CHEM 111 AND CHEM 113 (GENERAL CHEMISTRY I AND II)



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TABLE OF CONTENTS

Licensing

1: Chemistry Uses Specific Mathematical Tools

1.1: Overview and Objectives

1.2: Measurements

1.3: Dimensional Analysis for Calculations

1.4: Significant Figures for Measurements and Calculations

1.5: Accuracy and Precision of Experimental Results (lab topic)

2: Atoms Make Up Ionic and Covalent Compounds

2.1: Overview and Objectives

2.2: Atomic Structure and Symbolism

2.3: The Periodic Table

2.4: Molecular and Ionic Compounds

2.5: Chemical Nomenclature

3: Chemical Composition Involves Fixed Atomic Ratios

3.1: Overview and Objectives

3.2: Formula Mass and the Mole Concept

3.3: Determining Empirical and Molecular Formulas

3.4: Molarity

3.5: Writing and Balancing Chemical Equations

3.6: Classifying Chemical Reactions

3.7: Reaction Stoichiometry

3.8: Reaction Yields

4: Quantum Mechanics Describes Atomic Structure

4.1: Overview and Objectives

4.2: Electromagnetic Energy

4.3: Coulomb's Law and the Electrostatic Potential

4.3.1: Coulomb's Law and the Electrostatic Potential (Problems)

4.4: The Bohr Model

4.5: Development of Quantum Theory

4.6: Electronic Structure of Atoms (Electron Configurations)

4.7: Periodic Variations in Element Properties

5: Models for Chemical Bonding and Shape

5.1: Overview and Objectives

5.2: Ionic Bonding

5.3: Metallic Bonding

5.4: Covalent Bonding

5.5: Lewis Symbols and Structures
5.6: Strengths of Ionic and Covalent Bonds
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity
5.9: Valence Bond Theory Describes Bonds as Overlapping Atomic Orbitals
5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals
5.11: Valence Bond Treatment of Multiple Bonds
5.12: Molecular Orbital Theory Resolves Issues in Other Bonding Theories
5.13: Coordinate Covalent Bonding is Different
5.14: Spectroscopic and Magnetic Properties of Coordination Compounds

6: Intermolecular Interactions Drive Physical Properties

6.1: Overview and Objectives
6.2: Skeletal Structures For Representing Organic Compounds
6.3: Intermolecular Forces
6.4: Phase Transitions
6.5: Phase Diagrams
6.6: The Dissolution Process
6.7: Dissolution of Electrolytes
6.8: Solubility
6.9: Colligative Properties

7: The Gas Phase is Different

7.1: Overview and Objectives
7.2: Gas Pressure
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
7.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions
7.5: The Kinetic-Molecular Theory
7.6: Effusion and Diffusion of Gases
7.7: Non-Ideal Gas Behavior

8: Thermodynamics Describes the Flow of Energy

8.1: Overview and Objectives
8.2: Energy Changes in Chemical Reactions
8.3: Enthalpy and Reactions
8.4: Thermodynamics and Work
8.5: The First Law of Thermodynamics
8.6: Direction of Heat Flow and Enthalpy of Reaction
8.7: Calorimetry
8.8: Hess's Law
8.9: Heats of Formation
8.10: The Second Law of Thermodynamics
8.11: Entropy Changes and the Third Law of Thermodynamics

8.12: Spontaneity is Related to Entropy
8.13: Entropy
8.14: Free Energy is a Good Predictor of Spontaneity
8.15: Temperature Dependence of Free Energy
8.16: Free Energy

9: Processes Start Out Under Kinetic Control

9.1: Overview and Objectives
9.2: Chemical Reaction Rates
9.3: Rate Laws
9.4: Integrated Rate Laws
9.5: Factors Affecting Reaction Rates
9.6: Catalysis
9.7: Collision Theory
9.8: Reaction Mechanisms

10: Processes End Up At Equilibrium

10.1: Overview and Objectives
10.2: The Concept of Chemical Equilibrium
10.3: The Equilibrium Constant
10.4: Solving Equilibrium Problems
10.5: Non-equilibrium Conditions
10.6: Factors That Affect Equilibrium
10.7: Spontaneity and Equilibrium
10.8: Comparing Thermodynamics and Kinetics

11: Acids and Bases Have Common Properties and Reactions

11.1: Overview and Objectives
11.2: Definitions of Acids and Bases
11.3: Acid-Base Reactions
11.4: The Autoionization of Water and Solution pH
11.5: Equilibria and pH of Weak Acid and Salt Solutions
11.6: Buffers
11.7: Acid-Base Titrations

12: Ionic Compounds Have Common Properties and Reactions

12.1: Overview and Objectives
12.2: Solubility and Molecular Structure
12.3: Determining the Solubility of Ionic Compounds
12.4: Solubility and pH
12.5: Qualitative Analysis Using Selective Precipitation

13: Redox Reactions Describe The Movement of Electrons

13.1: Overview and Objectives

13.2: Oxidation-Reduction Reactions
13.3: Balancing Redox Reactions
13.4: Describing Electrochemical Cells
13.5: Standard Potentials
13.6: Comparing Strengths of Oxidants and Reductants
13.7: Electrochemical Cells and Thermodynamics
13.8: Electrolysis

14: Atomic Nuclei Can Change

14.1: Overview and Objectives
14.2: The Components of the Nucleus
14.3: Nuclear Reactions
14.4: Kinetics of Radioactive Decay

Index

Glossary

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1: CHEMISTRY USES SPECIFIC MATHEMATICAL TOOLS

1.1: Overview and Objectives
1.2: Measurements
1.3: Dimensional Analysis for Calculations
1.4: Significant Figures for Measurements and Calculations
1.5: Accuracy and Precision of Experimental Results (lab topic)

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1.1: Overview and Objectives

"Mathematics is the language with which God has written the universe." (Galileo Galilei)

Love it or hate it, chemistry contains a great deal of math. Everyone can do math, and you will do it here! Let's set the foundation for the important computational and algebra skills you need in General Chemistry.

