b) −23 °C
   (c) −42.1 °C
7. (a) London, dipole–dipole, hydrogen bonding
   (b) London, dipole–dipole, hydrogen bonding
   (c) London
   (d) London, dipole–dipole, hydrogen bonding
   (e) London, dipole–dipole
8. $H_2NCH_2CH_2NH_2$

4.8 Questions, p. 254

2. (a) metallic
   (b) molecular
   (c) ionic
   (d) molecular
6. (a) metallic
   (b) ionic
   (c) covalent network
   (d) molecular

Chapter 4 Self-Quiz, p. 261

1. (c)
2. (a)
3. (c)
4. (d)
5. (c)
6. (a)
7. (d)
8. (c)
9. (c)
10. T
11. T
12. F
13. T
14. F
15. T
16. T
17. T
18. F
19. T

Chapter 4 Review, pp. 262–267

1. (d)
2. (c)
3. (d)
4. (c)
5. (d)
6. (b)
7. (c)
8. (a)
9. (c)
10. (d)
11. (a)
12. (b)
13. T
14. T
15. F
16. T
17. T
18. F
19. F
20. F
21. T
22. T
23. F
32. $S-O > N-S = S-Cl > P-S > C-S$
33. (a) carbon tetrachloride and boron trifluoride
35. $CF_2H_2 > CCl_2H_2 > CF_2Cl_2 > CCl_4$
36. (b) sigma bond
37. (b) sp
   (c) C−Br bond is a sigma bond; C−C bond is a triple bond: one sigma and two pi bonds
39. (a) $SiCl_4$
   (b) NaCl
46. (a) one
   (b) one
   (c) none
   (d) two
48. (a) 8 e^- surround central atom; 3 bonding pairs, 6 lone pairs
   (b) 8 e^- surround central atom; 3 bonding pairs, 10 lone pairs
   (c) 6 e^- surround central atom; 3 bonding pairs, 9 lone pairs
   (d) 8 e^- surround central atom; 4 bonding pairs, 4 lone pairs
   (e) 12 e^- surround central atom; 6 bonding pairs, 18 lone pairs
   (f) 8 e^- surround central atom; 4 bonding pairs, 12 lone pairs
   (g) 2 e^- surround central atom; 1 bonding pair, 0 lone pairs
   (h) 6 e^- surround central atom; 3 bonding pairs, 18 lone pairs
50. (a) trigonal planar; 120°
   (b) V-shaped; 104°
51. (a) linear
   (b) tetrahedral around C; bent around S
   (c) tetrahedral around C bonded to H; linear C bonded to N
   (d) trigonal planar
53. (a) $B-H < N-H = Mg-H < Li-H < O-H$
   (b) $Ga-Br = Ge-Cl < Sn-F < Al-F$
   (c) $P-H < P-S < P-Cl < P-O < P-F$
54. (a) polar covalent
   (b) polar covalent
   (c) ionic
   (d) covalent
   (e) covalent
   (f) polar covalent
55. (a) Si: δ^+; Cl: δ^-
   (b) Li: δ^+; H: δ^-
   (c) Al: δ^+; I: δ^-
   (d) Ge: δ^+; H: δ^-
56. O, F
57. (a) no
   (b) yes
   (c) no
   (d) yes
   (e) yes
58. (a) no partial charge
   (b) no partial charge
   (c) H: δ^+; C: δ^-
   (d) C: δ^+; N: δ^-
60. (a) polar
   (b) polar
   (c) non-polar
   (d) non-polar
   (e) polar
62. (a) sp^3
   (b) no hybridization
   (c) sp^2
   (d) sp^2
63. (a) sp^3
   (b) sp
   (c) sp^2
   (d) sp^2
   (e) sp
64. (a) sigma
   (b) sigma
   (c) sigma
   (d) 1 sigma, 1 pi between C atoms; sigma between C and Cl
   (e) 1 sigma, 2 pi
65. (b) 1 sigma, 1 pi
66. (b) *p*
71. (a) *n*-pentane
   (b) HF
   (c) LiCl
   (d) hexane
72. (a) ethanol
   (b) SiH_4
   (c) H_2O
   (d) C_2H_5OH
   (e) C_4H_9OH
74. (a) ionic
   (b) ionic
   (c) metallic
   (d) molecular
75. (a) ionic
   (b) molecular
   (c) metallic
   (d) covalent network
76. (a) molecular
   (b) metallic
   (c) covalent network
   (d) ionic
78. (a) SiC
   (b) Na_3PO_4
   (c) H_2O
80. (b) trigonal planar; 120°
82. (a) 90°, octahedral
83. CH_3OH
84. water
85. (a) V-shaped; 104.5°; polar; sp^3
   (b) tetrahedral; 109.5°; non-polar; sp^3
   (c) linear; 180°; non-polar; sp
   (d) linear; 180°; non-polar; sp
86. (b) trigonal planar around C atoms; 120°; sp^2
   (c) non-polar
89. (a) no
   (b) 12 valence electrons

Unit 2 Self-Quiz, pp. 270–271

1. (d)
2. (b)
3. (a)
4. (c)
5. (d)
6. (b)
7. (b)
8. (b)
9. (a)
10. (b)
11. (c)
12. (b)
13. (a)
14. (d)
15. (a)
16. (a)
17. (b)
18. (d)
19. (a)
20. (c)
21. (d)
22. (a)
23. (a)
24. (d)
25. F
26. F
27. T
28. T
29. F
30. T
31. F
32. T
33. F
34. T
35. F
36. T
37. T
38. F
39. F
40. T
41. T
42. T
43. F

Unit 2 Review, pp. 272–279

1. (b)
2. (d)
3. (c)
4. (d)
5. (c)
6. (a)
7. (d)
8. (d)
9. (c)
10. (d)
11. (d)
12. (d)
13. (c)
14. (d)
15. (c)
16. (d)
17. (a)
18. (a)
19. (b)
20. (d)
21. (c)
22. (d)
23. (c)
24. (b)
25. (b)
26. (d)
27. (b)
28. (c)
29. (d)
30. F
31. T
32. T
33. F
34. T
35. T
36. T

37. T
38. F
39. T
40. T
41. T
42. F
43. T
44. F
45. F
46. F
47. T
48. F
49. T
50. F
51. T
52. F
53. F
54. F
55. F
56. F
57. (a) (i)
    (b) (v)
    (c) (x)
    (d) (iv)
    (e) (vii)
    (f) (ix)
    (g) (viii)
    (h) (ii)
    (i) (vi)
    (j) (iii)
58. (a) (ii)
    (b) (iv)
    (c) (iii)
    (d) (i)
67. no
68. 10, 11, 12
79. (a) n
    (b) n^2
    (c) $2n^2$
81. (a) 1
    (b) 2
    (c) $4n - 2$, where n is the principal quantum number
82. (a) Kr
    (b) Mg
    (c) Ru
    (d) Ar
84. (a) P
    (b) He
    (c) H
    (d) Ga
85. (a) 3
    (b) 6
    (c) 2
    (d) 7
88. (a) F: $1s^22s^22p^5$
    (b) C: $1s^22s^22p^2$
    (c) Sc: $1s^22s^22p^63s^23p^64s^23d^1$
    (d) He: $1s^2$
89. 2
91. (a) cation
    (b) anion
    (c) cation
    (d) anion
92. (a) lose 1 e^-
    (b) gain 3 e^-
    (c) gain 1 e^-
    (d) lose 2 e^-
101. K < Na < S < Br < O
102. (a) Ca
    (b) F
    (c) S
    (d) Ge
103. F–H > O–H > N–H > C–H > P–H
104. (a) ionic
    (b) non-polar covalent
    (c) polar covalent
    (d) ionic
    (e) polar covalent
    (f) non-polar covalent
106. (a) (i) P: $1s^22s^22p^63s^23p^3$
        (ii) S: $1s^22s^22p^63s^23p^4$
        (iii) Br: $1s^22s^22p^63s^23p^64s^23d^{10}4p^5$
        (iv) Si: $1s^22s^22p^63s^23p^2$
107. (a) $3p$
    (b) $3p$
    (c) $4p$
    (d) $3p$
108. (a) (i) B: $1s^22s^22p^1$
        (ii) N: $1s^22s^22p^3$
        (iii) C: $1s^22s^22p^2$
        (iv) F: $1s^22s^22p^5$
    (f) (i) B: sp^2
        (ii) N: sp^3
        (iii) C: sp^3
        (iv) F: sp^3
109. (a) Be: sp; $BeCl_2$: linear
    (b) S: sp^3; H_2S: bent
    (c) C: sp^2; H_2CO: trigonal planar
    (d) Si: sp^3; SiF_4: tetrahedral
110. $CH_3CH_2CH_2OH$
114. (a) (i) intermolecular
        (ii) intermolecular
        (iii) intermolecular
        (iv) intramolecular
        (v) intermolecular
        (vi) intramolecular
    (b) covalent bonds, ionic bonds, van der Waals (hydrogen bonds, dipole-dipole, London dispersion)
117. (a) metal
    (b) ionic
    (c) molecular
    (d) molecular
    (e) covalent network
    (f) covalent network
    (g) metal
119. (a) molecular
    (b) covalent network
    (c) covalent network
    (d) molecular
    (e) metal
    (f) molecular
    (g) ionic
    (h) molecular
    (i) ionic
    (j) metal
    (k) ionic
    (l) molecular
120. B_2H_6: molecular;
    SiO_2: network;
    CsI: ionic;
    W: metallic
123. (a) ionic
    (b) covalent
    (c) ionic
    (d) ionic
    (e) covalent
    (f) ionic
127. (b) biacetyl: all 120°;
        acetoin: C–C–O around double-bonded carbon: 120°;
        C–C–O around single-bonded carbon: 109.5°
    (c) biacetyl: 11 sigma bonds and 2 pi bonds
        acetoin: 13 sigma bonds and 1 pi bond

Unit 3

Are You Ready?, pp. 282–283

1. (a) chemical energy to kinetic energy
    (b) solar energy to electrical energy
    (c) electrical energy to thermal energy
2. absorb
5. (a) absorb
    (b) release
    (c) absorb
    (d) release
6. releases
8. (a) temperature
    (b) concentration
    (c) concentration
10. (a) $2\ C_8H_{18}(l) + 25\ O_2(g) \rightarrow 16\ CO_2(g) + 18\ H_2O(g)$
    (b) 1.74 L
    (c) 2.71 L
11. (a) $2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$: decomposition
    (b) $Fe_2O_3(s) + 2\ Al(s) \rightarrow 2\ Fe(s) + Al_2O_3(s)$: reduction
    (c) $2\ C_4H_{10}(g) + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(g)$: combustion
    (d) $4\ K(s) + O_2(g) \rightarrow 2\ K_2O(s)$: synthesis
12. (a) $2\ C(s) + O_2(g) \rightarrow 2\ CO(g)$
        $2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$
    (b) 50 L of CO and 50 L of CO_2
    (c) $C(s) + O_2(g) \rightarrow CO_2(g)$
    (d) 49 L of CO_2
13. (a) 24.4 kJ
    (b) 4.8×10^2 g
    (c) 1.52×10^{-2} mg
14. (a) $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$
    (b) 18.3 g
15. (a) 18 mol
    (b) 69 J
    (c) 23.1 J/mol

5.1 Questions, p. 291

1. (a) potential energy
    (b) potential energy
    (c) kinetic energy
    (d) potential energy
2. (a) endothermic
    (b) exothermic
    (c) exothermic
    (d) endothermic
    (e) endothermic
    (f) endothermic

5.2 Questions, p. 306

2. q_{system}: negative;
    ΔH: negative;
    $q_{surroundings}$: positive
3. (a) −446 kJ
    (b) −891 kJ
    (c) −446 kJ
4. 9.4 °C
6. (a) $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$
        $\Delta H°_c = -2220\ kJ$
    (b) $Cl_2(g) \rightarrow 2\ Cl(g)$
        $\Delta H°_r = 243\ kJ$
    (c) $2\ Fe(s) + 3\ O_2(g) \rightarrow Fe_2O_3(s)\ \Delta H°_f = -824\ kJ$
    (d) $HCl(g) \rightarrow \frac{1}{2}\ H_2(g) + \frac{1}{2}\ Cl_2(g)$
        $\Delta H°_r = 93\ kJ$
7. (a) $Cu(s) + Cl_2(g) \rightarrow CuCl_2(s) + 220.1\ kJ$
    (b) $C(graphite) + 2.0\ kJ \rightarrow C(diamond)$
    (c) $AgCl(s) + 127.1\ kJ \rightarrow Ag(s) + \frac{1}{2}\ Cl_2(g)$

5.3 Questions, p. 313

1. (a) −183 kJ
    (b) −109 kJ
2. (a) −158 kJ
    (b) -1.17×10^3 kJ
4. 327 kJ
8. −20 kJ
9. 485 kJ/mol
10. 5695 kJ
11. exothermic
12. (a) $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$
    (c) 137 kJ/mol
13. (a) propane: −2057 kJ/mol;
        methane: −824 kJ/mol
    (b) 2.5 mol

5.4 Questions, p. 318

4. (a) −2984 kJ
    (b) −746 kJ/mol
5. 29 kJ
6. −623 kJ
7. −713 kJ
8. −461.3 kJ

5.5 Questions, p. 324

1. (b), (d)
2. (a) −571.6 kJ
    (b) −393.5 kJ
    (c) 571.6 kJ
    (d) −1409.2 kJ
3. 5.45×10^3 kJ

4. -2672.7 kJ
5. -176 kJ/mol
6. 4360 kJ
7. 52.5 kJ
8. -30.58 kJ/g
9. (a) -22.7 kJ/g
   (c) ethanol
10. (a) $Ga(s) + 5.59\ kJ \rightarrow Ga(l)$
    (b) $\Delta H^{\circ}_{f_{Ga(s)}} = 0$, $\Delta H^{\circ}_{f_{Ga(l)}} = 5.59$ kJ

5.6 Questions, p. 330

3. T

Chapter 5 Self-Quiz, p. 337

1. (c)
2. (b)
3. (a)
4. (b)
5. (d)
6. (d)
7. (d)
8. (a)
9. T
10. F
11. F
12. F
13. T
14. T
15. T
16. F
17. F
18. T
19. F
20. T
21. F

Chapter 5 Review, pp. 338–343

1. (d)
2. (d)
3. (a)
4. (d)
5. (b)
6. (c)
7. (a)
8. (a)
9. F
10. T
11. T
12. F
13. T
14. F
15. F
16. F
17. F
18. T
19. F
20. T
21. (a) exothermic
    (b) exothermic
    (c) exothermic
    (d) endothermic
22. (a) 54 kJ
    (b) exothermic
26. 362 kJ
27. (a) $Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$
    (b) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(s)$
    (c) $Pb(s) + S(s) + 2\ O_2(g) \rightarrow PbSO_4(s)$
    (d) $6\ C(s) + 6\ H_2(g) + 3\ O_2(g) \rightarrow C_6H_{12}O_6(s)$
28. $2\ Al(s) + \frac{3}{2} O_2(g) \rightarrow Al_2O_3(s)$
    $\Delta H_f^{\circ} = -1676$ kJ/mol;
    $2\ Al(s) + \frac{3}{2} O_2(g) \rightarrow Al_2O_3(s) + 1676\ kJ$
34. (a) 363 kJ
    (b) 726 kJ
    (c) 484 kJ
    (d) -726 kJ
35. (a) 8.77 J/g
    (b) 43.9 J/g
36. (a) 5.9 kJ
    (b) 59 kJ/mol
37. (a) $HgO(s) \rightarrow Hg(l) + \frac{1}{2} O_2(g)$, $\Delta H = 90.7$ kJ/mol
    (b) $HgO(s) + 90.7\ kJ \rightarrow Hg(l) + \frac{1}{2} O_2(g)$
38. $+26.0$ kJ/mol
39. 120 kJ
40. (b) 77.2 kJ
    (c) 13.1 kJ
41. (a) -34 kJ/mol, -54 kJ/mol
    (b) $+20$ kJ/mol
42. (a) cyclohexane: $6\ C(s) + 6\ H_2(g) \rightarrow C_6H_{12}(l) + 156\ kJ$
    1-hexene: $6\ C(s) + 6\ H_2(g) \rightarrow C_6H_{12}(l) + 74.2\ kJ$
    (b) -3920 kJ, -4001.6 kJ
43. (a) 1504 kJ/mol
    (b) 1515 kJ/mol
    (c) 1665 kJ/mol
    (d) 2266 kJ/mol
44. (a) -1228 kJ/mol
45. (a) -183 kJ, exothermic
    (b) -1282 kJ, endothermic
    (c) -109 kJ, exothermic
    (d) -1930 kJ, exothermic
46. 218 kJ
47. (a) -27.7 kJ/g
48. -100.9 kJ
49. -852 kJ
50. 44 kJ
51. (a) -75 kJ/mol
    (b) warm
52. 129 kJ
53. 615 kJ
54. -117 kJ
56. (a) -1014.4 kJ
    (b) -282.9 kJ
    (c) -176.2 kJ
    (d) -1409.2 kJ
    (e) -21.3 kJ
    (f) -37.1 kJ
57. (a) -128 kJ
    (b) exothermic
58. (a) $3\ C(s) + 3\ H_2(g) + \frac{1}{2} O_2(g) \rightarrow C_3H_6O(l)$
    (b) -256 kJ
59. -256 kJ
60. (a) 2803 kJ
    (b) 2755 kJ
    (d) endothermic
61. (a) $C_{12}H_{22}O_{11}(s) \xrightarrow{catalyst} 12\ C(s) + 11\ H_2O(g)$
    (b) -434.3 kJ
62. (a) $C_8H_{18}(l) + 3\ H_2(g) \rightarrow CH_4(g) + 2\ C_2H_6(g) + C_3H_8(g)$
    (b) -96.6 kJ
64. 2900 g
66. (a) 2.1×10^{11} kJ
67. (a) propane: -50.4 kJ/g; gasoline: -47.7 kJ/g
    (b) propane
68. (a) -890.7 kJ/mol, -283.0 kJ/mol
    (b) -55.50 kJ/g, -10.10 kJ/g