Chapter Objectives

- Convert within SI base units (e.g. mm to km or MJ to J) between the prefixes pico- (p/10-12), nano- (n/10-9), micro- (μ/10-6), milli- (m/10-3), centi (c/10-2) kilo- (k/103), mega- (M/106), and giga- (G/109).
- Given non-SI conversion factors or equations, convert between units (e.g. cm to ft or psi to atm).
- Solve word problems requiring multiple dimensional analysis steps.
- Count significant figures and round numbers to an appropriate number of significant figures.

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1.2: Measurements

Learning Objectives

By the end of this section, you will have background information that helps you to be able to:

- Convert within SI base units (e.g. mm to km or MJ to J) between the prefixes pico- (p/10^{-12}), nano- (n/10^{-9}), micro- (μ/10^{-6}), milli- (m/10^{-3}), centi (c/10^{-2}) kilo- (k/10^{3}), mega- (M/10^{6}), and giga- (G/10^{9}).

Measurements provide much of the information that informs the hypotheses, theories, and laws describing the behavior of matter and energy in both the macroscopic and microscopic domains of chemistry. Every measurement provides three kinds of information: the size or magnitude of the measurement (a number); a standard of comparison for the measurement (a unit); and an indication of the uncertainty of the measurement. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

The number in the measurement can be represented in different ways, including decimal form and scientific notation. (Scientific notation is also known as exponential notation; a review of this topic can be found in Appendix B.) For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as 2.98 10^{5} kg. The mass of the average mosquito is about 0.0000025 kilograms, which can be written as 2.5 10^{-6} kg.

Units, such as liters, pounds, and centimeters, are standards of comparison for measurements. A 2-liter bottle of a soft drink contains a volume of beverage that is twice that of the accepted volume of 1 liter. The meat used to prepare a 0.25-pound hamburger weighs one-fourth as much as the accepted weight of 1 pound. Without units, a number can be meaningless, confusing, or possibly life threatening. Suppose a doctor prescribes phenobarbital to control a patient's seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg given three times per day can be effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

SI Base Units

The initial units of the metric system, which eventually evolved into the SI system, were established in France during the French Revolution. The original standards for the meter and the kilogram were adopted there in 1799 and eventually by other countries. This section introduces four of the SI base units commonly used in chemistry. Other SI units will be introduced in subsequent chapters.

The measurement units for the seven fundamental properties ("base units") are listed in Table 1.2.1. The standards for these units are fixed by international agreement, and they are called the **International System of Units** or SI Units (from the French, *Le Système International d'Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964. Units for other properties may be derived from these seven base units.

Table 1.2.1: Base Units of the SI System

Property Measured	Name of Unit	Symbol of Unit
length	meter	m
mass	kilogram	kg
time	second	s
temperature	kelvin	K
electric current	ampere	A
amount of substance	mole	mol

Property Measured	Name of Unit	Symbol of Unit
luminous intensity	candela	cd

Everyday measurement units are often defined as fractions or multiples of other units. Milk is commonly packaged in containers of 1 gallon (4 quarts), 1 quart (0.25 gallon), and one pint (0.5 quart). This same approach is used with SI units, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means "one thousand," which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in Table 1.2.2.

*Table 1.2.2: Common Unit Prefixes. The prefixes you are expected to memorize and use are in **bold** print.*

Prefix	Symbol	Factor	Example
femto	f	10^{-15}	1 femtosecond (fs) = 1 x 10^{-15} s (0.000000000000001 s)
pico	**p**	**10^{-12}**	**1 picometer (pm) = 1 x 10^{-12} m (0.000000000001 m)**
nano	**n**	**10^{-9}**	**4 nanograms (ng) = 4 x 10^{-9} g (0.000000004 g)**
micro	**μ**	**10^{-6}**	**1 microliter (μL) = 1 x 10^{-6} L (0.000001 L)**
milli	**m**	**10^{-3}**	**2 millimoles (mmol) = 2 x 10^{-3} mol (0.002 mol)**
centi	**c**	**10^{-2}**	**7 centimeters (cm) = 7 x 10^{-2} m (0.07 m)**
deci	d	10^{-1}	1 deciliter (dL) = 1 x 10^{-1} L (0.1 L)
kilo	**k**	**10^3**	**1 kilometer (km) = 1 x 10^3 m (1000 m)**
mega	**M**	**10^6**	**3 megahertz (MHz) = 3 x 10^6 Hz (3,000,000 Hz)**
giga	**G**	**10^9**	**8 gigayears (Gyr) = 8 x 10^9 yr (8,000,000,000 yr)**
tera	T	10^{12}	5 terawatts (TW) = 5 x 10^{12} W (5,000,000,000,000 W)

Derived SI Units

We can derive many units by combining the seven SI base units in useful ways. Here are a few examples of derived units that we use in chemistry.

Volume

Volume is the measure of the amount of space occupied by an object. There are different equations for finding volume depending on the object: for example, the volume of a rectangular prism is *length x width x height*, while the volume of a sphere is $(4/3)\pi r^3$. Regardless, several very common units for volume are given below. Make sure that you are aware of these units and their equivalencies.

- **cubic meter (m^3)**
- **cubic decimeter (dm^3)**, which is equal to 1 **liter (L)**
- **cubic centimeter (cm^3)**, which is equal to 1 **milliliter (mL).** Sometimes, like in health professions, this unit is called a **cc**.