6.1 Questions, p. 361

1. 5×10^{-3} mol/L·s
2. $Fe^{2+}(aq)$: 0.20 mol/(L·min);
   $H^{+}(aq)$: 0.32 mol/(L·min);
   $Mn^{2+}(aq)$: 0.040 mol/(L·min);
   $Fe^{3+}(aq)$: 0.20 mol/(L·min);
   $H_2O(l)$: 0.16 mol/(L·min)
3. (a) (i) 2.5×10^{-2} mol/L·s
       (ii) 3.0×10^{-2} mol/L·s
4. (a) rate $= \left(\frac{\Delta[NO_2]}{\Delta t}\right)$; 4.0×10^{-3} mol/L·s
5. (a) $H_2SO_4(aq) + 2\ NaHCO_3(aq) \rightarrow Na_2SO_4(aq) + 2\ CO_2(g) + 2\ H_2O(l)$
   (b) (i) 0.16 g/s
       (ii) 9.5×10^{-4} mol/s
       (iii) 1.9×10^{-3} mol/s

6.2 Questions, p. 365

1. (a) nature of reactant
   (b) temperature
   (c) surface area
   (d) nature of reactant
   (e) catalyst
   (f) concentration
   (g) temperature
   (h) temperature
   (i) surface area
   (j) catalyst

6.3 Questions, p. 372

1. (a) rate decreases
   (b) rate increases
   (c) rate increases
   (d) rate increases
   (e) no change
5. (c) heterogeneous
6. (a) $C_2H_4(g) + HCl(g) \rightarrow CH_3CH_2Cl(g)$

6.5 Questions, p. 382

1. rate $= k[N_2O_5(g)]$;
   $k = 1.19 \times 10^{-2}\ s^{-1}$
2. (a) rate $= k[NOCl(g)]^2$
   (b) 6.6×10^{-5} L/(mol·s)
3. (a) rate $= k[I^{-}(aq)][OCl^{-}(aq)]$
   (b) 3.7 L/(mol·s)
   (c) 8.2×10^{-2} mol/(L·s)
4. (a) $Cl_2(g)$: 1; $NO(g)$: 2
   (b) triple
   (c) increase four-fold
   (d) 3.0 $L^2/(mol^2 \cdot s)$
   (e) 8.2×10^{-4} mol/(L·s)

6.6 Questions, p. 387

4. (a) rate $= k[O_3(g)]^2$
   (b) $2\ O_3(g) \rightarrow 3\ O_2(g)$
   (c) $O(g)$
5. (a) rate $= k[C_4H_9Br(aq)]$
   (b) $C_4H_9Br(aq) + 2\ H_2O(l) \rightarrow Br^{-}(aq) + C_4H_9OH + H_3O^{+}(aq)$
   (c) $C_4H_9^{\ +}(aq)$; $C_4H_9OH_2^{\ +}(aq)$
8. (a) $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$
   (b) $N_2O_2(g)$
   (c) second step
9. (a) $HNO_2(aq) + NH_4^{\ +}(aq) \rightarrow N_2(g) + 2\ H_2O(l) + H^{+}(aq)$
   (b) $NH_3(aq)$, $NO^{+}(aq)$, $NH_3NO^{+}(aq)$
   (c) no

Chapter 6 Self-Quiz, p. 395

1. (b)
2. (d)
3. (a)
4. (b)
5. (c)
6. (c)
7. (a)
8. (d)
9. (b)
10. (d)
11. T
12. F
13. T
14. F
15. F
16. T
17. T
18. T
19. F
20. F

Chapter 6 Review, pp. 396–402

1. (a)
2. (d)
3. (d)
4. (b)
5. (c)
6. (b)
7. (c)
8. (c)
9. (c)
10. F
11. T
12. T
13. F
14. T
15. T
16. F
17. F
18. F
19. F
20. T
38. 2
45. 1 or 2
49. $P_4(g)$: 0.00060 mol/L·s;
    $H_2(g)$: 0.0036 mol/L·s
50. (a) 1.83×10^{-5} mol/L·s
    (b) 2.74×10^{-5} mol/L·s
51. 1.94×10^{-5} mol/L·s
52. (a) 2
    (b) 1
    (c) reactants: 0.100 00 mol/L, 0.05 000 mol/L; product: 0.00 mol/L
    (d) $2A + B \rightarrow 3C$
53. (b) 4.0×10^{-3} mol/L·s
    (c) 7.0×10^{-3} mol/L·s
    (d) 1.6×10^{-3} mol/L·s
54. (a) increase
    (b) decrease
    (c) increase
    (d) increase
63. (a) $r = k[ClO_2(aq)]^2[OH^{-}(aq)]$
    (b) third order
    (c) quadruple
    (d) double
65. first order; rate $= k[RX][OH^{-}]$
66. (a) zero order
    (b) first order
    (c) order greater than 1
    (d) second order

67. (a) Cl_2: 1; NO: 2
(b) third order
(c) $L^2/(mol^2 \cdot s)$
68. rate law: rate $= k[Mg][O_2]^2$;
rate constant: 2.0 $L^2/(mol^2 \cdot s)$;
overall reaction order: 3
70. (a) rate $= k[CH_3CSNH_2][OH^-]$
(b) 2
(c) $CH_3CONH_2 + OH^- \rightarrow CH_3CO_2^- + NH_3$
71. (a) A: 2; B: 0; C: 1
(b) rate $= (440\ L^2/(mol^2 \cdot s))[A]^2[C]$
(c) step 3
(d) F, G
(f) yes
(g) no
72. $A + B \rightarrow P$
73. (b) 3.0×10^{-3} mol/(L·s)
(c) oxalic acid:
7.4×10^{-3} mol/(L·s),
carbon dioxide:
0.014 mol/(L·s)

Unit 3 Self-Quiz, pp. 404–405

1. (d)
2. (c)
3. (b)
4. (b)
5. (a)
6. (b)
7. (a)
8. (a)
9. (c)
10. (c)
11. (c)
12. (d)
13. (c)
14. (a)
15. (a)
16. (c)
17. T
18. F
19. T
20. T
21. F
22. F
23. F
24. T
25. F
26. F
27. T
28. F
29. T
30. F
31. T
32. F

Unit 3 Review, pp. 406–413

1. (a)
2. (c)
3. (c)
4. (d)
5. (c)
6. (d)
7. (d)
8. (b)
9. (d)
10. (d)
11. (d)
12. (d)
13. F
14. F
15. T
16. F
17. T
18. T
19. F
20. T
21. F
23. (a) open
(b) closed
(c) closed
(d) closed
24. (a) endothermic
(b) endothermic
(c) exothermic
(d) exothermic
30. forming a P–Cl bond
36. (a) chemical nature of reactants
(b) temperature
(c) presence of catalyst
(d) surface area
(e) concentration
43. 3.4×10^5 J; 340 kJ
44. 657 kJ
45. 35 J/(g·°C)
46. 1100 J/g
47. (a) −46.0 kJ/mol
48. 614 kJ
49. 1.96×10^3 kJ/mol
50. −183 kJ
51. (a) −101.5 kJ/mol H_2O_2
(b) −274.5 kJ/mol CH_3OH
(c) −1140 kJ/mol $C_2H_2F_4$
52. −643.1 kJ
53. (a) $C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(g)$
(b) −2802.7 kJ/mol
(c) −2425 kJ/mol
(d) −2790 kJ/mol
55. (a) $S(s) + O_2(g) \rightarrow SO_2(g)$
$\Delta H = -296.8$ kJ/mol
(c) 44.6 kJ
56. (a) $C_5H_{12}(g) + 8\ O_2(g) \rightarrow 5\ CO_2(g) + 6\ H_2O(l)$
(b) −3536.3 kJ/mol
(c) 1000 kJ
59. (b) 0.170 mol/L
60. (c) (i) 0.092 mol/(L·h)
(ii) 0.046 mol/(L·h)
(iii) 0.18 mol/(L·h)
(d) 0.14 mol/(L·h);
0.058 mol/(L·h)
61. 0.2 mol/(L·min)
62. (a) 2.5×10^{-2} mol/(L·s)
(b) 3.0×10^{-2} mol/(L·s)
63. (a) −5.0 mL/s
(b) 5.8 mL/s
(c) reactant: methane
product: oxygen
64. the first reaction
66. (a) 1.47 mL/s
(b) (i) faster
(ii) slower
(iii) slower
73. (a) (i) double
(ii) halved
(iii) quadruple
74. (a) 1
(b) either
75. 0.006 3 mol/(L·s)
76. 1.0×10^9 mol/(L·s)
77. (b) $[O_2(g)]$:
2×10^{-1} mol/(L·s);
$[CO_2(g)]$:
1×10^{-1} mol/(L·s)
78. (a) $2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$
(b) $N_2O_2(g)$; $N_2O(g)$
(c) $r = k[NO]^2$
79. (a) $r = k[NO_2Cl]$
(b) (ii), (iii)
(c) no
80. (a) 2
(b) 1
(c) 3
(d) yes
87. mechanism 1 or mechanism 3
88. step 2

Unit 4

Are You Ready?, pp. 416–417

1. (a) standard ambient temperature and pressure
(b) liquid, solid
(c) day 5
(d) evaporate
(e) yes
2. (a) $Zn(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
(b) 14 g
(c) 0.40 mol/L
3. (b) $H^+(aq)$, $NO_3^-(aq)$
7. 200 g
8. (a) $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$
$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$
$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(aq)$
(b) 16 mol/L
10. (a) 2.7×10^{-2} mol/L
(b) no
11. (a) balanced chemical:
$2\ NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$;
total ionic: $2\ Na^+(aq) + 2\ OH^-(aq) + 2\ H^+(aq) + SO_4^{2-}(aq) \rightarrow 2\ Na^+(aq) + SO_4^{2-}(aq) + H_2O(l)$;
net ionic: $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$
(b) double displacement or neutralization
(c) burette
(d) titration
(e) 60.0 mL
12. (a) $x = 2.6 \times 10^4$
(b) $x = 0.15$
(c) $x = -2.6$ and $x = 0.88$

7.1 Questions, p. 428

2. (c) dynamic
3. (a) $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$
4. $[SO_2] = 0.75$ mol/L;
$[O_2] = 1.1$ mol/L;
$[SO_3] = 1.8$ mol/L
5. $[PCl_5(g)] = 1.80$ mol/L;
$[Cl_2(g)] = 0.200$ mol/L
6. (a) no

7.2 Tutorial 1 Practice, p. 431

(a) $K = \dfrac{[CO(g)]^2[O_2(g)]}{[CO_2(g)]^2}$
(b) $K = \dfrac{[HCl(g)]^4[O_2(g)]}{[Cl_2(g)]^2[H_2O(g)]^2}$
(c) $K = \dfrac{[O_2(g)]^3}{[O_3(g)]^2}$
(d) $K = \dfrac{[N_2(g)]^2[H_2O(g)]^6}{[NH_3(g)]^4[O_2(g)]^3}$

7.2 Questions, p. 436

1. (a) $K = \dfrac{[SiCl_4(g)][H_2(g)]}{[SiH_2(g)][Cl_2(g)]^2}$
(b) $K = \dfrac{[PCl_3(g)]^2[Br_2(g)]^3}{[PBr_3(g)]^2[Cl_2(g)]^3}$
(c) $K = [H_2O(g)]$
(d) $K = [CO_2(g)]$
2. 1.6×10^{-5}
3. 8.0×10^9
5. (a) $CO(g) + 2\ H_2(g) \rightarrow CH_4O(l)$
(d) 160
6. (a) $C(s) + CO_2(g) \rightarrow 2\ CO(g)$
(b) $K = \dfrac{[CO(g)]^2}{[CO_2(g)]}$
(c) 1000 °C

7.4 Questions, p. 446

3. increase
4. (a) left, K decreases
(b) right, K increases
(c) exothermic

7.5 Tutorial 1 Practice, p. 452

2. Time 1: no, shift left
Time 2: yes, no shift
3. (a) $K = [O_2(g)]$
(b) no, shift left

7.5 Questions, p. 459

1. (a) $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$
(b) 0.500
(c) no; right
2. (a) no; left
(b) yes; no shift
(c) no; left
3. $[NO_2(g)] = 4.28 \times 10^{-1}$ mol/L;
$[N_2O_4(g)] = 2.11 \times 10^{-1}$ mol/L
4. 3.4
5. 5.6×10^{-2}
6. $[SO_2(g)] = 5.45 \times 10^{-1}$ mol/L;
$[NO_2(g)] = 5.45 \times 10^{-1}$ mol/L;
$[SO_3(g)] = 1.06$ mol/L;
$[NO(g)] = 1.06$ mol/L
7. 0.20 mol/L
8. 3.0×10^{-6} mol/L

7.6 Tutorial 1 Practice, p. 462

1. $K_{sp} = [Mg^{2+}(aq)][CO_3^{2-}(aq)]$
2. $K_{sp} = [Fe^{3+}(aq)][OH^-(aq)]^3$

7.6 Tutorial 2 Practice, p. 464

4. copper(I) chloride

7.6 Tutorial 3 Practice p. 468

1. yes
2. yes
3. no
4. yes

7.6 Questions, p. 471

3. (a) $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$
(b) $K_{sp} = [Ba^{2+}(aq)][SO_4^{2-}(aq)]$
4. AgBr(s)

5. 8.31×10^{-17}
6. 2.2×10^{-6}
7. yes, $Ca_3(PO_4)_2(s)$
8. yes
9. 1.7×10^{-6} mol/L
11. (a) $CaCl_2(aq)$ or $Sr(NO_3)_2(aq)$

Chapter 7 Self-Quiz, p. 479

1. (d)
2. (a)
3. (c)
4. (c)
5. (c)
6. (a)
7. (a)
8. (d)
9. F
10. F
11. F
12. T
13. F
14. T
15. F
16. F