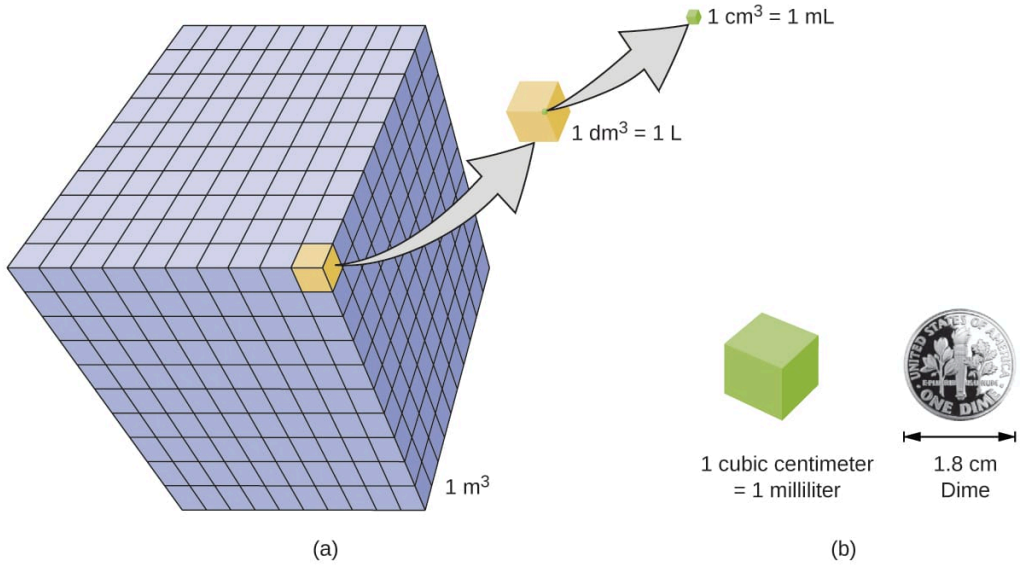


Figure 1.2.3: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

Density

The **density** of a substance is the ratio of the mass of a sample of the substance to its volume. There are two density units we will use in this course:

- **grams per milliliter (g/mL)** for talking about solids and liquids
- **grams per liter (g/L)** for talking about gases

Table 1.2.3 shows the densities of some common substances. Notice that

Table 1.2.3: Densities of Common Substances

Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L (0.00120 g/cm^3)
oak (wood) 0.60–0.90 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L (0.00131 g/cm^3)
iron 7.9 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L (0.00114 g/cm^3)
copper 9.0 g/cm^3	glycerin 1.26 g/cm^3	carbon dioxide 1.80 g/L (0.0018 g/cm^3)
lead 11.3 g/cm^3	olive oil 0.92 g/cm^3	helium 0.16 g/L (0.00016 g/cm^3)
silver 10.5 g/cm^3	gasoline 0.70–0.77 g/cm^3	neon 0.83 g/L (0.00083 g/cm^3)
gold 19.3 g/cm^3	mercury 13.6 g/cm^3	radon 9.1 g/L (0.0091 g/cm^3)

While there are many ways to determine the density of an object, perhaps the most straightforward method involves separately finding the mass and volume of the object, and then dividing the mass of the sample by its volume. In the following example, the mass is found directly by weighing, but the volume is found indirectly through length measurements.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.2.1}$$

Example 1.2.1: Calculation of Density

Gold—in bricks, bars, and coins—has been a form of currency for centuries. In order to swindle people into paying for a brick of gold without actually investing in a brick of gold, people have considered filling the centers of hollow gold bricks with lead to fool buyers into thinking that the entire brick is gold. It does not work: Lead is a dense substance, but its density is not as great as that of gold, 19.3 g/cm^3. What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g?

Solution

The density of a substance can be calculated by dividing its mass by its volume. The volume of a cube is calculated by cubing the edge length.

$$\text{volume of lead cube } = 2.00 \text{ cm} \times 2.00 \text{ cm} \times 2.00 \text{ cm} = 8.00 \text{ cm}^3$$

$$\text{density } = \frac{\text{mass}}{\text{volume}} = \frac{90.7 \text{ g}}{8.00 \text{ cm}^3} = 11.3 \text{ g/cm}^3$$

(We will discuss the reason for rounding to the first decimal place in the next section.)

Exercise 1.2.1

a. To three decimal places, what is the volume of a cube (cm^3) with an edge length of 0.843 cm?
b. If the cube in part (a) is copper and has a mass of 5.34 g, what is the density of copper to two decimal places?

Answer available at the end of this section.

Footnotes

- 1For details see https://www.nist.gov/pml/weights-and.../si-units-mass

Answers

Exercise 1.2.1

a. 0.599 cm^3
b. 8.91 g/cm^3

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1.3: Dimensional Analysis for Calculations

Learning Objectives

By the end of this section, you will have background information that helps you be able to:

- Given non-SI conversion factors or equations, convert between units (e.g. cm to ft or psi to atm).
- Solve word problems requiring multiple dimensional analysis steps.

In chemistry, we will often deal with quantities that we cannot measure directly but are instead calculated from other measurable properties and mathematical relationships like equations or conversion factors.

One non-chemistry example measuring the average speed of an athlete running sprints. Instead of directly measuring speed, we are measuring the *time* required for the athlete to run from the starting line to the finish line. The *speed* comes from the equation that relates these three properties:

$$\text{speed} = \frac{\text{distance}}{\text{time}}$$

An Olympic-quality sprinter can run 100 m in approximately 10 s, corresponding to an average speed of

$$\frac{100\,\text{m}}{10\,\text{s}} = 10\,\text{m/s}$$

What if we wanted to know the time it would take for a person running at this speed to travel a distance of 25 m? We will use the same equation, but rearrange it to solve for time:

$$\text{time} = \frac{\text{distance}}{\text{speed}}$$

The time can then be computed as:

$$\frac{25\,\text{m}}{10\,\text{m/s}} = 2.5\,\text{s}$$

We have done nothing more than arithmetic - division, in this case of (25/10 = 2.5). However, we have also done arithmetic on the units (m/(m/s) = s) to yield the number and unit of the result, 2.5 s. Note that, just as for numbers, when a unit is divided by an identical unit (in this case, m/m), the result is "1"—or, as commonly phrased, the units "cancel."

These calculations are examples of a versatile mathematical approach known as **dimensional analysis** (or the **factor-label method**). Dimensional analysis is based on this premise: *the units of quantities must be subjected to the same mathematical operations as their associated numbers*. This method can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities.

Conversion Factors and Dimensional Analysis

A ratio of two equivalent quantities expressed with different measurement units can be used as a **unit conversion factor**. For example, the lengths of 2.54 cm and 1 in. are equivalent (by definition), and so a unit conversion factor may be derived from the ratio,

$$\frac{2.54\,\text{cm}}{1\,\text{in.}}(2.54\,\text{cm} = 1\,\text{in.}) \text{ or } 2.54\frac{\text{cm}}{\text{in.}}$$

Several other commonly used conversion factors are given in Example 1.3.1.

Example 1.3.1: Common US-Metric Conversion Factors. All such conversion factors will be given to you on quizzes and exams; you do not need to memorize them.

Length	Volume	Mass
1 m = 1.0936 yd	1 L = 1.0567 qt	1 kg = 2.2046 lb
1 in. = 2.54 cm (exact)	1 qt = 0.94635 L	1 lb = 453.59 g
1 km = 0.62137 mi	1 ft^3 = 28.317 L	1 (avoirdupois) oz = 28.349 g
1 mi = 1609.3 m	1 tbsp = 14.787 mL	1 (troy) oz = 31.103 g

When a quantity (such as distance in inches) is multiplied by an appropriate unit conversion factor, the quantity is converted to an equivalent value with different units (such as distance in centimeters). For example, a basketball player's vertical jump of 34 inches can be converted to centimeters by:

$$34 \cancel{\text{ in.}} \times \frac{2.54\,\text{cm}}{1 \cancel{\text{ in.}}} = 86\,\text{cm}$$

Dimensional analysis helps us know whether we have appropriately used unit conversion factors as demonstrated in the following example.

Example 1.3.1: Using a Unit Conversion Factor

The mass of a competition frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g (Example 1.3.1).

Solution

Given the conversion factor, the mass in ounces may be derived using an equation similar to the one used for converting length from inches to centimeters.

$$xoz = 125g \times \text{ unit conversion factor}$$

The unit conversion factor may be represented as:

$$\frac{1\,\text{oz}}{28.349\,\text{g}} \text{ and } \frac{28.349\,\text{g}}{1\,\text{oz}}$$

The correct unit conversion factor is the ratio that cancels the units of grams and leaves ounces.

$$\begin{aligned} x\,\text{oz} &= 125\,\text{g} \times \frac{1\,\text{oz}}{28.349\,\text{g}} \\ &= \left(\frac{125}{28.349}\right)\,\text{oz} \\ &= 4.41\,\text{oz (three significant figures)} \end{aligned}$$

Exercise 1.3.1

Convert a volume of 9.345 qt to liters.

Answer available at the end of this section.

Beyond simple unit conversions, dimensional analysis, which is also called the factor-label method, can be used to solve more complex problems involving computations. Regardless of the details, the basic approach is the same—all the *factors* involved in the calculation must be appropriately oriented to ensure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

Example 1.3.2: Computing Quantities from Measurement Results and Known Mathematical Relations

What is the density of common antifreeze in units of g/mL? A 4.00-qt sample of the antifreeze weighs 9.26 lb.

Solution

Since $\text{density} = \frac{\text{mass}}{\text{volume}}$, we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A × unit conversion factor. The necessary conversion factors are given in Example 1.3.1: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. Mass may be converted from pounds to grams as follows:

$$9.26 \cancel{\text{ lb}} \times \left(\frac{453.59\,\text{g}}{1\ \cancel{\text{lb}}} \right) = 4.20 \times 10^3\,\text{g}$$

Volume may be converted from quarts to milliliters via two steps:

Step 1: Convert quarts to liters.

$$4.00\ \cancel{\text{qt}} \times \left(\frac{1\,\text{L}}{1.0567\ \cancel{\text{qt}}} \right) = 3.78\,\text{L}$$

Step 2: Convert liters to milliliters.

$$3.78\ \cancel{\text{L}} \times \left(\frac{1000\,\text{mL}}{1\ \cancel{\text{L}}} \right) = 3.78 \times 10^3\,\text{mL}$$

Then,

$$\text{density} = \frac{4.20 \times 10^3\,\text{g}}{3.78 \times 10^3\,\text{mL}} = 1.11\,\text{g/mL}$$

Alternatively, the calculation could be set up in a way that uses three unit conversion factors sequentially as follows:

$$\frac{9.26 \cancel{\text{ lb}}}{4.00\ \cancel{\text{qt}}} \times \frac{453.59\,\text{g}}{1\ \cancel{\text{lb}}} \times \frac{1.0567\ \cancel{\text{qt}}}{1\ \cancel{\text{L}}} \times \frac{1\ \cancel{\text{L}}}{1000\,\text{mL}} = 1.11\,\text{g/mL}$$

Exercise 1.3.2

What is the volume in liters of 1.000 oz, given that 1 L = 1.0567 qt and 1 qt = 32 oz (exactly)?