Chapter 7 Review, pp. 480–485

1. (b)
2. (b)
3. (a)
4. (c)
5. (c)
6. (b)
7. (c)
8. T
9. F
10. F
11. T
12. F
13. T
14. T
15. F
16. T
17. (a) (iii)
    (b) (iv)
    (c) (ii)
    (d) (i)
18. Reaction A: products;
    Reaction B: reactants
20. $[N_2O(g)] = 1.00$ mol/L;
    $[O_2(g)] = 5.00 \times 10^{-1}$ mol/L;
    $[NO(g)] = 1.00$ mol/L
21. 9.7×10^{-1} mol/L
23. (a) $K = \dfrac{[O_2(g)]^3}{[O_3(g)]^2}$
    (b) $K = \dfrac{[H_2(g)]^4}{[H_2O(g)]^4}$
    (c) $K = [N_2(g)][H_2O(g)]^2$
    (d) $K = \dfrac{[NO(g)]^2[Cl_2(g)]}{[NOCl(g)]^2}$
24. (a) $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$
    (b) $2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$
    (c) $3\,H_2(g) + CO(g) \rightleftharpoons CH_4(g) + H_2O(g)$
    (d) $CS_2(g) + 4\,H_2(g) \rightleftharpoons CH_4(g) + 2\,H_2S(g)$
25. 1.02×10^1
26. 1.66×10^{-1} mol/L
27. 2.9×10^2
28. 4.30×10^{-1} mol/L
29. 7.57×10^{-1} mol/L
30. 2.7×10^{-3} mol/L
31. (a) $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + \text{energy}$
    (b) right
    (c) left
32. left
33. left
34. (a) $3\,Z \rightleftharpoons 2\,X + Y$
37. (a) reactants
    (b) products
    (c) products
    (d) reactants
39. no; right
40. 2.5×10^{-1}
41. 7.0×10^{-1}
42. $[CO_2(g)] = 4.42 \times 10^{-2}$ mol/L;
    $[H_2(g)] = 4.42 \times 10^{-2}$ mol/L;
    $[CO(g)] = 5.58 \times 10^{-2}$ mol/L;
    $[H_2O(g)] = 5.58 \times 10^{-2}$ mol/L
43. $[I_2(g)] = 4.5 \times 10^{-2}$ mol/L;
    $[Cl_2(g)] = 4.5 \times 10^{-2}$ mol/L;
    $[ICl(g)] = 4.1 \times 10^{-1}$ mol/L
44. 3.48×10^{-3} mol/L
45. $[H_2(g)] = 3.6 \times 10^{-17}$ mol/L;
    $[Cl_2(g)] = 3.6 \times 10^{-17}$ mol/L;
    $[HCl(g)] = 2.0$ mol/L
46. (a) $K_{sp} = [Zn^{2+}(aq)][OH^-(aq)]^2$
    (b) 2.7×10^{-6} mol/L
47. yes
49. no
50. lower
51. $\frac{2}{3}x$
52. (b) 5.5
56. invalid
57. K is small
58. 6.4×10^{-4} g

8.1 Questions, p. 494

2. (a) equal
   (b) greater
   (c) less
4. (a) $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
   (b) $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$
   (c) $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$
   (d) $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$
6. (a) acid: $HNO_2(aq)$; conjugate base: $NO_2{}^-(aq)$; base: $H_2O(l)$; conjugate acid: $H_3O^+(aq)$
   (b) acid: H_2O, conjugate base: OH^-;
       base: NH_3, conjugate acid: $NH_4{}^+$
7. (a) $H_3PO_4(aq) + NH_3(aq) \rightleftharpoons H_2PO_4^-(aq) + NH_4^+(aq)$;
       acid: $H_3PO_4(aq)$;
       base: $NH_3(aq)$;
       conjugate acid: $NH_4^+(aq)$;
       conjugate base: $H_2PO_4^-(aq)$;
       amphiprotic entity: $H_2PO_4{}^-(aq)$
   (b) $HCHO_2(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + CHO_2^-(aq)$;
       acid: $HCHO_2(aq)$;
       base: $CN^-(aq)$;
       conjugate acid: $HCN(aq)$;
       conjugate base: $CHO_2^-(aq)$
8. (a) $K_a = \dfrac{[H^+(aq)][F^-(aq)]}{[HF(aq)]}$
   (b) $K_a = \dfrac{[H^+(aq)][CO_3^{2-}(aq)]}{[HCO_3^-(aq)]}$
   (c) $K_a = \dfrac{[H^+(aq)][C_4H_7O_2^-(aq)]}{[HC_4H_7O_2(aq)]}$
9. (a) $HCHO_2(aq) + H_2O(l) \rightleftharpoons CHO_2^-(aq) + H_3O^+(aq)$;
       acid: $HCHO_2(aq)$;
       base: $H_2O(l)$;
       conjugate acid: H_3O^+;
       conjugate base: $CHO_2^-(aq)$
   (b) $C_{17}H_{23}NO_3(aq) + H_2O(l) \rightleftharpoons HC_{17}H_{23}NO_3^+(aq) + OH^-(aq)$;
       acid: $H_2O(l)$;
       base: $C_{17}H_{23}NO_3(aq)$;
       conjugate acid: $HC_{17}H_{23}NO_3{}^+(aq)$;
       conjugate base: $OH^-(aq)$
   (c) $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$;
       acid: $H_2O(l)$;
       base: $HCO_3{}^-(aq)$;
       conjugate acid: $H_2CO_3(aq)$;
       conjugate base: $OH^-(aq)$
10. disagree

8.2 Questions, p. 509

1. $H_2O < H_2S < HC_2H_3O_2 < H_3O^+ < HCl$
2. $Cl^- < NO_2{}^- < F^- < CN^-$
3. (a) 5.6×10^{-11}
   (b) 2.3×10^{-8}
   (c) 3.0×10^{-7}
   (d) 1.7×10^{-5}
4. (a) 5.9×10^{-6}
   (b) 5.9×10^{-9}
   (c) 1.3×10^{-8}
   (d) 1.0×10^{-11}
5. (a) $[H^+(aq)] = 1.0 \times 10^{-9}$ mol/L; basic
   (b) $[OH^-(aq)] = 1.00 \times 10^{-15}$ mol/L; acidic
   (c) $[OH^-(aq)] = 2.0 \times 10^{-8}$ mol/L; acidic
   (d) $[H^+(aq)] = 1.3 \times 10^{-4}$ mol/L; acidic
   (e) $[OH^-(aq)] = 1.4 \times 10^{-1}$ mol/L; basic
   (f) $[H^+(aq)] = 8.3 \times 10^{-9}$ mol/L; basic
6. (a) $[H^+(aq)] = 5.9 \times 10^{-4}$; $[OH^-(aq)] = 1.7 \times 10^{-11}$
   (b) $[H^+(aq)] = 3.8 \times 10^{-14}$; $[OH^-(aq)] = 2.6 \times 10^{-1}$
   (c) $[H^+(aq)] = 6.0 \times 10^{-3}$; $[OH^-(aq)] = 1.7 \times 10^{-12}$
   (d) $[H^+(aq)] = 1.1 \times 10^{-9}$; $[OH^-(aq)] = 8.9 \times 10^{-6}$
7. (a) 10.21
   (b) 0.85
   (c) 9.02
8. (a) 3.51
   (b) 7.00
   (c) 10.16
9. (a) $[H^+(aq)] = 1.0 \times 10^{-12}$ mol/L; $[OH^-(aq)] = 1.0 \times 10^{-2}$ mol/L
   (b) $[H^+(aq)] = 2.9 \times 10^{-2}$ mol/L; $[OH^-(aq)] = 3.5 \times 10^{-13}$ mol/L
   (c) $[H^+(aq)] = 1.0 \times 10^{-3}$ mol/L; $[OH^-(aq)] = 1.0 \times 10^{-11}$ mol/L
   (d) $[H^+(aq)] = 4.9 \times 10^{-10}$ mol/L; $[OH^-(aq)] = 2.0 \times 10^{-5}$ mol/L

8.4 Questions, p. 525

1. (a) 2.5×10^{-6} mol/L, 5.60
   (b) 1.3×10^{-2} mol/L, 1.89
   (c) 3.7×10^{-4} mol/L, 3.43
   (d) 5.3×10^{-3} mol/L, 2.28
2. (a) 0.50 %
   (b) 0.021 %
   (c) 4.0 %
3. (a) 7.9×10^{-5}
   (b) 6.3×10^{-4}
4. 0.42%
5. 480 mL
6. 1.42×10^{-4}
7. 2.61
8. sodium bicarbonate
9. (a) 6.3×10^{-5}
   (b) less
10. (a) 5.1 %

8.5 Questions, p. 530

1. (a) 11.47
   (b) 11.60
   (c) 11.49
   (d) 10.31
2. (a) 9.1×10^{-8}
   (b) 1.4×10^{-11}
   (c) 1.6×10^{-5}
   (d) 1.5×10^{-11}
3. (a) 9.94
   (b) 9.50
4. (a) $[H^+(aq)] = 1.1 \times 10^{-12}$ mol/L; $[OH^-(aq)] = 1.1 \times 10^{-2}$ mol/L; pH = 11.95
   (b) $[H^+(aq)] = 2.1 \times 10^{-10}$ mol/L; $[OH^-(aq)] = 4.7 \times 10^{-5}$ mol/L; pH = 9.67
5. [OH -(aq)] = 0.00080 mol/L; pOH = 3.10; pH = 10.90
6. (a) $[OH^-(aq)] = 0.45$ mol/L; pOH = 0.35; pH = 13.65
   (b) $[OH^-(aq)] = 3.75$ mol/L; pOH = −0.57; pH = 14.57
7. 2.2 mol/L
9. (a) $HCO_2^-(aq) + H_2O(l) \rightleftharpoons HCO_2H(aq) + OH^-(aq)$;
       $K_b = \dfrac{[HCO_2H(aq)][OH^-(aq)]}{[HCO_2^-(aq)]}$

    (b) $HCO_2H(aq) + H_2O \rightleftharpoons HCO_2^-(aq) + H_3O^+(aq)$; $K_a = \frac{[HCO_2^-(aq)][H^+(aq)]}{[HCO_2H(aq)]}$
10. (a) no
    (b) too dilute

8.6 Tutorial 3 Practice, p. 538

1. basic
2. acidic

8.6 Questions, p. 539

1. (a) neutral
    (b) basic
    (c) acidic
2. (a) greater
    (b) less
    (c) 7
4. (a) 4.88
    (b) 7.00
    (c) 7.00
    (d) 0.767
    (e) 9.60
    (f) 10.71
5. (a) 2.81
    (b) calcium oxide

8.7 Questions, p. 557

1. 1.447 mol/L
2. (a) 0.00375 mol; pH = 0.602
    (b) 0.00125 mol; pH = 2.903
    (c) 7.000
3. (a) 0.31 mol/L
    (b) 4.88
4. (a) 0.59 mol/L
    (b) 1.5×10^{-2} mol
    (c) 8.63
5. (a) 50.0 mL
    (b) 2.01
    (c) 8.49
6. 4.90
7. yes
8. (a) 5.00×10^{-3} mol; pH = 2.872
    (b) 7.2×10^{-3} mol; pH = 2.833
    (c) 1.73
    (d) amount: 5.00 mmol; volume: 50.00 mL

8.8 Questions, p. 567

2. weak acid or base and its salt
3. (a) $H_3PO_4 + H_2O(l) \rightarrow H_3O^+(aq) + H_2PO_4^-(aq)$; conjugate base: $H_2PO_4^-(aq)$
    (b) $H_2CO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HCO_3^-$; conjugate base: $HCO_3^-(aq)$
    (c) $HSO_3^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_3^{2-}(aq)$; conjugate base: $SO_3^{2-}(aq)$
    (d) $ClO^-(aq) + H_2O(l) \rightarrow HClO(aq) + OH^-(aq)$; conjugate acid: $HClO(aq)$
7. 4.02
8. 8.73

Chapter 8 Self-Quiz, p. 575

1. (a)
2. (c)
3. (c)
4. (b)
5. (b)
6. (d)
7. (c)
8. (d)
9. (d)
10. F
11. T
12. F
13. F
14. F
15. F
16. F
17. T
18. F
19. F
20. F
21. T

Chapter 8 Review, pp. 576–581

1. (b)
2. (b)
3. (a)
4. (b)
5. (d)
6. (c)
7. (c)
8. (d)
9. (c)
10. (b)
11. (d)
12. (b)
13. (b)
14. F
15. T
16. F
17. F
18. T
19. F
20. T
21. F
22. T
23. F
24. T
25. (a) (vi)
    (b) (vii)
    (c) (iii)
    (d) (xi)
    (e) (iv)
    (f) (ix)
    (g) (x)
    (h) (viii)
    (i) (i)
    (j) (ii)
    (k) (v)
27. (a) base
    (b) acid
    (c) base
    (d) acid
28. (a) acid: $H_3PO_4(aq)$; base: $H_2O(l)$; conjugate acid: $H_3O^+(aq)$; conjugate base: $H_2PO_4^-(aq)$
    (b) acid: $H_2O(l)$; base: $NH_3(aq)$; conjugate acid: $NH_4^+(aq)$; conjugate base: $OH^-(aq)$
    (c) acid: $HBr(aq)$; base: $H_2O(l)$; conjugate acid: $H_3O^+(aq)$; conjugate base: $Br^-(aq)$
    (d) acid: $H_2O(l)$; base: CN-(aq); conjugate acid: $HCN(aq)$; conjugate base: $OH(aq)$
29. (a) fluoride ion; F^-
    (b) hydronium ion; H_3O^+
    (c) hydroxide ion; OH^-
    (d) ammonium ion; NH_4^+
30. $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$; $HSO_4^-(aq) + HNO_3^+(aq) \rightleftharpoons H_2SO_4(aq) + NO_3^-(aq)$
31. (a) 2.4
    (b) 7
    (c) 5.14
    (d) 0.60
    (e) 13.65
    (f) 10.08
    (g) 11.8
32. pOH = 14.00 − pH
33. $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
34. 1.0×10^{-6} mol/L
36. large
37. 1.80×10^{-5}
39. 6.4
40. (a) $[OH^-(aq)] = 1.0 \times 10^{-7}$ mol/L; neutral
    (b) [OH-(aq)] = 1.2×10^{-9} mol/L; acidic
    (c) $[OH^-(aq)] = 1.0 \times 10^{-2}$ mol/L; basic
    (d) $[OH^-(aq)] = 1.9 \times 10^{-10}$ mol/L; acidic
41. 1×10^{-10} mol/L
42. (a) products
    (b) reactants
    (c) reactants
43. (a) endothermic
    (b) $[H^+(aq)] = 2.3 \times 10^{-7}$ mol/L; $[OH^-(aq)] = 2.3 \times 10^{-7}$ mol/L
45. 11 %
46. $[HCO_3^-(aq)] = 1.5 \times 10^{-4}$ mol/L; $[CO_3^{2-}(aq)] = 4.7 \times 10^{-11}$ mol/L; $[OH^-(aq)] = 4.7 \times 10^{-11}$ mol/L
47. 1.80×10^{-5}
48. 2.9
49. (a) neutral
    (b) acidic
    (c) basic
52. (a) colourless
    (b) green
    (c) yellow
53. 3.38
54. 8.4 mL
55. (a) $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
    (b) right
56. citrate ion
61. acid with K_a of 1×10^{-6}
66. hydrofluoric acid
67. $K_{a1} > K_{a2} > K_{a3}$
68. no
69. (a) stronger
72. (a) 2.72
    (b) 2.87
    (c) 3.02
    (d) 3.22
    (e) 8.78
    (f) 12.15
74. methyl yellow
76. no
77. (a) 7.93
78. (a) lungs: $Hb(O_2)_4$; cells: $HbH_4^{4+}(aq)$
79. (a) $[H^+(aq)] = 9.0 \times 10^{-7}$ mol/L; pH = 3.02
    (b) 0.079 %
80. (a) $3\ NO_2(g) + H_2O(l) \rightarrow NO(g) + 2\ HNO_3(aq)$; $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$; acidic solutions
81. (a) 200 mL
    (b) (i) $H_2A(aq)$, $H_2O(l)$
        (ii) $H_2A(aq)$, $HA^-(aq)$, $H_2O(l)$, $Na^+(aq)$
        (iii) $HA^-(aq)$, $H_2O(l)$, $Na^+(aq)$
        (iv) $HA^-(aq)$, $A^{2-}(aq)$, $H_2O(l)$, $Na^+(aq)$
        (v) $A^{2-}(aq)$, $H_2O(l)$, $Na^+(aq)$
        (vi) $A^{2-}(aq)$, $H_2O(l)$, $Na^+(aq)$, $OH^-(aq)$
    (c) $K_{a1} = 1.0 \times 10^{-4}$; $K_{a2} = 1.0 \times 10^{-8}$
89. no
90. no

Unit 4 Self-Quiz, pp. 584–585

1. (a)
2. (b)
3. (c)
4. (c)
5. (a)
6. (b)
7. (d)
8. (b)
9. (a)
10. (b)
11. (b)
12. (d)
13. (c)
14. (a)
15. (c)
16. (c)
17. (b)
18. (c)
19. T
20. T
21. F
22. T
23. F
24. F
25. F
26. T
27. T
28. F
29. F
30. T
31. F
32. F
33. T
34. T
35. F
36. T
37. F
38. T
39. F
40. T

Unit 4 Review, pp. 586–593

1. (d)
2. (c)
3. (a)
4. (b)
5. (b)
6. (d)
7. (b)
8. (b)
9. (c)
10. (d)
11. (a)
12. (c)
13. (c)
14. (c)
15. (c)
16. (b)
17. (a)
18. (a)
19. (d)
20. (b)
21. (a)
22. (d)
23. F
24. T
25. F
26. T
27. F
28. F
29. T
30. T