Answer available at the end of this section.

Example 1.3.3: Computing Quantities from Measurement Results and Known Mathematical Relations

While being driven from Philadelphia to Atlanta, a distance of about 1250 km, a 2014 Lamborghini Aventador Roadster uses 213 L gasoline.

a. What (average) fuel economy, in miles per gallon, did the Roadster get during this trip?
b. If gasoline costs $3.80 per gallon, what was the fuel cost for this trip?

Solution

(a) First convert distance from kilometers to miles:

$$1250\ \cancel{\text{km}} \times \frac{0.62137\ \text{mi}}{1\ \cancel{\text{km}}} = 777\ \text{mi}$$

and then convert volume from liters to gallons:

$$213\ \cancel{\text{L}} \times \frac{1.0567\ \cancel{\text{qt}}}{1\ \cancel{\text{L}}} \times \frac{1\ \text{gal}}{4\ \cancel{\text{qt}}} = 56.3\ \text{gal}$$

Finally,

$$(\text{average})\ \text{mileage} = \frac{777\ \text{mi}}{56.3\ \text{gal}} = 13.8\ \text{miles}\ /\ \text{gallon} = 13.8, \text{mpg}$$

Alternatively, the calculation could be set up in a way that uses all the conversion factors sequentially, as follows:

$$\frac{1250\ \cancel{\text{km}}}{213\ \cancel{\text{L}}} \times \frac{0.62137\ \text{mi}}{1\ \cancel{\text{km}}} \times \frac{1\ \cancel{\text{L}}}{1.0567\ \cancel{\text{qt}}} \times \frac{4\ \cancel{\text{qt}}}{1\ \text{gal}} = 13.8\ \text{mpg}$$

(b) Using the previously calculated volume in gallons, we find:

$$56.3\ \cancel{\text{gal}} \times \frac{\$3.80}{1\ \cancel{\text{gal}}} = \$214$$

Exercise 1.3.3

A Toyota Prius Hybrid uses 59.7 L gasoline to drive from San Francisco to Seattle, a distance of 1300 km (two significant digits).

a. What (average) fuel economy, in miles per gallon, did the Prius get during this trip?
b. If gasoline costs $3.90 per gallon, what was the fuel cost for this trip?

Answer available at the end of this section.

Footnotes

- 2 Strictly speaking, the ounce and pound are units of weight, *W* (a force equal to the product of mass and gravitational acceleration, *W* = *mg*). The conversion relations in this table are commonly used to equate masses and weight assuming a nominal value for *g* at the surface of the earth.

Answers

Exercise 1.3.1

8.844 L

Exercise 1.3.2

2.956×10^{-2} L

Exercise 1.3.3

a. 51 mpg
b. $62

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1.4: Significant Figures for Measurements and Calculations

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Count significant figures and round numbers to an appropriate number of significant figures.

Significant Figures in Measurement

Nearly all measurements are limited by the certainty of the measurement tool. There are only two exceptions to this principle:

- **Counting discrete objects.** You either have 11 eggs or 12 eggs. You can't have some partial number in between.
- **Conversion factors.** These are defined equivalencies within or between two unit systems, like 1 foot = exactly 12 inches, 1 gram = exactly 0.001 kg, or 1 in = exactly 2.54 cm.

Significant figures don't apply to these cases. Instead, numbers like this are called **exact numbers** and have an infinite number of significant figure.

All other quantities you'll encounter in chemistry are derived from measurements, which are not exact and instead uncertain to varying extents due to practical limitations of the measurement process used. For example, let's look at the amount of liquid in a graduated cylinder. You should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.

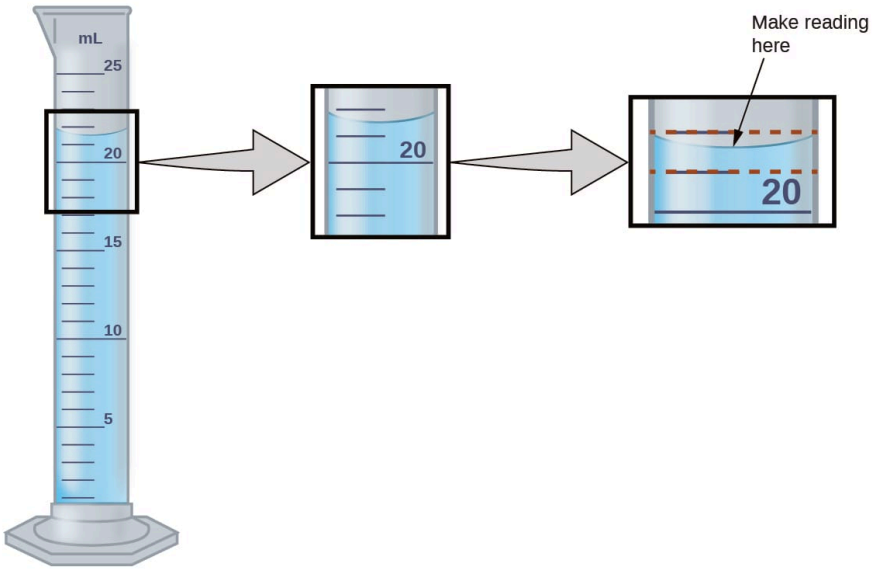


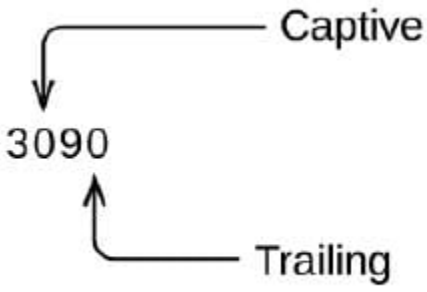
Figure 1.4.1: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

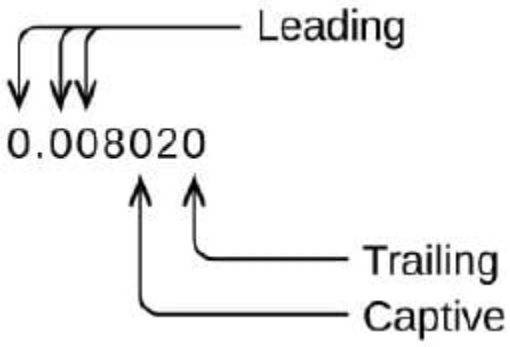
The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

Even if you personally did not make an estimate with your eye, this principle holds true for any measuring tool. For example, if you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. The quarter weighs *about* 6.72 grams, with a nominal uncertainty in the measurement of ± 0.01 gram. If the coin is weighed on a more sensitive balance, the mass might be 6.723 g. This means its mass lies between 6.722 and 6.724 grams, an uncertainty of 0.001 gram. Every measurement has some **uncertainty**, which depends on the device used (and the user's ability). All of the digits in a measurement, including the uncertain last digit, are called **significant figures** or **significant digits**. Note that zero may be a measured value; for example, if you stand on a scale that shows weight to the nearest pound and it shows "120," then the 1 (hundreds), 2 (tens) and 0 (ones) are all significant (measured) values.

Rules for Counting Significant Figures

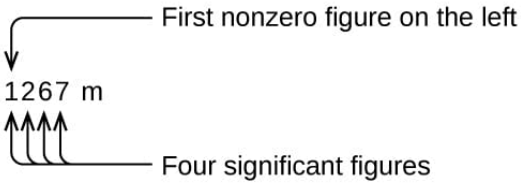
Before we can look at the rules, we need to acknowledge that there are several different types of zeros in a measured quantity: "leading," "trailing," and "captive" are the terms we will use going forward - see the figure below.

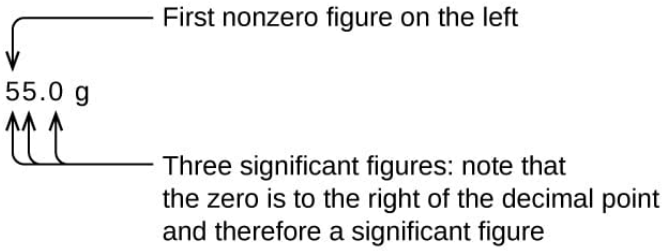




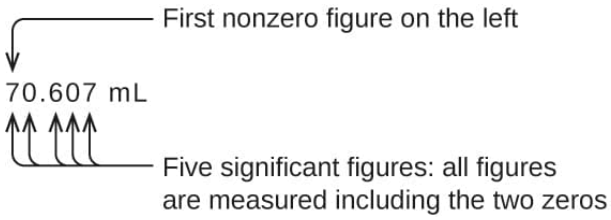
Now that we have the definitions, here are the rules:

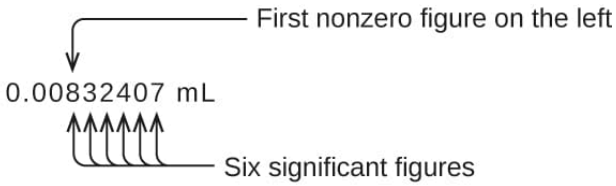
1. **All nonzero digits are significant.** Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.





2. **Captive zeros are always significant.** This is because they result from measurement. See the left-hand example below.
3. **Leading zeros are never significant.** This is because they only tell us where the decimal point is located. See the right-hand example below.

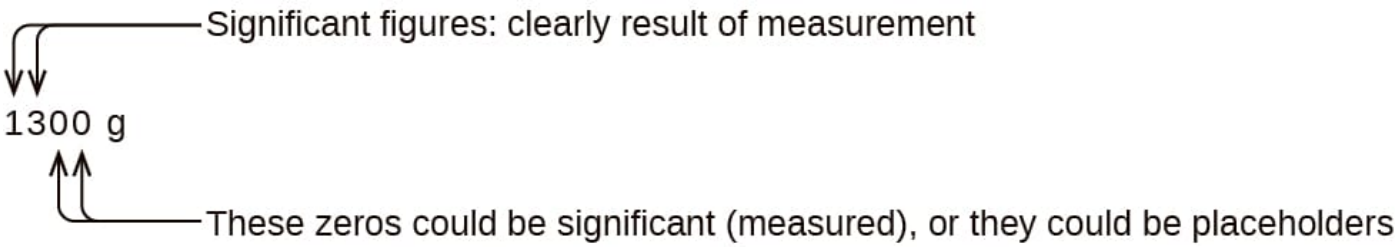




If you are having trouble telling whether to use rule 2 or rule 3, try rewriting the number in scientific notation. In the right-hand example above, we express that number as 8.32407×10^{-3}. This shows that the number 8.32407 contains all of the significant

figures, and 10^{-3} locates the decimal point (non-significant zeros).

4. **Trailing zeros without a decimal point are ambiguous.** For example, the zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located. This number *could* be 1.3×10^3 (two significant figures), 1.30×10^3 (three significant figures, if the tens place was measured), or 1.300×10^3 (four significant figures, if the ones place was also measured). Unless someone tells us, we can't know. Write your answers in scientific notation to resolve this ambiguity. If you come across examples that are ambiguous, ask for more clarity.