31. F
32. T
33. F
34. F
35. T
36. T
37. F
38. F
39. T
40. F
41. F
42. F
43. T
44. T
45. T
46. F
47. F
48. F
49. T
50. T
51. F
52. F
53. T
54. (a) (i)
(b) (iv)
(c) (iii)
(d) (ii)
58. no
59. $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
60. (a) $K = \frac{[NO]^2}{[N_2][O_2]}$
(b) $K = \frac{[NO_2]^2}{[N_2O_4]}$
(c) $K = \frac{[SiCl_4][H_2]^2}{[SiH_4][Cl_2]^2}$
(d) $K = \frac{[PCl_3]^2[Br_2]^3}{[PBr_3]^2[Cl_2]^3}$
61. 4 molecules H_2O;
2 molecules CO;
4 molecules H_2;
4 molecules CO_2
62. (a) left
(b) left
(c) right
(d) no shift
64. no; right
65. (a) $H_2SO_4(aq)$
(b) $H_2O(l)$
(c) $H_3O^+(aq)$
(d) $HSO_4^-(aq)$
66. (a) $HBr(aq) \rightleftharpoons H^+(aq) + Br^-(aq)$
(b) $HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$
(c) $HCHO_2 \rightleftharpoons H^+(aq) + CHO_2^-(aq)$
67. (a) $CH_3NH_3^+(aq)$, $CH_3NH_2(aq)$; $ClO^-(aq)$, $HClO(aq)$
(b) $HSO_4^-(aq)$, $SO_4^{2-}(aq)$; $HC_2O_4^-(aq)$, $C_2O_4^{2-}(aq)$
68. $C_6H_5NH_3^+(aq)$
69. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
70. pH + pOH = 14.00
71. 100 times
72. (a) 5.62
(b) 6.00
(c) 6.636
(d) 8.04
73. (a) $[H^+(aq)] = 7.9 \times 10^{-7}$ mol/L; $[OH^-(aq)] = 1.3 \times 10^{-8}$ mol/L
(b) $[H^+(aq)] = 9.8 \times 10^{-11}$ mol/L; $[OH^-(aq)] = 1.0 \times 10^{-4}$ mol/L
74. (a) $[H^+(aq)] = 1.0 \times 10^{-7}$ mol/L; neutral
(b) $[H^+(aq)] = 1.5 \times 10^{-6}$ mol/L; acidic
(c) $[OH^-(aq)] = 1.6 \times 10^{-3}$ mol/L; basic
75. (a) 12.25
(b) 0.59
(c) 4.00
76. 5.0×10^{-12} mol/L
77. 11.33
78. (a) 2.5×10^{-3} mol/L
(b) acid
79. 1.0×10^{-7} mol/L
80. $H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$; $HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$
81. basic; $K_2O(s) + H_2O(l) \rightleftharpoons 2\ K^+(aq) + 2\ OH^-(aq)$
82. (a) basic
(b) acidic
(c) neutral
(d) acidic
87. (a) $K = [CO_2(g)]$
88. (a) $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$
89. (a) yes
(b) right
(c) yes
(d) no
94. (a) (i) sulfurous acid; $H_2SO_3(aq)$
(ii) perchloric acid; $HClO_4(aq)$
(iii) phosphoric acid; $H_3PO_4(aq)$
95. products
101. (b) high temperatures
103. $[H_2(g)] = 0.141$ mol/L; $[Br_2(g)] = 0.021$ mol/L; $[HBr(g)] = 0.398$ mol/L
105. acid rain
106. 13.504
107. 1.89
108. 2.24
110. (a) 2.09
(b) yes
111. (a) 2.4
(b) 6.54
(c) 10.09
(d) 5.14
(e) 0.60
(f) 13.65
112. 10.7
115. 8.42
116. (b) yes
117. (a) 5.0
(b) 1×10^{-10}
118. 4.74
119. (a) 8.1
(b) pH 7.00: 0.083; pH 9.00: 8.30
(c) buffer pH: 8.08; pH after: 7.95
120. (a) 9.26
(b) 9.17
(c) drop from 7 to 2
121. highest: b; lowest: a

Unit 5

Are You Ready?, pp. 596–597

1. (a) atom
(b) ion
(c) ion
(d) atom
(e) atom
2. (a) loses 1 electron
(b) gains 1 electron
(c) gains 2 electrons
(d) loses 2 electrons
4. (a) gains electrons; negative
(b) lose electrons; positive
6. (a) acidic
(b) neutralization
7. (a) acid–base neutralization or double displacement
(b) single displacement
(c) complete combustion
(d) double displacement
9. (a) $4\ K(s) + O_2(g) \rightarrow 2\ K_2O(s)$
(b) $2\ Al(s) + 6\ HCl(aq) \rightarrow 3\ H_2(g) + 2\ AlCl_3(aq)$
(c) $C_2H_4(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 2\ H_2O(g)$
(d) $2\ Fe(NO_3)_3(aq) + 3\ K_2CO_3(aq) \rightarrow 6\ KNO_3(aq) + Fe_2(CO_3)_3(s)$
10. (a) reactants: hydrogen ions, hydroxide ions; products: water, ionic compound (a salt)
(b) $H_2SO_4(aq) + 2\ KOH(aq) \rightarrow K_2SO_4(aq) + 2\ H_2O(l)$
(c) 4 mol
11. (a) $Zn(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
(c) $Zn(s) + 2\ H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
12. (a) precipitate forms
(b) $Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$
13. (a) 1.0 mol/L $AgNO_3(aq)$
(b) $2\ AgNO_3(aq) + K_2CO_3(aq) \rightarrow Ag_2CO_3(s) + 2\ KNO_3(aq)$
(c) $2\ Ag^+(aq) + CO_3^{2-}(aq) \rightarrow Ag_2CO_3(s)$
16. (a) $2\ H_2O_2(aq) \xrightarrow{MnO_2} 2\ H_2O(l) + 2\ O_2(g)$

9.1 Tutorial 1 Practice, pp. 601–602

1. (a) oxidation: $Co(s) \rightarrow Co^{2+}(aq) + 2e^-$; reduction: $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$
(b) oxidation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$; reduction: $Ag^+(aq) + e^- \rightarrow Ag(s)$
(c) oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$; reduction: $I_2(s) + 2e^- \rightarrow 2I^-(aq)$
2. (a) oxidized: Co(s); reduced: $Sn^{2+}(aq)$
(b) oxidized: Pb(s); reduced: $Ag^+(aq)$
(c) oxidized: $Fe^{2+}(aq)$ reduced: $I_2(s)$
3. (a) oxidation: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$; reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; spectator ion: $Cl^-(aq)$
(b) oxidation: $Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + e^-$; reduction: $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$; spectator ion: $NO_3^-(aq)$
4. (a) $Cl_2(g) + 2KI(aq) \rightarrow I_2(s) + 2KCl(aq)$
(b) $Cl_2(g) + 2I^-(aq) \rightarrow I_2(s) + 2Cl^-(aq)$
(c) oxidation: $2I^-(aq) \rightarrow I_2(s) + 2e^-$; reduction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
(d) oxidized: chlorine; reduced: iodide

9.1 Tutorial 2 Practice, p. 604

1. (a) 0
(b) +4
(c) +1
(d) +5
(e) −3
2. (a) +2
(b) −4
(c) +4
(d) 0
3. (a) +4
(b) +4
(c) +6
(d) +7
4. (a) Na: +1; C: +4; O: −2
(b) K: +1; Cr: +6; O: −2
(c) H: +1; Cl: +7; O: −2
(d) Cu: +2; P: +5; O: −2

9.1 Tutorial 3 Practice, p. 606

1. (a) oxidized: Cu(s); reduced: $Ag^+(aq)$
(b) oxidized: Fe(s); reduced: $O_2(g)$
2. (a) oxidizing agent: HCl(aq); reducing agent: Zn(s)
(b) oxidizing agent: $SnO_2(s)$; reducing agent: C(s)
3. (a) H: +1; S: −2; O: 0; S: +4; O: −2; H: +1; oxidizing agent: $O_2(g)$; reducing agent: $H_2S(g)$
(b) C: −4; H: +1; O: 0; C: +4; O: −2; H: +1; oxidizing agent: $O_2(g)$; reducing agent: $CH_4(g)$

9.1 Questions, p. 607

2. (a) oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2\ e^-$;

reduction: $2 H^{+}(aq) + 2 e^{-} \rightarrow H_2(g)$
   (b) oxidation: $2 Al(s) \rightarrow 2 Al^{3+}(aq) + 6 e^{-}$; reduction: $2 Fe^{3+}(aq) + 6 e^{-} \rightarrow 2 Fe(l)$

3. (a) 0
   (b) +6
   (c) −2
   (d) −1
   (e) +2
   (f) −3
   (g) +3
   (h) +7
   (i) −2
   (j) +4
4. (a) oxidized: carbon; reduced: hydrogen
   (b) oxidized: iron; reduced: manganese
   (c) oxidized: copper; reduced: silver
5. (a) increases
   (b) decreases
6. (b) oxidizing agent: $SiCl_4$; reducing agent: Mg; reduced: Si; oxidized: Mg
   (c) oxidizing agent: H_2O; reducing agent: CO; reduced: H; oxidized: C
7. (a) reactants: $P = -3$; $H = +1$; $O = 0$; products: $P = +5$, $O = -2$; $H = +1$
   (b) reactants: $K = +1$; $Cl = +5$; $O = -2$; products: $K = +1$; $Cl = -1$, $O = 0$
   (c) reactants: $Pb = 0$, Pb in $PbO_2 = +4$; $O = -2$; $H = +1$; $S = +6$; products: $Pb = +2$; $S = +6$; $O = -2$; $H = +1$
9. (a) $CO_2 = +4$; $C_6H_{12}O_6 = 0$
10. $CO_2 = +4$; $CH_2O_2 = +2$; CH_2O: 0; CH_4O: −2; CH_4: −4

9.2 Tutorial 1 Practice, pp. 613–614

1. $3 PbO_2(s) + 4 NH_3(g) \rightarrow 2 N_2(g) + 6 H_2O(l) + 3 Pb(s)$
2. $2 H_2S(g) + O_2(g) \rightarrow 2 S(s) + 2 H_2O(l)$
3. (a) $2 MnO_4^{-}(aq) + Br^{-}(aq) + 2 H^{+}(aq) \rightarrow 2 MnO_2(s) + BrO_3^{-}(aq) + H_2O(l)$
   (b) $I_2(s) + 5 OCl^{-}(aq) + H_2O(l) \rightarrow 2 IO_3^{-}(aq) + 5 Cl^{-}(aq) + 2 H^{+}(aq)$
4. (a) $2 MnO_4^{-}(aq) + 3 SO_3^{2-}(aq) + H_2O(l) \rightarrow 3 SO_4^{2-}(aq) + 2 MnO_2(s) + 2 OH^{-}(aq)$
   (b) $S^{2-}(aq) + 4 I_2(s) + 8 OH^{-}(aq) \rightarrow SO_4^{2-}(aq) + 8 I^{-}(aq) + 4 H_2O(l)$
5. (a) iodine gains 5 electrons, sulfur loses 2 electrons.
   (b) $2 IO_3^{-}(aq) + 5 SO_3^{2-}(aq) + 2 H^{+}(aq) \rightarrow 5 SO_4^{2-}(aq) + I_2(s) + H_2O(l)$
6. (a) chromium loses 3 electrons, chlorine gains 6 electrons.
   (b) $2 Cr(OH)_3(s) + ClO_3^{-}(aq) + 4OH^{-}(aq) \rightarrow 2CrO_4^{2-}(aq) + Cl^{-}(aq) + 5H_2O(l)$

9.2 Tutorial 2 Practice, p. 616

1. (a) $Zn(s) + 2 H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
   (b) $2 HNO_3(aq) + Cu(s) + 2 H^{+}(aq) \rightarrow 2 NO_2(g) + Cu^{2+}(aq) + 2 H_2O(l)$
2. (a) oxidation: $CH_3OH(aq) + 8 OH^{-}(aq) \rightarrow CO_3^{2-}(aq) + 4 e^{-} + 6 H_2O(l)$; reduction: $MnO_4^{-}(aq) + e^{-} \rightarrow MnO_4^{2-}(aq)$
   (b) $CH_3OH(aq) + 4 MnO_4^{-}(aq) + 8 OH^{-}(aq) \rightarrow CO_3^{2-}(aq) + 4 MnO_4^{2-}(aq) + 6 H_2O(l)$

9.2 Questions, p. 617

1. (a) oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2 e^{-}$; reduction: $2 H^{+}(aq) + 2 e^{-} \rightarrow H_2(g)$
   (b) $Mg(s) + 2 HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$
   (c) 2
2. (a) oxidation: $Cu(s) \rightarrow Cu^{+}(aq) + 2 e^{-}$; reduction: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$
   (b) oxidation: $2 Cr^{3+}(aq) + 7 H_2O(l) \rightarrow Cr_2O_7^{2-}(aq) + 14 H^{+}(aq) + 6 e^{-}$; reduction: $Cl_2(g) + 2e^{-} \rightarrow 2 Cl^{-}(aq)$
   (c) oxidation: $Ca(s) \rightarrow Ca^{2+}(aq) + 2 e^{-}$; reduction: $2 H^{+}(aq) + 2 e^{-} \rightarrow H_2(g)$
3. (a) $3 H_2O(l) + 5 ClO_3^{-}(aq) + 3 I_2(aq) \rightarrow 5 Cl^{-}(aq) + 6 IO_3^{-}(aq) + 6 H^{+}(aq)$
   (b) $Cr_2O_7^{2-}(aq) + 6 Cl^{-}(aq) + 14 H^{+}(aq) \rightarrow 2 Cr^{3+}(aq) + 3 Cl_2(aq) + 7 H_2O(l)$
4. (a) $Pb(OH)_4^{2-}(aq) + ClO^{-}(aq) \rightarrow PbO_2(s) + Cl^{-}(aq) + 2 OH^{-}(aq) + H_2O(l)$
   (b) $5 H_2O(l) + NO_2^{-}(aq) + 2 Al(s) + OH^{-}(aq) \rightarrow NH_3(aq) + 2 Al(OH)_4^{-}(aq)$
5. (a) 5 electrons
   (b) 2 electrons
   (c) $16 H^{+}(aq) + 2 MnO_4^{-}(aq) + 5 C_2O_4^{2-}(aq) \rightarrow 2 Mn^{2+}(aq) + 10 CO_2(aq) + 8 H_2O(l)$
6. (a) $4 Ag(s) + 8 CN^{-}(aq) + O_2(g) + 2 H_2O(l) \rightarrow 4 Ag(CN)_2^{-}(aq) + 4 OH^{-}(aq)$
7. (a) $16 H^{+}(aq) + 2Cr_2O_7^{2-}(aq) + C_2H_5OH(l) \rightarrow 4 Cr^{3+}(aq) + 2 CO_2(g) + 11 H_2O(l)$
8. (a) oxidation: $H_2O_2(aq) \rightarrow O_2(g) + 2 H^{+}(aq) + 2 e^{-}$; reduction: $5 e^{-} + 8 H^{+}(aq) + MnO_4^{-}(aq) \rightarrow Mn^{2+}(aq) + 4 H_2O(l)$
   (b) $6 H^{+}(aq) + 2 MnO_4^{-}(aq) + 5 H_2O_2(aq) \rightarrow 2 Mn^{2+}(aq) + 5 O_2(g) + 8 H_2O(l)$
9. $2 H^{+}(aq) + 2 NO_3^{-}(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2 NO_2(g) + H_2O(l)$
10. (a) $3 Cl_2(g) + 6 OH^{-}(aq) \rightarrow 5 Cl^{-}(aq) + ClO_3^{-}(aq) + H_2O(l)$
    (b) Cl_2: $Cl = 0$; OH^{-}: $O = -2$, $H = +1$; $Cl^{-} = -1$; ClO_3^{-}: $Cl = +5$, $O = -2$; H_2O: $H = +1$, $O = -2$