Significant Figures in Calculations

As we've said before, most quantities of interest in chemistry are calculated from other measured values. That means it's important to set out rules for performing mathematical operations with significant figures and for rounding the results.

1. **Addition and subtraction:** round the result to the same number of decimal places as the number with the least number of decimal places (the least certain value in terms of addition and subtraction). For example, 1.01 cm + 102 cm = 103.01 cm. However, 102 cm is the least certain number, since it ends at the ones place (versus the hundredths place). Therefore, we report our final calculated result as **103 cm** to reflect the least certain measurement.
2. **Multiplication and division:** round the result to the same number of digits as the number with the least number of significant figures (the least certain value in terms of multiplication and division). For example, 7.505 g/20.1 mL = 0.37338... g/mL. We acknowledge that an infinite number of decimal places is a really silly way to report an answer that came from uncertain measurements. Then, we recognize that 20.1 mL (3 significant figures) is the least certain measurement and round or final answer to **0.373 g/mL**.
3. **Rounding:** we'll have to look at the digit to be dropped
   - If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, “round down” and leave the retained digit unchanged. Examples: 18.3384 rounds “down” to 18.3 (the dropped digit, 3, is less than 5)
   - if the digit to be dropped is more than 5, “round up” and increase the retained digit by 1. Example: 0.028675 rounds “up” to 0.0287 (the dropped digit, 7, is greater than 5)
   - If the dropped digit is 5, and it’s either the last digit in the number or it’s followed only by zeros, round up or down, whichever yields an even value for the retained digit. If any nonzero digits follow the dropped 5, round up. (The last part of this rule may strike you as a bit odd, but it’s based on reliable statistics and is aimed at avoiding any bias when dropping the digit “5,” since it is equally close to both possible values of the retained digit.)
     - 6.8752 rounds “up” to 6.88 (the dropped digit is 5, and a nonzero digit follows it)
     - 92.85 rounds “down” to 92.8 (the dropped digit is 5, and the retained digit is even)

Let’s work through these rules with a few examples.

Example 1.4.1: Rounding Numbers

Round the following to the indicated number of significant figures:

a. 31.57 (to two significant figures)
b. 8.1649 (to three significant figures)
c. 0.051065 (to four significant figures)
d. 0.90275 (to four significant figures)

Solution

a. 31.57 rounds “up” to 32 (the dropped digit is 5, and the retained digit is even)
b. 8.1649 rounds “down” to 8.16 (the dropped digit, 4, is less than 5)
c. 0.051065 rounds “down” to 0.05106 (the dropped digit is 5, and the retained digit is even)
d. 0.90275 rounds “up” to 0.9028 (the dropped digit is 5, and the retained digit is even)

Exercise 1.4.1

Round the following to the indicated number of significant figures:

a. 0.424 (to two significant figures)
b. 0.0038661 (to three significant figures)
c. 421.25 (to four significant figures)
d. 28,683.5 (to five significant figures)

Answer available at the end of this section.

Example 1.4.2: Addition and Subtraction with Significant Figures

Rule: When adding or subtracting numbers, round the result to the same number of decimal places as the number with the fewest decimal places (i.e., the least certain value in terms of addition and subtraction).

a. Add 1.0023 g and 4.383 g.
b. Subtract 421.23 g from 486 g.

Solution

(a)

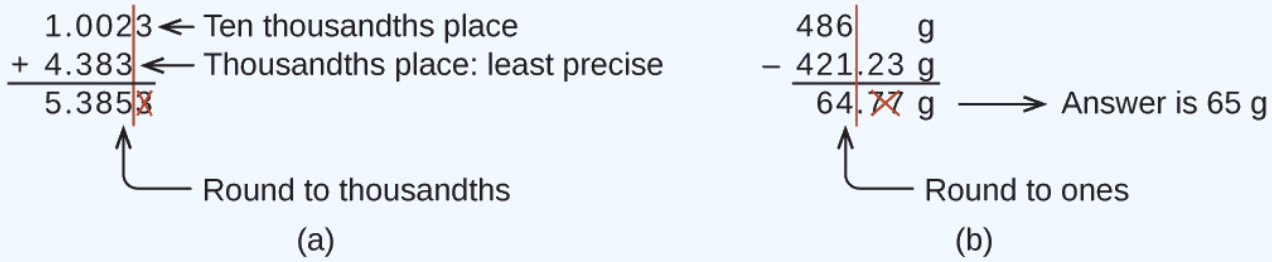
$$\begin{array}{rr} & 1.0023\,\text{g} \\ + & 4.383\,\text{g} \\ \hline & 5.3853\,\text{g} \end{array}$$

Answer is 5.385 g (round to the thousandths place; three decimal places)

(b)

$$\begin{array}{rr} & 486\,\text{g} \\ - & 421.23\,\text{g} \\ \hline & 64.77\,\text{g} \end{array}$$

Answer is 65 g (round to the ones place; no decimal places)



Exercise 1.4.2

a. Add 2.334 mL and 0.31 mL.
b. Subtract 55.8752 m from 56.533 m.

Answer available at the end of this section.

Example 1.4.3: Multiplication and Division with Significant Figures

Rule: When multiplying or dividing numbers, round the result to the same number of digits as the number with the fewest significant figures (the least certain value in terms of multiplication and division).

a. Multiply 0.6238 cm by 6.6 cm.
b. Divide 421.23 g by 486 mL.