9.3 Tutorial 1 Practice, p. 622

1. (a) oxidation: $Co(s) \rightarrow Co^{2+}(aq) + 2 e^{-}$, reduction: $Cu^{2+}(aq) + 2 e^{-} \rightarrow Cu(s)$; spontaneous
   (b) oxidation: $2 I^{-}(aq) \rightarrow I_2(s) + 2 e^{-}$, reduction: $Br_2(l) + 2 e^{-} \rightarrow 2 Br^{-}(aq)$; spontaneous
   (c) oxidation: $Ni(s) \rightarrow Ni^{2+}(aq) + 2 e^{-}$, reduction: $Zn^{2+}(aq) + 2 e^{-} \rightarrow Zn(s)$; not spontaneous
2. not spontaneous
3. yes, oxidation: $Ca(s) \rightarrow Ca^{2+}(aq) + 2 e^{-}$, reduction: $2 H_2O(l) + 2 e^{-} \rightarrow H_2(g) + 2 OH^{-}(aq)$; spontaneous; $Ca(s) + 2 H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$
4. $MnO_4^{-}(aq) + 8 H^{+}(aq) + 5 Cr^{2+}(aq) \rightarrow 5 Cr^{3+}(aq) + Mn^{2+}(aq) + 4 H_2O(l)$

9.3 Questions, p. 623

1. $Au^{3+}(aq) > Hg^{2+}(aq) > Cu^{2+}(aq) > Sn^{2+}(aq)$
3. (a), (b)
4. (a) $Cu^{2+}(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + Cu(s)$
   (b) yes
5. (a) $H^{+}(aq)$, $K^{+}(aq)$, $H_2O(l)$, $Fe^{2+}(aq)$, $SO_4^{2-}(aq)$, $MnO_4^{-}(aq)$; strongest: $MnO_4^{-}(aq)$
   (b) $H_2O(l)$, $Fe^{2+}(aq)$; strongest: $Fe^{2+}(aq)$
6. (a) oxidation: $Au(s) \rightarrow Au^{3+}(aq) + 3 e^{-}$; reduction: $NO_3^{-}(aq) + 2 H^{+}(aq) + e^{-} \rightarrow NO_2(g) + H_2O(l)$
   (b) no
7. (a) Cu: Cu^{+}, Au^{3+}; Au: none; Zn: Cu^{+}, Au^{3+}, Co^{2+}; Co: Cu^{+}, Au^{3+}
   (b) oxidizing agent: Au^{3+}; reducing agent: Zn(s)
8. (a) $Cu^{2+}(aq)$, $Pb^{2+}(aq)$, $Fe^{2+}(aq)$, $Ba^{2+}(aq)$
   (b) $Cu^{2+}(aq) + Pb(s) \rightarrow 2 Cu(s) + Pb^{2+}(aq)$

Chapter 9 Self-Quiz, p. 627

1. (b)
2. (c)
3. (d)
4. (b)
5. (c)
6. (a)
7. (b)
8. (c)
9. F
10. T
11. F
12. T
13. F
14. T
15. F
16. F
17. F

Chapter 9 Review, pp. 628–633

1. (a)
2. (c)
3. (a)
4. (c)
5. (b)
6. (d)
7. (a)
8. (b)
9. (a)
10. F
11. T
12. F
13. T
14. T
15. F
16. F
17. F
18. T
19. (a) (iii)
    (b) (ii)
    (c) (v)
    (d) (vii)
    (e) (i)
    (f) (vi)
    (g) (iv)
20. (a) oxidation: $Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + e^{-}$; reduction: $Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$
    (b) oxidation: $Fe(s) \rightarrow Fe^{3+}(aq) + 3e^{-}$; reduction: $Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$
    (c) oxidation: $2 I^{-}(aq) \rightarrow I_2(s) + 2e^{-}$; reduction: $Br_2(l) + 2e^{-} \rightarrow 2 Br^{-}(aq)$
21. (a) −1
    (b) −2
    (c) −3
    (d) +3
    (e) +4

22. (a) N: + 3; Cl: −1
  (b) Se: + 4; O: −2
  (c) Si: + 4; S: −2
  (d) S: + 6; F: −1
  (e) S: + 2; Cl: −1

23. (a) O: −2; H: +1
  (b) Cl: + 5; O: −2
  (c) Cl: + 3; O: −2
  (d) S: + 6; O: −2
  (e) S: +7; O: −2
  (f) C: 0; H: +1: O: −2

24. a, d, e

25. (a) oxidation: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e^-$; reduction: $Au^{3+}(aq) + 3e^- \rightarrow Au(s)$
  (b) $6\ H_2O(l) + 4Au^{3+}(aq) \rightarrow 3\ O_2(g) + 4Au(s) + 12\ H^+(aq)$

26. (a) oxidation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2\ e^-$; reduction: $Cu\ ^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$
  (b) oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$; reduction: $2\ HNO_2\ (aq) + 4\ H^+(aq) + 4\ e^- \rightarrow N_2O(g) + 3\ H_2O(l)$
  (c) oxidation: : $Co(s) \rightarrow Co^{2+}(aq) + 2\ e^-$; reduction: $O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4OH^-(aq)$
  (d) oxidation: $Ag(s) \rightarrow Ag^+(aq) + e^-$; reduction: $Br_2(l) + 2e^- \rightarrow 2\ Br^-(aq)$
  (e) oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3\ e^-$; reduction: $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
  (f) oxidation: $H_2S(aq) \rightarrow S(s) + 2H^+(aq) + 2e^-$; reduction: $Na^+(aq) + e^- \rightarrow Na(s)$
  (g) oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e$; reduction: $MnO_4{}^-(aq) + 2\ H_2O(l) + 3\ e^- \rightarrow MnO_2(s) + 4OH^-(aq)$

27. (a) 2 electrons
  (b) 1 electron
  (c) $Ni(s) + Cl_2(g) \rightarrow NiCl_2(g)$

28. oxidation: $Ca(s) \rightarrow Ca^{2+}(aq) + 2\ e^-$; reduction: $2\ H_2O(l) + 2\ e^- \rightarrow 2\ OH^-\ (aq) + H_2(g)$; net ionic: $Ca(s) + 2\ H_2O(l) \rightarrow Ca^{2+}(aq) + 2\ OH^-(aq) + H_2(g)$

29. $K^+(aq) < H_2O(l) < Cd^{2+}(aq) < I_2(s) < IO_3{}^-(aq) < AuCl_4{}^-(aq)$

30. $F^-(aq) < I_2(aq) < H_2O(l) < Cu^+(aq) < K(s)$

31. (a) ii, iii
  (b) (ii) $Cr^{2+}(aq) + 2\ K(s) \rightarrow Cr(s) + 2\ K^+(aq)$
    (iii) $Pb^{2+}(aq) + Fe(s) \rightarrow Pb(s) + Fe^{2+}(aq)$

32. Li(s), K(s), Cs(s), Ba(s), Ca(s), Na(s), La(s), Mg(s)

34. yes

35. $HNO_3 > NO_2 > NaNO_2 > N_2O > NH_4Cl$

38. no

39. no; $2\ AgNO_3(aq) + Cu(s) \rightarrow 2\ Ag(s) + Cu(NO_3)_2(aq)$

40. (a) $NH_3(g) + O_2(g) \rightarrow NO_2(g) + H_2O(g)$
  (b) in reactants, N: −3; H: + 1; O: 0; in products: N: + 4; H: +1; O: −2
  (c) oxidation: $NH_3 + 2\ H_2O \rightarrow NO_2 + 7\ H^+ + 7\ e^-$; reduction: $O_2 + 4\ H^+ + 4e^- \rightarrow 2\ H_2O$
  (d) $4\ NH_3(g) + 7\ O_2(g) \rightarrow 4\ NO_2(g) + 6H_2O(g)$

42. (a) oxidation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2\ e$; reduction: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$; balanced net ionic: $Cu^{2+}(aq) + Pb(s) \rightarrow Pb^{2+}(aq) + Cu(s)$
  (b) oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$; reduction: $2\ HNO_2\ (aq) + 4\ H^+(aq) + 4e^- \rightarrow N_2O(g) + 3\ H_2O(l)$; balanced net ionic: $2\ HNO_2\ (aq) + 4\ H^+(aq) + 2\ Fe(s) \rightarrow 2\ Fe^{2+}(aq) + N_2O(g) + 3\ H_2O(l)$
  (c) oxidation: $Co(s) \rightarrow Co^{2+}(aq) + 2\ e^-$; reduction: $O_2(g) + 2\ H_2O(l) + 4e^- \rightarrow 4\ OH^-(aq)$; balanced net ionic: $O_2(g) + 2\ H_2O(l) + 2\ Co(s) \rightarrow 2\ Co^{2+}(aq) + 4\ OH^-(aq)$

43. (b) $2\ NO_3{}^-(aq) + 3\ AsO_3{}^{3-}(aq) + H_2O(l) \rightarrow 2\ NO(g) + 3\ AsO_4{}^{3-}(aq) + 2\ OH^-(aq)$

44. (a) $3\ Ni^{2+}(aq) + 2\ Al(s) \rightarrow 2\ Al^{3+}(aq) + 3\ Ni(s)$
  (b) $2\ MnO_4{}^-(aq) + 3\ Ni(s) + 8\ H^+ \rightarrow 2\ MnO_2(s) + 3\ Ni^{2+}(aq) + 4\ H_2O(l)$
  (c) $SO_4{}^{2-}(aq) + Sn^{2+}(aq) + 2H^+(aq) \rightarrow SO_3{}^{2-}(aq) + Sn^{4+}(aq) + H_2O(l)$
  (d) $Br_2(l) + 2\ Ag(s) \rightarrow 2\ Br\ ^-(aq) + 2\ Ag^+(aq)$
  (e) $3\ Fe^{2+}(aq) + 2\ Al(s) \rightarrow 2\ Al^{3+}(aq) + 3\ Fe(s)$
  (f) $H_2S(aq) + 2\ Na^+(aq) \rightarrow S(s) + 2\ Na(s) + 2\ H^+(aq)$
  (g) $2\ MnO_4{}^-(aq) + 3\ Zn(s) + 4\ H_2O(l) \rightarrow 2\ MnO_2(s) + 3\ Zn^{2+}(aq) + 8\ OH^-(aq)$

45. (a) $2\ MnO_4{}^-(aq) + 5\ C_2O_4{}^{2-}(aq) + 16\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(g) + 8\ H_2O(l)$
  (b) $2\ MnO_4{}^-(aq) + 3CN^-(aq) + H_2O(l) \rightarrow 2\ MnO_2(s) + 3\ OCN^-(aq) + 2\ OH^-(aq)$
  (c) $Pb(s) + PbO_2(s) + 4\ H^+(aq) \rightarrow 2\ Pb^{2+}(aq) + 2\ H_2O(l)$

46. yes

47. Ca(s) > Al(s) > Cr(s) > Cd(s) > Pb(s) > Cu(s)

50. (a) reactants: Fe = 0, O = 0; products: Fe = +3, O = −2; electron transfer: 12; oxidizing agent: O_2; reducing agent: Fe
  (b) reactants: Ni = +2, O = −2, H = 0; products: Ni = 0, H = +1, O = −2; electron transfer: 2; oxidizing agent: NiO; reducing agent: H_2
  (c) reactants: Fe = +3, O = −2, C = +2, O = −2; products: Fe = 0, C = +4, C = −2; electron transfer: 6; oxidizing agent: Fe_2O_3; reducing agent: CO
  (d) reactants: Cu = 0, H = +1, N = +5, O = −2; products: Cu = +2, N = +5, O = −2, H = +1, N = +4; electron transfer: 2; oxidizing agent: HNO_3; reducing agent: Cu

52. yes

53. (a) oxidized: $Cr^{2+}(aq)$ by 1 electron; reduced: Ag by 1 electron
  (b) oxidized: Al(s) by 3 electrons; reduced: $Ni^{2+}(aq)$ by 2 electrons
  (c) oxidized: Ni(s) by 2 electrons; reduced: Mn by 3 electrons
  (d) oxidized: $Sn^{2+}(aq)$ by 2 electrons; reduced: S by 2 electrons

54. (a) oxidation: $Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$; reduction: $2\ H_2O(l) + 2e^- \rightarrow H_2(g) + 2\ OH^-(aq)$
  (b) yes; $Ca(s) + 2H_2O(l) \rightarrow H_2(g) + 2\ OH^-(aq)$
  (c) bubbles
  (d) pH test

55. (b) (i) $2\ AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2\ Ag(s)$
    (ii) $2\ HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$
    (iii) $Fe_3O_4(s) + 4\ CO(g) \rightarrow 4\ CO_2(g) + 3\ Fe(s)$
    (iv) $8\ HNO_3(aq) + 3\ Cu(s) \rightarrow 2\ NO(g) + 3\ Cu(NO_3)_2(aq) + 4\ H_2O(l)$

56. (a) first equation: reactants, H: +1, O: −2, Cl: +1, N: −3, H: +1; products: H: +1, O: −2, Cl: +1, N: −3; $4HOCl(aq) + 2NH_3(aq) \rightarrow 2\ NHCl_2(g) + 4\ H_2O(l)$; second equation: reactants, H: +1, O: −2, Cl: +1, N: −3, products:, O: −2, Cl: −1, N: + 3, H: +1; $3\ HOCl(aq) + NH_3(aq) \rightarrow NCl_3(aq) + 3\ H_2O(l)$

57. (a) (i) yes
    (ii) yes
    (iii) no
    (iv) yes
  (c) (i) $Fe_2(SO_4)_3(aq) + Cu(s) \rightarrow 2FeSO_4(aq) + CuSO_4(aq)$
    (ii) $CuCl_2(aq) + Fe(s) \rightarrow FeCl_2(aq) + Cu(s)$
    (iv) $2\ AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2\ Ag(s)$

58. (a) Metal X
  (b) Ag^+

59. (a) $NO_3{}^-$: +5; $NO_2{}^-$: +3; N_2: 0; NO: +2; NO_2: +4; HNO_3: +5; HNO_2: +3
  (b) oxidized
  (c) reaction with oxygen: $O_2(g)$ oxidizing agent; reaction with water: $NO_2(g)$ reducing agent and oxidizing agent

62. no

63. (a) Ca(s)

64. no

74. (a) (i) no
    (ii) yes
  (b) (i) $Fe_2O_3(s) + 3\ H_2S(g) \xrightarrow{H_2O} Fe_2S_3(s) + 3\ H_2O(l)$
    (ii) $2\ Fe_2S_3(s) + 3\ O_2(g) \xrightarrow{H_2O} 2\ Fe_2O_3(s) + 6\ S(s)$

10.1 Questions, p. 641

4. (d) oxidizing agent: nickel(II) ions; reducing agent: magnesium metal
  (e) reduction: $Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$; oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2\ e^-$
  (f) $Ni^{2+}(aq) + Mg(s) \rightarrow Ni(s) + Mg^{2+}(aq)$

5. (a) (i) oxidizing agent: copper(I) ions; reducing agent: zinc metal
    (ii) cathode: $Cu^+(aq) + e^- \rightarrow Cu(s)$; anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

(iii) $Mg(s) + 2\,Cu^{+}(aq) \rightarrow Mg^{2+}(aq) + 2\,Cu(s)$
(b) (i) reducing agent: iron metal; oxidizing agent: silver ions
(ii) anode: $Fe(s) \rightarrow Fe^{2+} + 2\,e^{-}$; cathode: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$
(iii) $Fe(s) + 2\,Ag^{+}(aq) \rightarrow Fe^{2+}(aq) + 2\,Ag(s)$
6. (b) $Fe^{2+}(aq) + 2\,e^{-} \rightarrow Fe(s)$; $Mg(s) \rightarrow Mg^{2+}(aq) + 2\,e^{-}$
(c) $Fe^{2+}(aq) + Mg(s) \rightarrow Fe(s) + Mg^{2+}(aq)$
7. (b) $Mg(s) \rightarrow Mg^{2+}(aq) + 2\,e^{-}$; $2\,H_2O(l) + 2\,e^{-} \rightarrow H_2(g) + 2\,OH^{-}(aq)$; $Mg(s) + 2\,H_2O(l) \rightarrow Mg^{2+}(aq) + 2\,OH^{-}(aq)$

10.2 Questions, p. 648

4. $Cl_2(g) + 2Br^{-}(aq) \rightarrow 2\,Cl^{-}(aq) + Br_2(g)$; $\Delta E° = 0.27$ V
5. (a) anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}$; cathode: $Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$; net ionic equation: $Mg(s) + 2\,Fe^{+}(aq) \rightarrow Mg^{2+}(aq) + 2\,Fe^{2+}(aq)$
(b) $\Delta E° = 3.14$ V
6. −0.23 V; Ni
7. (a) $Cr_2O_7^{2-}$: 1.33 V; Pd^{2+}: 1.05 V; Tl^{+}: −0.24 V; Ti^{+}: −1.53 V
8. (a) $3\,Mg(s) + 2\,Au^{3+}(aq) \rightarrow 3\,Mg^{2+}(aq) + 2\,Au(s)$; $\Delta E° = 3.87$ V
(b) $2\,Cu^{+}(aq) + Mg(s) \rightarrow 2\,Cu(s) + Mg^{2+}(aq)$; $\Delta E° = 2.89$ V
(c) $Zn(s) + Sn^{2+}(aq) \rightarrow Zn^{2+}(aq) + Sn(s)$; $\Delta E° = 0.62$ V

10.3 Questions, p. 654

3. 1.2 V

10.6 Questions, p. 662

1. (a) zinc
3. (b) magnesium > zinc > iron > gold

10.7 Questions, p. 670

3. (a) cathode: $Ni^{2+} + 2e^{-} \rightarrow Ni(s)$; anode: $2\,Br^{-} \rightarrow Br_2 + 2\,e^{-}$
(b) cathode: $Al^{3+} + 3\,e^{-} \rightarrow Al(s)$; anode: $6F^{-} \rightarrow 3\,F_2 + 6\,e^{-}$;
(c) cathode: $Mn^{2+} + 2e^{-} \rightarrow Mn(s)$; anode: $2\,I^{-} \rightarrow I_2 + 2e^{-}$
7. cathode: $Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$; anode: $2\,Cl^{-}(aq) \rightarrow Cl_2(g) + 2e^{-}$; net ionic: $Sn^{2+}(aq) + 2\,Cl^{-}(aq) \rightarrow Cl_2(g) + Sn(s)$
9. (a) $6\,Al_2OF_6^{2-}(l) + 12\,F^{-}(l) + 3\,C(s) \rightarrow 4\,Al(s) + 8\,AlF_6^{3-}(l) + 3\,CO_2(g)$

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1. (a)
2. (d)
3. (b)
4. (a)
5. (a)
6. (c)
7. (b)
8. (b)
9. (d)
10. T
11. F
12. F
13. F
14. T
15. F
16. T
17. F

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1. (b)
2. (b)
3. (d)
4. (c)
5. (a)
6. (d)
7. F
8. T
9. T
10. F
11. F
12. F
13. F
14. F
15. T
16. (a) (v)
(b) (iii)
(c) (vi)
(d) (viii)
(e) (iv)
(f) (i)
(g) (vii)
(h) (ii)
17. (b) $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$; $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$
(c) $Cu(s) + 2\,Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$
(d) $Cu(s)|Cu^{2+}(aq)\,||\,Ag^{+}(aq)\,|\,Ag(s)$
18. (a) anode
(b) negative
19. oxidizing agent: $Cu^{+}(aq)$; reducing agent: $Zn(s)$
21. (a) $Al(s)\,|\,Al^{3+}(aq)\,||\,Fe^{2+}(aq)\,|\,Fe(s)$
(b) $Pt(s)\,|\,Cr^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Pt(s)$
22. (a) no
(b) yes
(c) no
23. (a) hydrogen fuel cell
30. (a) no
(b) yes
(c) yes
33. anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$; cathode: $2\,H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$
34. (a) $Cd^{2+}(aq) + Zn(s) \rightarrow Cd(s) + Zn^{2+}(aq)$ $\Delta E°_{r\,(cell)} = 0.36$ V
(b) $3\,Ag^{+}(aq) + Al(s) \rightarrow 3\,Ag(s) + Al^{3+}(aq)$ $\Delta E°_{r\,(cell)} = 2.46$ V
(c) $3\,Fe^{2+}(aq) + 2\,Al(s) \rightarrow 3\,Fe(s) + 2\,Al^{3+}(aq)$ $\Delta E°_{r\,(cell)} = 1.22$ V
35. (a) $2\,Al(s) + 6\,H^{+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,H_2(g)$; $\Delta E°_{r\,(cell)} = 1.66$ V
(b) $2\,Cr^{3+}(aq) + H_2O(l) + 3\,H_2O_2(aq) \rightarrow Cr_2O_7^{2-}(aq) + 8\,H^{+}(aq)$ $\Delta E°_{r(cell)} = 0.45$ V
36. (a) $\Delta E°_{r(cell)} = -0.47$V; not spontaneous
(b) $\Delta E°_{r(cell)} = +0.70$ V; spontaneous
(c) $\Delta E°_{r(cell)} = +0.37$ V; spontaneous
37. (a) $16\,H^{+}(aq) + 2\,MnO_4^{-}(aq) + 10\,I^{-}(aq) \rightarrow 5\,I_2(s) + 2\,Mn^{2+}(aq) + 8\,H_2O(l)$; $\Delta E°_{r(cell)} = 0.97$ V; spontaneous
(b) $16\,H^{+}(aq) + 2\,MnO_4^{-}(aq) + 10\,F^{-}(aq) \rightarrow 5\,F_2(g) + 2\,Mn^{2+}(aq) + 8\,H_2O(l)$; $\Delta E°_{r(cell)} = -1.36$ V; not spontaneous
38. (a) potassium hydroxide
39. (a) oxygen and water
42. (a) anode: $2\,F^{-}(l) \rightarrow F_2(g) + 2\,e^{-}$; cathode: $2\,K^{+}(l) + 2\,e^{-} \rightarrow 2\,K(l)$
(b) anode: $2\,Cl^{-}(l) \rightarrow Cl_2(g) + 2\,e^{-}$; cathode: $Cu^{2+}(l) + 2\,e^{-} \rightarrow Cu(l)$
(c) anode: $2\,I^{-}(l) \rightarrow I_2(l) + 2\,e^{-}$; cathode: $Mg^{2+}(l) + 2e^{-} \rightarrow Mg(l)$
43. (b) $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $E°_{r(cell)} = 0.34$ V $Cr(s) \rightarrow Cr^{2+}(aq) + 2e^{-}$ $E°_{r(cell)} = 0.91$ V net: $Cu^{2+}(aq) + Cr(s) \rightarrow Cu(s) + Cr^{2+}(aq)$ $\Delta E°_{r(cell)} = 1.25$ V
45. (a) $Ag^{+}(aq) + Fe^{2+}(aq) \rightarrow Ag(s) + Fe^{3+}(aq)$ $\Delta E°_{r(cell)} = 0.03$ V
(b) $Au^{3+}(aq) + 3\,Cu^{+}(aq) \rightarrow 3\,Cu^{2+}(aq) + Au(s)$ $\Delta E°_{r\,(cell)} = 1.34$ V
(c) $2\,VO^{2+}(aq) + 4\,H^{+}(aq) + Cd(s) \rightarrow Cd^{2+}(aq) + 2\,VO^{2+}(aq) + 2\,H_2O(l)$ $\Delta E°_{r\,(cell)} = 1.40$ V
46. (a) $2\,IO_3^{-}(aq) + 10\,Fe^{2+}(aq) + 12\,H^{+}(aq) \rightarrow 10\,Fe^{3+}(aq) + I_2(aq) + 6\,H_2O(l)$; $\Delta E°_{r(cell)} = 0.43$ V
(b) $Zn(s) + 2\,Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2\,Ag(s)$; $\Delta E°_{r(cell)} = 1.56\ V$
47. (a) aluminum
(b) $3Cu^{2+}(aq) + 2Al(s) \rightarrow 3\,Cu(s) + 2\,Al^{3+}(aq)$
48. (a) $Ag^{+}(aq)$
(b) $Zn(s)$
(c) $Pb(s)$, $Zn(s)$
(d) $Ag^{+}(aq)$, $Zn^{2+}(aq)$
49. (a) $Br_2(l)$
(b) $Ca(s)$
(c) $Br^{-}(aq)$, $H_2(g)$, $Ca(s)$, $Cd(s)$
(d) $Br_2(l)$, $H^{+}(aq)$
50. (c) $Ag(s)$, $Cl^{-}(aq)$
51. (a) $\Delta E°_{r\,(cell)} = 0.10$ V; anode
(b) $\Delta E°_{r\,(cell)} = 0.53$ V; anode
(c) $\Delta E°_{r\,(cell)} = 0.02$ V; cathode
(d) $\Delta E°_{r\,(cell)} = 1.42$ V; cathode
(e) $\Delta E°_{r\,(cell)} = 0.01$ V; cathode
52. (a) 0.41 V
(b) no
59. $Au(s) + HNO_3(aq) + 4\,HCl(aq) \rightarrow AuCl_4^{-}(aq) + NO(g) + 2\,H_2O(l) + H^{+}(aq)$
60. (a) anode: $2\,Br^{-}(aq) \rightarrow Br_2(g) + 2e^{-}$; cathode: $Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$; yes
(b) anode: $2\,H_2O(l) \rightarrow O_2(g) + 4\,H^{+}(aq) + 4\,e^{-}$; cathode: $2\,H_2O(l) + 2\,e^{-} \rightarrow H_2 + 2\,OH^{-}(aq)$; no
(c) anode: $2\,I^{-}(aq) \rightarrow I_2(s) + 2\,e^{-}$; cathode: $2\,H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2\,OH^{-}(aq)$; no
61. no

Unit 5 Self-Quiz, pp. 686–687

1. (a)
2. (c)
3. (d)
4. (c)
5. (a)
6. (a)
7. (c)
8. (d)
9. (c)
10. (b)
11. (d)
12. (c)
13. (b)
14. (c)
15. (b)
16. (a)
17. (a)
18. (a)
19. (c)
20. F
21. F
22. T
23. T
24. T
25. T
26. F
27. T
28. T
29. F
30. T
31. F
32. F
33. T
34. T
35. F
36. F
37. F
38. F

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1. (a)
2. (a)
3. (a)
4. (c)
5. (a)
6. (d)
7. (d)
8. (b)
9. (c)
10. (d)
11. (a)
12. (c)
13. (b)
14. (d)
15. (a)
16. (c)
17. (b)
18. (c)
19. (d)
20. (b)

21. (c)
22. T
23. F
24. F
25. F
26. F
27. T
28. F
29. T
30. F
31. T
32. T
33. T
34. F
35. T
36. F
37. T
38. T
39. T
40. F
41. (a) (iii)
    (b) (vii)
    (c) (vi)
    (d) (iv)
    (e) (viii)
    (f) (i)
    (g) (v)
    (h) (ii)
42. (a) P: +5; O: −2
    (b) N: +4; O: −2
    (c) Na: +1; S: +6; O: −2
    (d) Cu: +2; N: +5; O: −2
    (e) K: +1; Mn: +7; O: −2
    (f) Na: +1; Fe: +3; O: −2; H: +1
    (g) Xe: +6; O: −2; F: −1
43. (a) +6
    (b) +7
    (c) +2
    (d) +4
46. (a) $Cl_2(g)$
    (b) $O_2(g)$
    (c) $Cl_2(g)$
    (d) $F_2(g)$
47. (a) oxidized: I; reduced: Pb; oxidizing agent: $PbO_2(aq)$; reducing agent: HI(aq)
    (b) oxidized: Mg; reduced: Cu; oxidizing agent: $Cu(NO_3)_2(aq)$; reducing agent: Mg(s)
    (c) oxidized: As; reduced: Cl; oxidizing agent: $Cl_2(g)$; reducing agent: $As_2O_3(s)$
    (d) oxidized: C; reduced: I; oxidizing agent: $I_2O_5(s)$; reducing agent: CO(g)
48. (a) $Cl_2(g) + 2\,e^- \rightarrow 2Cl^-(aq)$
    (b) $S_8(s) + 16\,e^- \rightarrow 8\,S^{2-}(aq)$
    (c) $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$
    (d) $Na(s) \rightarrow Na^+(aq) + e^-$
49. oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2\,e^-$; reduction : $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$
50. (a) one
    (b) two
    (c) $2\,Na(s) + F_2(g) \rightarrow 2\,NaF(s)$
51. (a) yes
    (b) no
    (c) yes
    (d) yes
    (e) yes
    (f) yes
    (g) yes
52. (a) cathode: iron; anode: magnesium
55. (a) $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
    $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
    Net: $Fe^{2+}(aq) + Mg(s) \rightarrow Mg^{2+}(aq) + Fe(s)$
    (b) 1.93 V
56. (a) $Ni^{2+}(aq) + Zn(s) \rightarrow Ni(s) + Zn^{2+}(aq)$
    (b) 0.53 V
    (c) $Zn(s) \mid Zn^{2+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$
57. $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$
58. −0.83 V; −0.23 V; +1.50 V; +1.20 V; −3.05 V
    ranking: Au(s), $I_2(s) + H_2O$, (l) Ni(s), $H_2(g) + OH^-(aq)$, Li(s)
62. $4\,Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$
63. ions
64. (a) cathode: $Ni^{2+}(l) + 2\,e^- \rightarrow Ni(s)$; anode: $2\,Br(l) \rightarrow Br_2(g) + 2\,e^-$
    (b) cathode: $Al^{3+}(l) + 3\,e^- \rightarrow Al(s)$; anode: $2\,F(l) \rightarrow F_2(g) + 2\,e^-$
    (c) cathode: $Mg^{2+}(l) + 2\,e^- \rightarrow Mg(s)$; anode: $2\,I(l) \rightarrow I_2(g) + 2\,e^-$
69. reduced
72. (a) $2\,C_2H_6(g) + 7\,O_2(g) \rightarrow 4\,CO_2(g) + 6\,H_2O(g)$
    (b) $Mg(s) + 2\,HCl(aq) \rightarrow Mg^{2+}(aq) + 2\,Cl^-(aq) + H_2(g)$
    (c) $KIO_4(aq) + 7\,KI(aq) + 8\,HCl(aq) \rightarrow 8\,KCl(aq) + 4\,I_2(s) + 4\,H_2O(l)$
    (d) $3\,Cl_2(g) + 6\,KOH(aq) \rightarrow KClO_3(aq) + 5\,KCl(aq) + 3\,H_2O(l)$
    (e) $2\,K_2CrO_7(s) + 28\,HCl(g) \rightarrow 4\,KCl(aq) + 2\,CrCl_3(aq) + 9\,Cl_2(g) + 14\,H_2O(l)$
    (f) $MnO_2(s) + H_2C_2O_4(aq) + H_2SO_4(aq) \rightarrow MnSO_4(aq) + 2\,CO_2(g) + 2\,H_2O(l)$
74. (a) $2\,MnO(s) + 5\,PbO_2(s) + 8\,H^+(aq) \rightarrow 2\,MnO_4^-(aq) + 5\,Pb^{2+}(aq) + 4\,H_2O(l)$
    (b) $3\,I^-(aq) + ClO^-(aq) + 2\,H^+(aq) \rightarrow I_3^-(aq) + Cl^-(aq) + H_2O(l)$
    (c) $3\,As_2O_3(s) + 4\,NO_3^-(aq) + 4H^+ + 7\,H_2O \rightarrow 6\,H_3AsO_4(aq) + 4\,NO(g)$
    (d) $16\,H^+(aq) + 10\,Br^-(aq) + 2\,MnO_4^-(aq) \rightarrow 5\,Br_2(l) + 2\,Mn^{2+}(aq) + 8\,H_2O(l)$
    (e) $8\,H^+(aq) + 3\,CH_3OH(aq) + Cr_2O_7^{2-}(aq) \rightarrow 3\,CH_2O(aq) + 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
75. (a) $Au^{3+}(aq) + Mn(s) \rightarrow Au(s) + Mn^{2+}(aq)$
    (b) $Au^{3+}(aq)$
    (c) Mn(s)
    (d) $Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$, $Mn(s) \rightarrow Mn^{2+}(aq) + 2\,e^-$
    (e) $2\,Au^{3+}(aq) + 3\,Mn(s) \rightarrow 2\,Au(s) + 3\,Mn^{2+}(aq)$
76. $2\,MnO_4^-(aq) + 3\,CN^-(aq) + H_2O(l) \rightarrow 2\,MnO_2(aq) + 3\,CNO^-(aq) + 2\,OH^-(aq)$
77. (a) no reaction
    (b) $Cl_2(g) + 2\,I^-(aq) \rightarrow I_2(s) + 2\,Cl^-(aq)$
    (c) no reaction
    (d) $4\,Fe^{2+}(aq) + 4\,H^+(aq) + O_2(g) \rightarrow 4\,Fe^{3+}(aq) + 2\,H_2O(l)$
78. (a) $MnO_4{}^-(aq) + 8\,H+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$; $Fe^{2+}(aq) \rightarrow e^- + Fe^{3+}(aq)$; $5\,Fe^{2+}(aq) + MnO_4{}^-(aq) + 8\,H^+(aq) \rightarrow 4\,H_2O(l) + Mn^{2+}(aq) + 5\,Fe^{3+}(aq)$
    (b) no reaction
    (c) $O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$; $Fe(s) \rightarrow 2\,e^- + Fe^{2+}(aq)$; $O_2(g) + 2\,H_2O(l) + 2\,Fe(s) \rightarrow 4\,OH^-(aq) + 2\,Fe^{2+}(aq)$
80. (a) oxidizing agent: hydrochloric acid; reducing agent: magnesium
    (b) $Mg(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$
    (c) 2
    (d) no
86. (b) $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
    (c) $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$
    (d) $Zn(s) \mid Zn^{2+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$
87. $3\,Ag^+(aq) + Al(s) \rightarrow 3\,Ag(s) + Al^{3+}(aq)$; $\Delta E^\circ_{r(cell)} = 2.46\ V$
93. (a) no
98. (a) $Cl_2(g)$
    (b) Sn(s)
    (d) $Sn^{2+}(aq) + 2\,Cl^-(aq) \rightarrow Sn(s) + Cl_2(g)$
    (e) 1.50 V
102. (a) $2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g)$
    (b) oxygen
    (c) 2
    (d) 2
104. (a) reactant oxidation numbers: H: +1; O: −2; C: −2; Cr: +6 product oxidation numbers: H: +1; O: −2; single-bonded C: −2; double-bonded C: +2; Cr: +3
    (b) $3\,CH_3CH_2OH(g) + 2\,Cr_2O_7^{2-}(aq) + 16\,H^+(aq) \rightarrow 3\,CH_3CO_2H(aq) + 4\,Cr^{3+}(aq) + 11\,H_2O(l)$
    (c) orange–green
105. no
108. (b) 0.21 V
109. (b) $Zn(s) | Zn^{2+}(aq) || Ag^+(aq) | Ag(s)$
    (c) anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$
    (d) cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$
    (e) 1.56 V
    (f) less
110. $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2\,Ag(s)$
112. (a) −0.40 V
114. (a) reactant oxidation numbers: Zn: +2; S in ZnS: −2; S in H_2SO_4: +6; O in H_2SO_4: −2; O in O_2: 0; H: +1 product oxidation numbers: Zn: +2; S in $ZnSO_4$: +6; elemental S: 0; H: +1; O: −2
    (b) $2\,ZnS(s) + 2\,H_2SO_4(aq) + O_2(g) \rightarrow 2\,ZnSO_4(aq) + 2\,S(s) + 2\,H_2O(l)$
    (c) zinc metal and sulfuric acid
    (d) 0.47V
115. (a) produce electricity
    (b) drive chemical process
    (c) drive chemical process
    (d) drive chemical process
116. (a) anode: $2I^-(aq) \rightarrow I_2(s) + 2\,e^-$ cathode: $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$
117. no
120. spoon: cathode; $Ag^+(aq) + e^- \rightarrow Ag(s)$; silver: anode; $Ag(s) \rightarrow Ag^+(aq) + e^-$
121. (a) $2\,H_2O(l) + 2\,Br^-(aq) \rightarrow H_2(g) + 2\,OH^-(aq) + Br_2(g)$
    (b) potassium bromide, KBr(aq); water, $H_2O(l)$
129. (a) chlorine

Glossary

A

acid–base indicator a substance that changes colour within a specific pH range (p. 506)

acid ionization constant (K_a) the equilibrium constant for the ionization of an acid; also called the acid dissociation constant (p. 492)

activated complex an unstable arrangement of atoms containing partially formed and unformed bonds that represents the maximum potential energy point in the change; also called the transition state (p. 367)

activation energy (E_a) the minimum energy that reactant molecules must possess for a reaction to be successful (p. 367)

addition polymer a very long organic molecule formed as the result of addition reactions between monomers with unsaturated carbon–carbon bonds (p. 84)

addition reaction a reaction in which the atoms from one molecule are added to another molecule to form a single molecule (p. 23)

alcohol organic compound that contains the hydroxyl (–OH) functional group (p. 32)

aldehyde an organic molecule containing a carbonyl group that is bonded to at least 1 hydrogen atom (p. 40)

aliphatic hydrocarbon a compound that has a structure based on straight or branched chains or rings of carbon atoms (p. 18)

alkane a saturated hydrocarbon (p. 8)

alkene a hydrocarbon that contains at least one carbon–carbon double bond (p. 18)

alkyl group one or more carbon atoms that form a branch off the main chain of a hydrocarbon (p. 10)

alkyl halide an alkane in which one or more hydrogen atoms have been substituted with one or more halogen atoms (p. 16)

alkyne a hydrocarbon that contains at least one carbon–carbon triple bond (p. 18)

amide an organic compound that contains a carbonyl group bonded to a nitrogen atom (p. 59)

amine an organic compound, related to ammonia, that contains a nitrogen atom bonded to one or more alkyl groups on each molecule (p. 56)

amino acid a compound with a carboxyl group and an amino group attached to the same carbon atom; the building blocks of all protein (p. 102)

amphiprotic (amphoteric) able to donate or accept a hydrogen ion (proton) and thus act as both a Brønsted–Lowry acid and a Brønsted–Lowry base (p. 491)

anode the electrode where oxidation occurs (p. 638)

aromatic hydrocarbon an unsaturated cyclic hydrocarbon with a pattern of bonding that makes it chemically stable (p. 28)

Arrhenius theory a theory stating that, in an aqueous solution, an acid is a substance that produces hydrogen ions and a base is a substance that produces hydroxide ions (p. 488)

atomic number (Z) the number of protons in a nucleus (p. 138)

aufbau principle the theory that an atom is “built up” by the addition of electrons, which fill orbitals starting at the lowest available energy orbital before filling higher energy orbitals (for example, 1*s* before 2*s*) (p. 162)

autoionization of water the transfer of a hydrogen ion from one water molecule to another (p. 499)

average reaction rate the change in reactant or product concentration over a given time interval (p. 347)

B

base ionization constant (K_b) the equilibrium constant for the ionization of a base; also called the base dissociation constant (p. 498)

battery a group of two or more galvanic cells connected in series (p. 649)

biological catalyst a catalyst made by a living system (p. 364)

bond dissociation energy the energy required to break a given chemical bond (p. 307)

bonding electron pair an electron pair that is involved in bonding, found in the space between 2 atoms (p. 195)

Bose–Einstein condensate (BEC) a state of matter that consists of a collection of atoms near absolute zero; all the atoms have the lowest possible quantum energy state (p. 175)

Brønsted–Lowry theory a theory stating that an acid is a hydrogen ion (proton) donor and a base is a hydrogen ion (proton) acceptor (p. 488)

buckyball a spherical arrangement of carbon atoms that forms a hollow, cage-like structure (p. 252)

buffer an aqueous solution containing a conjugate acid–base pair that maintains a nearly constant pH when an acid or base is added (p. 558)

buffering capacity the ability of a buffer to resist changes in pH by reacting with added hydrogen ions or hydroxide ions (p. 566)

burette a calibrated tube used to deliver variable known volumes of a liquid during a titration (p. 540)

C

calorimeter a device that is used to measure thermal energy changes during a chemical or physical change (p. 293)

calorimetry the experimental process of measuring the thermal energy change during a chemical or physical change (p. 293)

capillary action the spontaneous rising of a liquid in a narrow tube (p. 245)

carbohydrate a polymer food source and structural material for plants with the empirical formula $C_x(H_2O)_y$ (p. 101)

carbon nanotube a solid made of carbon atoms similar to graphite rolled into a cylinder (p. 252)

carbonyl group a carbon atom double-bonded to an oxygen atom, found in organic compounds such as aldehydes and ketones (p. 40)

carboxyl group a carbon atom that is double-bonded to 1 oxygen atom and single-bonded to a hydroxyl group (p. 47)

carboxylic acid a weak organic acid containing at least one carboxyl group (p. 47)

catalyst a substance that alters the rate of a chemical reaction without itself being permanently changed (p. 364)

cathode the electrode where reduction occurs (p. 638)

cathodic protection a form of corrosion prevention in which electrons are continually supplied to the metal that is being protected, making the metal a cathode (p. 660)

cell a system in which two connected electrodes are in contact with an electrolyte (p. 636)

cell potential the electric potential difference (voltage) between the two half-cells in a galvanic cell; the SI unit is the volt, and the unit symbol is V (1 V = 1 J/C) (p. 642)

chemical equilibrium the state of a reaction in which all reactants and products have reached constant concentrations in a closed system (p. 420)

chemical kinetics the area of chemistry that deals with rates of reaction (p. 346)

chemical system a group of reactants and products being studied (p. 287)

***cis* isomer** a stereoisomer in which the groups of interest are located on the same side of a double bond (p. 22)

closed system a system in which energy can enter and leave the system, but matter cannot (p. 287)

coal slurry a suspension of pulverized coal in water (p. 327)

collision theory the theory that chemical reactions can occur only if reactants collide with proper orientation and with enough kinetic energy to break reactant bonds and form product bonds (p. 366)

common ion effect a reduction in the solubility of an ionic compound due to the presence of a common ion in solution (p. 469)

complete combustion a chemical reaction in which a compound reacts with oxygen, O_2; if the compound is a hydrocarbon, the products of the reaction are carbon dioxide, water, and thermal energy (p. 15)

composite material a material composed of two or more distinct materials that remain separate from each other in the solid phase (p. 248)

condensation polymer a very long organic molecule formed as a result of condensation reactions between monomers with two functional groups (p. 95)

condensation reaction a chemical reaction in which two molecules combine to form a larger molecule and a small molecule, such as water (p. 37)

conjugate acid the substance that forms when a base, according to the Brønsted–Lowry theory, accepts a hydrogen ion (proton) (p. 490)

conjugate acid–base pair two substances related to each other by the donating and accepting of a single hydrogen ion (p. 490)

conjugate base the substance that forms when an acid loses a hydrogen ion (proton) (p. 490)

continuous spectrum an emission spectrum that contains all the wavelengths in a specific region of the electromagnetic spectrum (p. 144)

coordinate covalent bond a covalent bond in which the electrons involved in bonding are from one atom (p. 204)

copolymer a polymer made of two or more different types of monomers combined (p. 81)

corrosion the deterioration of a metal by a redox reaction (p. 658)

covalent bond a chemical bond in which atoms share the bonding electrons (p. 195)

covalent network crystal a solid in which the atoms form covalent bonds in an interwoven network (p. 250)

cyclic alkane a hydrocarbon in which the main structure consists of a chain of carbon atoms joined to form a closed ring (p. 9)

D

dehydration reaction a reaction that involves the removal of a hydrogen atom and a hydroxyl group from the reactant, producing a slightly smaller molecule and water (p. 35)

dipole a separation of positive and negative charges in a region in space (p. 219)

dipole–dipole force the intermolecular force that is caused when the dipoles of polar molecules position their positive and negative ends near each other (p. 239)

DNA deoxyribonucleic acid; a polymer in the cell nucleus that stores and transmits genetic information (p. 104)

duet rule the rule that precribes the complete outer shell of valence electrons when hydrogen and period 2 metals are involved in bonding (p. 196)

dynamic equilibrium a balance between forward and reverse processes that are occurring simultaneously at equal rates (p. 420)

E

efficiency the ratio of the energy output to the energy input of any system (p. 329)

electrochemical cell a general term that is used to refer to both a galvanic cell and an electrolytic cell (p. 665)

electrode a solid electrical conductor (p. 636)

electrolysis the application of current through a cell to produce a chemical change (p. 663)

electrolytic cell a cell that uses electrical energy to produce a chemical change that would not occur spontaneously (p. 663)

electron a negatively charged subatomic particle (p. 134)

electron configuration the location and number of electrons in the electron energy levels of an atom (p. 162)

electron-pair repulsion the repulsive force that occurs between electron pairs, causing them to be positioned as far apart as possible in a molecule (p. 206)

electron probability density the probability of finding an electron at a given location, derived from wave equations and used to determine the shapes of orbitals; also called electron probability distribution (p. 151)

electron sea theory a theory that states that the electrons in a metallic crystal move freely around the positively charged nuclei (p. 249)

electronegativity the ability of an atom in a molecule to attract shared electrons to itself (p. 218)

elementary step a step involving a one-, two-, or three-entity collision that cannot be explained by simpler reactions (p. 383)

emission spectrum the spectrum of electromagnetic radiation emitted by an atom; results when an atom is returned to a lower energy state from a higher energy state (p. 144)

endothermic absorbing energy from the surroundings (p. 288)

endpoint the point in a titration at which a sharp change in a measurable and characteristic property occurs (for example, a colour change in an acid–base indicator) (p. 540)

energy the ability to do work; SI units joules (J) (p. 286)

energy-level diagram (orbital diagram) a diagram that represents the relative energies of the electrons in an atom (p. 163)

enthalpy (*H*) the total amount of thermal energy in a substance (p. 298)

enthalpy change (ΔH) the energy released to or absorbed from the surroundings during a chemical or physical change (p. 298)

equilibrium constant (*K*) a constant numerical value defining the equilibrium law for a given system; units are not included when giving the value of K (p. 429)

equilibrium law the mathematical description of a chemical system at equilibrium (p. 429)

equilibrium position the relative concentrations of reactants and products in a system in dynamic equilibrium (p. 421)

equilibrium shift a change in concentrations of reactants and products in order to restore an equilibrium state (p. 439)

equivalence point the point in a titration when neutralization is complete (p. 540)

ester an organic compound that contains a carbonyl group bonded to a second oxygen atom which is bonded to another carbon atom (p. 49)

esterification the reaction of a carboxylic acid and alcohol to form an ester and water (p. 51)

ether an organic compound containing an oxygen atom between 2 carbon atoms in a chain (p. 37)

exothermic releasing energy to the surroundings (p. 288)

F

fatty acid a long-chain carboxylic acid (p. 53)

ferromagnetism the very strong magnetism commonly exhibited by materials that contain nickel, iron, and cobalt; applies to a collection of atoms (p. 171)

fission the process of using a neutron to split a nucleus of high atomic mass into two nuclei with smaller masses (p. 289)

fuel cell a galvanic cell for which the reactants are continuously supplied (p. 652)

functional group a group of atoms within a molecule that determines the properties of the molecule (p. 23)

fusion the process of combining two or more nuclei of low atomic mass to form a heavier, more stable nucleus (p. 289)

G

galvanic cell an arrangement of two connected half-cells that spontaneously produces electric current (p. 638)

galvanizing the process in which steel is coated with a thin layer of zinc to protect the steel from corrosion (p. 660)

ground state the lowest energy state for an atom (p. 146)

H

half-cell an electrode and an electrolyte that form half of a complete cell (p. 636)

half-reaction equation the part of an oxidation–reduction reaction equation representing either the oxidation reaction or the reduction reaction (p. 600)

heat the transfer of thermal energy from a warm object to a cooler object (p. 287)

Heisenberg's uncertainty principle the idea that it is impossible to know the exact position and speed of an electron at a given time (p. 150)

Hess's law the enthalpy change for the conversion of reactants to products is the same whether the conversion occurs in one step or in several steps (p. 314)

heterogeneous catalyst a catalyst in a reaction in which the reactants and the catalyst are in different physical states (p. 364)

heterogeneous equilibrium a chemical equilibrium system in which the reactants and products are present in at least two different states, such as gases and solids (p. 433)

homogeneous catalyst a catalyst in a reaction in which the reactants and the catalyst are in the same physical state (p. 364)

homogeneous equilibrium a chemical equilibrium system in which all reactants and products are in the same state of matter, such as the gas state (p. 433)

homopolymer a polymer of a single type of monomer (p. 80)

Hund's rule a rule stating that in a particular set of orbitals of the same energy, the lowest energy configuration for an atom is the one with the maximum number of unpaired electrons allowed by the Pauli exclusion principle; unpaired electrons are represented as having parallel spins (p. 164)

hybrid orbital an orbital that forms from the combination of at least two different orbitals (p. 233)

hybridization the process of forming hybrid orbitals from the combination of at least two different orbitals (p. 233)

hydrocarbon a compound containing only carbon and hydrogen atoms (p. 8)

hydrogen bond the strong dipole–dipole force that occurs when a hydrogen atom bonded to a highly electronegative atom (oxygen, nitrogen, or fluorine) is attracted to a partially negative atom on a nearby molecule (p. 240)

hydrogen bonding a strong dipole–dipole force between a hydrogen atom attached to a highly electronegative atom (N, O, or F) in one molecule and a highly electronegative atom in another molecule (p. 35)

hydrolysis (1) the breaking of a covalent bond in a molecule by the addition of the elements of water (hydrogen and oxygen); the splitting of an ester into carboxylic acid and alcohol components (p. 51); (2) a chemical reaction of an ion with water to produce an acidic or basic solution by the production of hydronium or hydroxide ions (p. 532)

hydronium ion a water molecule that has accepted a hydrogen ion, H_3O^+ (p. 489)

I

ideal gas a hypothetical gas composed of entities that have no size, travel in straight lines, and have no attraction to each other (no intermolecular forces); a gas that obeys all gas laws (p. 443)

impressed current a form of cathodic protection in which electrons from a DC power source are pumped into the metal that is being protected (p. 661)

initial rate the rate determined just after the reaction begins (just after $t = 0$ s) (p. 376)

instantaneous concentrations concentrations that occur together at a particular instant in time in the progress of a chemical reaction (p. 450)

instantaneous reaction rate the rate of a chemical reaction at a single point in time (p. 353)

intermolecular force a force that causes one molecule to interact with another molecule; occurs between molecules (p. 239)

intramolecular bond the chemical bond within a molecule (p. 239)

ion-product constant for water (K_w) the equilibrium constant for the autoionization of water (p. 500)

ionic bond the electrostatic attraction between oppositely charged ions (p. 194)

isoelectronic having the same number of electrons per atom, ion, or molecule (p. 195)

isolated system an ideal system in which neither matter nor energy can move in or out (p. 287)

isotopes atoms with the same number of protons but different numbers of neutrons (p. 138)

K

ketone an organic compound that contains a carbonyl group bonded to 2 carbon atoms (p. 40)

kinetic energy the energy of an object due to its motion (p. 286)

L

laser (light amplification by stimulated emission of radiation) a device that produces light of a single colour with all waves travelling parallel to each other (p. 174)

Law of Conservation of Energy energy cannot be created or destroyed (p. 287)

Le Châtelier's principle a generalization that states that chemical systems at equilibrium shift to restore equilibrium when a change occurs that disturbs the equilibrium (p. 439)

Lewis structure a diagram that represents the arrangement of covalent electrons and bonds in a molecule or polyatomic ion (p. 196)

line spectrum an emission spectrum that contains only those wavelengths characteristic of the element being studied (p. 144)

lipid a class of organic compound that includes fats and oils (p. 53)

London dispersion forces the intermolecular forces that exist in non-polar molecules; they increase as the molecular mass increases (p. 242)

lone electron pair a pair of valence electrons that is localized to a given atom but not involved in bonding (p. 197)

M

magnetic quantum number (m_l) the quantum number that describes the orientation of an atomic orbital in space relative to the other orbitals in the atom, with whole-number values between $+l$ and $-l$, including 0 (p. 154)

magnetic resonance imaging (MRI) a medical tool in which magnetic fields interact with atoms in the human body, producing images that doctors can use to diagnose injuries and diseases (p. 175)

Markovnikov's rule the rule for predicting the products of addition reactions: when a hydrogen halide or water is added to an alkene, the hydrogen atom generally bonds to the carbon atom within the double bond that already has more hydrogen atoms bonded to it (p. 25)

mass number (*A*) the total number of protons and neutrons in a nucleus (p. 138)

metallic bonding the bonding that holds the nuclei and electrons of metals together (p. 249)

metallic crystal a solid with closely packed atoms held together by electrostatic interactions and free-moving electrons (p. 249)

molar enthalpy change (ΔH_r) the enthalpy change associated with a physical, chemical, or nuclear change involving 1 mol of a substance; SI units J/mol (p. 299)

molecular crystal a solid composed of individual molecules held together by intermolecular forces of attraction (p. 250)

monomer one of the repeating small molecules that make up polymers (p. 80)

monoprotic acid an acid that possesses only one ionizable (acidic) hydrogen atom (p. 521)

monosaccharide an aldehyde or ketone with 5 or 6 carbon atoms and many hydroxyl groups; a simple sugar that is the monomer of a carbohydrate (p. 101)

N

neutron an electrically neutral subatomic particle (p. 137)

non-polar covalent bond a covalent bond in which the electrons are shared equally between atoms (p. 217)

non-polar molecule a molecule that has only non-polar bonds, or a bond dipole sum of zero (p. 225)

nucleic acid the polymer molecules that make up DNA and RNA (p. 104)

nucleotide an ester created when the DNA or RNA base combines with phosphoric acid (p. 104)

nucleus the dense centre of an atom with a positive charge (p. 137)

O

octet rule the observation that many atoms tend to form the most stable substances when they are surrounded by 8 electrons in their valence shells (p. 196)

open system a system in which both matter and energy are free to enter and leave the system (p. 287)

orbital the region around the nucleus where an electron has a high probability of being found (p. 150)

order of reaction the exponent used to describe the relationship between the initial concentration of a particular reactant and the rate of the reaction (p. 375)

organic acid an acid (except carbonic acid, $H_2CO_3(aq)$) containing carbon, oxygen, and hydrogen atoms; also called carboxylic acid (p. 497)

organic base an organic compound that increases the concentration of hydroxide ions in aqueous solution (p. 499)

organic compound a molecular compound of carbon, not including $CO(g)$, $CO_2(g)$, and $HCN(g)$ (p. 8)

oxidation the process in which one or more electrons is lost by a chemical entity (p. 600)

oxidation number a number used to keep track of electrons in oxidation–reduction reactions according to certain rules; also known as oxidation state (p. 602)

oxidation–reduction (redox) reaction the reaction in which one or more electrons are transferred between chemical entities (p. 600)

oxidizing agent the reactant that is reduced (gains electrons from another substance) during an oxidation–reduction reaction (p. 605)

oxyacid an acid in which the acidic hydrogen atom is attached to an oxygen atom (p. 496)

P

paramagnetism the weak attraction of a substance to a magnet; applies to individual atoms (p. 171)

partial pressure the pressure that a gas, in a mixture of gases, would exert if it alone occupied the whole volume occupied by the mixture (p. 443)

Pauli exclusion principle the principle that no two electrons in the same atom can be in the same quantum state (p. 157)

peptide two or more amino acids linked together (p. 102)

percentage ionization the percentage of a solute that ionizes when it dissolves in a solvent (p. 514)

pH the negative logarithm of the concentration of hydrogen ions in an aqueous solution (p. 502)

pH curve a graph of pH plotted against volume of titrant added in an acid–base titration; titration curve (p. 544)

pH meter a device that measures the acidity or alkalinity of a solution electronically and displays the result as a pH value (p. 505)

phenyl group a benzene ring (minus 1 hydrogen atom) that behaves as a substituent in an organic compound (p. 28)

photoelectric effect electrons are emitted by matter that absorbs energy from shortwave electromagnetic radiation (for example, visible or UV light) (p. 139)

photon a unit of light energy (p. 141)

pi (π) bond a bond that is formed when the sides of the lobes of two orbitals overlap (p. 235)

plastic a synthetic substance that can be moulded (often under heat and pressure) and that then retains its given shape (p. 88)

pOH the negative logarithm of the concentration of hydroxide ions in an aqueous solution (p. 502)

polar covalent bond a covalent bond in which the electrons are not shared equally because 1 atom attracts them more strongly than the other atom (p. 217)

polar molecule a molecule that has a net dipole (p. 225)

polarizability the ability of a substance to form a dipolar charge distribution (p. 243)

polyamide a polymer formed by condensation reactions resulting in amide linkages between monomers (p. 96)

polyester a polymer formed by a condensation reaction that results in ester linkages between monomers (p. 95)

polymer a large, usually chain-like molecule that is built from small molecules (p. 80)

polyprotic acid an acid that possesses more than one ionizable (acidic) hydrogen atom (p. 521)

polysaccharide a large polymer consisting of many monosaccharides; can form when each ring forms two glycosidic bonds (p. 101)

potential energy the energy of a body or system due to its position or composition (p. 286)

potential energy diagram a graphical representation of the energy transferred during a physical or a chemical change (p. 302)

primary alcohol an alcohol in which the hydroxyl group is bonded to a terminal carbon atom (p. 32)

primary cell a cell that cannot be recharged (p. 649)

primary standard a highly pure and stable chemical used to determine the precise concentration of acids or bases (p. 540)

principal quantum number (*n*) the quantum number that describes the size and energy of an atomic orbital (p. 153)

proton a positively charged subatomic particle (p. 137)

Q

quantum a unit or packet of energy (plural: quanta) (p. 140)

quantum mechanical model a model for the atom based on quantum theory and the calculation of probabilities for the location of electrons (p. 151)

quantum mechanics the application of quantum theory to explain the properties of matter, particularly electrons in atoms (p. 148)

quantum numbers numbers that describe the quantum mechanical properties of orbitals; from the solutions to Schrödinger's wave equation (p. 153)

R

radioactivity the spontaneous decay or disintegration of the nucleus of an atom (p. 136)

radioisotope an isotope that emits radioactive gamma rays and/or subatomic particles (for example, alpha and/or beta particles) (p. 138)

rate constant a constant determined empirically that is unique for a single reaction at a specified temperature (p. 375)

rate-determining step the step in a reaction mechanism that determines the rate of the overall reaction; the slowest step in a reaction mechanism (p. 383)

rate law the mathematical expression that allows the calculation of reaction rate as a function of the reactant concentration (p. 375)

rate law equation the relationship among rate, the rate constant, the initial concentrations of reactants, and the orders of reaction with respect to the reactants (p. 375)

reaction intermediate an entity that is neither a reactant nor a product but is formed and consumed during the reaction sequence (p. 383)

reaction mechanism a series of elementary steps by which a chemical reaction occurs (p. 383)

reaction quotient (Q) the product of the concentrations of the products, divided by the product of the concentrations of the reactants, for a chemical reaction that is not necessarily at equilibrium (p. 449)

reaction rate the change in concentration of a reactant or a product of a chemical reaction per unit time (p. 346)

redox table a table listing standard reduction potentials of common oxidizing agents and reducing agents in order from strongest to weakest; standard reduction potentials table (p. 620)

reducing agent the reactant that is oxidized (loses electrons to another substance) during an oxidation–reduction reaction (p. 605)

reduction the process in which one or more electrons is gained by a chemical entity (p. 600)

representative elements those elements in the main blocks of the periodic table, which are Groups 1 to 18 (the *s* and *p* blocks) (p. 169)

reversible reaction a chemical reaction that proceeds in both the forward and reverse directions, setting up an equilibrium in a closed system (p. 421)

RNA ribonucleic acid; a polymer in the cell cytoplasm that stores and transmits genetic information (p. 104)

S

sacrificial anode a form of cathodic protection in which the oxidation of a more active metal that is attached to the steel prevents the iron in the steel from being oxidized (p. 661)

salt bridge a tube that contains an electrolyte solution and connects the two half-cells in a galvanic cell (p. 637)

sample the solution being analyzed in a titration (p. 540)

saponification the process of making soap by heating fats or oils with a strong base (p. 54)

saturated hydrocarbon a hydrocarbon with only single covalent bonds between its carbon atoms (p. 8)

secondary alcohol an alcohol in which the hydroxyl group is bonded to a carbon atom with two alkyl groups bonded to it (p. 32)

secondary cell a cell that can be recharged by being attached to an external source of electrical energy; recharging reverses the chemical reaction that generates the electrical energy (p. 650)

secondary quantum number (l) the quantum number that describes the shape and energy of an atomic orbital, with whole-number values from 0 to $n - 1$ for each value of n (p. 154)

semiconductor a substance that conducts a slight electric current at room temperature but has increasing conductivity at higher temperatures (p. 252)

shell an atom's main energy level, where the shell number is given by the principal quantum number, $n = 1, 2, 3, \ldots$ (p. 153)

sigma (σ) bond a bond that is formed when the lobes of two orbitals directly overlap end to end (p. 235)

simplified Lewis structure a Lewis structure in which bonding electron pairs are represented by solid lines and lone electron pairs by dots (p. 200)

solubility the quantity of solute that dissolves in a given quantity of solvent at a particular temperature; the concentration of a saturated solution at a particular temperature (p. 460)

solubility equilibrium a dynamic equilibrium between a solute and a solvent in a saturated solution in a closed system (p. 461)

solubility product constant (K_{sp}) the value obtained from the equilibrium law applied to a saturated solution (p. 461)

space-filling model a model of a molecule showing the relative sizes of the atoms and their relative orientations (p. 201)

specific heat capacity (c) the quantity of thermal energy required to raise the temperature of 1 g of a substance by 1 °C; SI units J/(g·°C) (p. 292)

spectroscopy the analysis of spectra to determine properties of their source (p. 143)

spin quantum number (m_s) the quantum number that relates to the spin of the electron; limited to $+\frac{1}{2}$ or $-\frac{1}{2}$ (p. 157)

standard cell a galvanic cell in which all the entities involved in the half-cell reactions are at SATP and the solutions have a concentration of 1.0 mol/L (p. 643)

standard cell potential ($\Delta E°_{r\,(cell)}$) the electric potential difference of a galvanic cell that is operating under standard conditions (p. 643)

standard enthalpy of formation ($\Delta H_f°$) the change in enthalpy that accompanies the formation of 1 mol of a compound from its elements in their standard states (p. 319)

standard hydrogen half-cell the galvanic cell from which all the half-cell potentials are determined; $E°_r = 0$ V (by definition) (p. 643)

standard reduction potential ($E°_r$) the ability of a half-cell to attract electrons in a cell that is operating under standard conditions (p. 643)

standard solution a solution whose concentration is accurately and precisely known (p. 540)

standard state the most stable form of a substance under standard conditions, 25 °C and 100 kPa (p. 319)

stereoisomers molecules that have the same chemical formula and structural backbone, but with a different arrangement of atoms in space (p. 22)

strong acid an acid that ionizes almost 100 % in water, producing hydrogen ions (p. 495)

strong base a base that dissociates completely in water, producing hydroxide ions (p. 497)

structural isomer a compound that has the same molecular formula as another compound, but a different structure (p. 10)

subshells orbitals of different shapes and energies, as given by the secondary quantum number; often referred to as *s*, *p*, *d*, and *f* (p. 153)

substituent group an atom or group that replaces a hydrogen atom in an organic compound (p. 10)

surface tension the resistance of a liquid to increase its surface area (p. 245)

surroundings all the matter that is not part of the system (p. 287)

syngas a synthetic fuel produced from the gasification of coal (p. 327)

T

temperature a measure of the average kinetic energy of the entities in a substance (p. 287)

tertiary alcohol an alcohol in which the hydroxyl group is bonded to a carbon atom with three alkyl groups bonded to it (p. 32)

thermal energy the total quantity of kinetic and potential energy in a substance (p. 287)

thermochemistry the study of the energy changes that accompany physical or chemical changes in matter (p. 286)

thiol an organic compound that contains the sulfhydryl (–SH) group (p. 38)

three-dimensional structure the three-dimensional arrangement of atoms in a molecule (p. 206)

titrant the solution in a burette during a titration (p. 540)

titration the addition of precise volumes of a solution in a burette to a measured volume of a sample solution; often used to determine the concentration of a substance in the sample (p. 540)

total order of reaction the sum of the exponents in the rate law equation (p. 375)

***trans* isomer** a stereoisomer in which the groups of interest are located on opposite sides of a double bond (p. 22)

transition the movement of an electron from one energy level to another (p. 146)

transition metal an element whose highest-energy electrons are in *d* orbitals (p. 167)

trial ion product (*Q*) the product of the concentrations of ions in a specific solution raised to powers equal to their coefficients in the balanced chemical equation; can be used to predict the formation of a precipitate (p. 466)

triglyceride an ester formed from long-chain fatty acids and glycerol (p. 53)

U

unsaturated hydrocarbon an organic compound, consisting of carbon and hydrogen, with one or more double or triple bonds joining pairs of carbon atoms within the molecules (p. 18)

V

valence bond theory a theory stating that atomic orbitals overlap to form a new orbital with a pair of opposite-spin electrons (p. 231)

valence electron an electron in the outermost principal quantum level of an atom (p. 167)

valence shell electron-pair repulsion (VSEPR) theory a method to determine the geometry of a molecule based on the idea that electron pairs are as far apart as possible (p. 206)

van der Waals forces many types of intermolecular forces, including dipole–dipole forces, London dispersion forces, and hydrogen bonding (p. 239)

viscosity the measure of a liquid's resistance to flow (p. 246)

W

wave function the mathematical probability of finding an electron in a certain region of space (p. 151)

weak acid an acid that only partly ionizes in water, producing hydrogen ions (p. 495)

weak base a base that only partially reacts with water to produce hydroxide ions (p. 498)

work the amount of energy transferred by a force over a distance; SI units joules (J) (p. 286)

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