Solution

(a)

$$\underbrace{0.6238\,\text{cm}}_{\text{four significant figures}} \times \underbrace{6.6\,\text{cm}}_{\text{two significant figures}} = 4.11708\,\text{cm}^2 \rightarrow \underbrace{4.1\,\text{cm}^2}_{\text{round to two significant figures}}$$

(b)

$$\underbrace{421.23\,\text{g}}_{\text{five significant figures}} \div \underbrace{486\,\text{mL}}_{\text{three significant figures}} = 0.866728\ldots\,\text{g/mL} \rightarrow \underbrace{0.867\,\text{g/mL}}_{\text{round to three significant figures}}$$

Exercise 1.4.3

a. Multiply 2.334 cm and 0.320 cm.
b. Divide 55.8752 m by 56.53 s.

Answer available at the end of this section.

In the midst of all these technicalities, it is important to keep in mind the reason for these rules about significant figures and rounding—to correctly represent the certainty of the values reported and to ensure that a calculated result is not represented as being more certain than the least certain value used in the calculation.

Example 1.4.4: Calculation with Significant Figures

One common bathtub is 13.44 dm long, 5.920 dm wide, and 2.54 dm deep. Assume that the tub is rectangular and calculate its approximate volume in liters.

Solution

$$\begin{aligned} V &= l \times w \times d \\ &= 13.44\,\text{dm} \times 5.920\,\text{dm} \times 2.54\,\text{dm} \\ &= 202.09459\ldots\,\text{dm}^3 \text{ (value from calculator)} \\ &= 202\,\text{dm}^3 \text{ or } 202\,\text{L} \text{ (answer rounded to three significant figures)} \end{aligned}$$

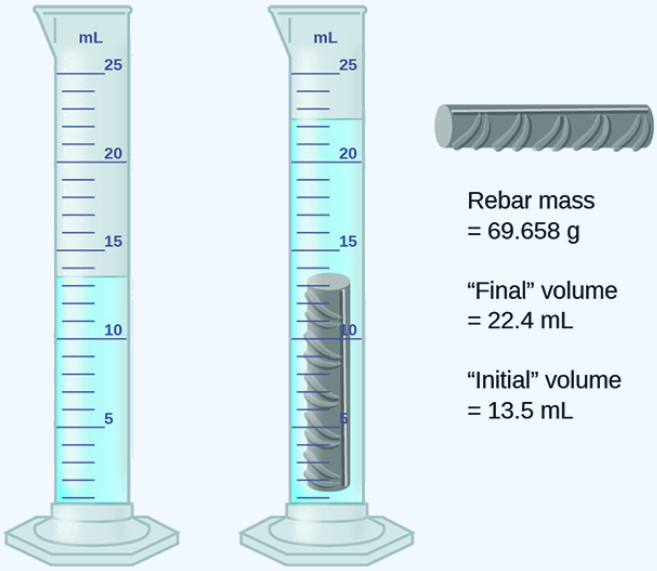
Exercise 1.4.4

What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer available at the end of this section.

Example 1.4.5: Experimental Determination of Density Using Water Displacement

A piece of rebar is weighed and then submerged in a graduated cylinder partially filled with water, with results as shown.



a. Use these values to determine the density of this piece of rebar.
b. Rebar is mostly iron. Does your result in (a) support this statement? How?

Solution

The volume of the piece of rebar is equal to the volume of the water displaced:

$$\text{volume} = 22.4\,\text{mL} - 13.5\,\text{mL} = 8.9\,\text{mL} = 8.9\,\text{cm}^3$$

(rounded to the nearest 0.1 mL, per the rule for addition and subtraction)

The density is the mass-to-volume ratio:

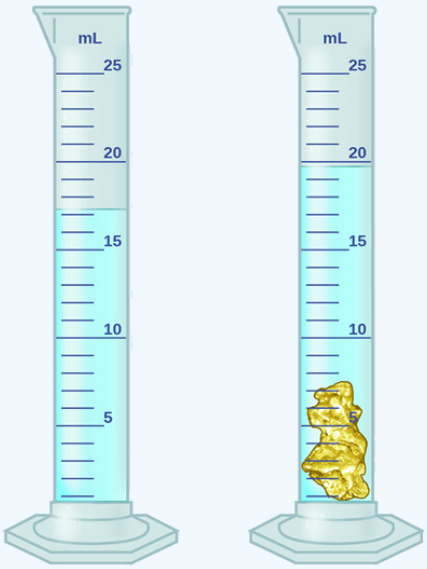
$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658\,\text{g}}{8.9\,\text{cm}^3} = 7.8\,\text{g/cm}^3$$

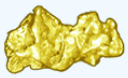
(rounded to two significant figures, per the rule for multiplication and division)

The density of iron is 7.9 g/cm^3, very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

Exercise 1.4.5

An irregularly shaped piece of a shiny yellowish material is weighed and then submerged in a graduated cylinder, with results as shown.





Mass
= 51.842 g

“Final” volume
= 19.8 mL

“Initial” volume
= 17.1 mL

a. Use these values to determine the density of this material.
b. Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

Answer available at the end of this section.

Answers

Exercise 1.4.1

a. 0.42
b. 0.00387
c. 421.2
d. 28,684

Exercise 1.4.2

a. 2.64 mL
b. 0.658 m

Exercise 1.4.3

a. 0.747 cm^2
b. 0.9884 m/s

Exercise 1.4.4

1.034 g/mL

Exercise 1.4.5

19 g/cm^3

It is likely gold; the right appearance for gold and very close to the known density of gold at $19.3\ g/cm^3$

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1.5: Accuracy and Precision of Experimental Results (lab topic)

Learning Objectives

By the end of this section, you will have background that will help you be able to:

- Define accuracy and precision
- Identify whether experimental datasets are accurate/inaccurate or precise/imprecise

Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to evaluate both the precision and the accuracy of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 1.5.2).

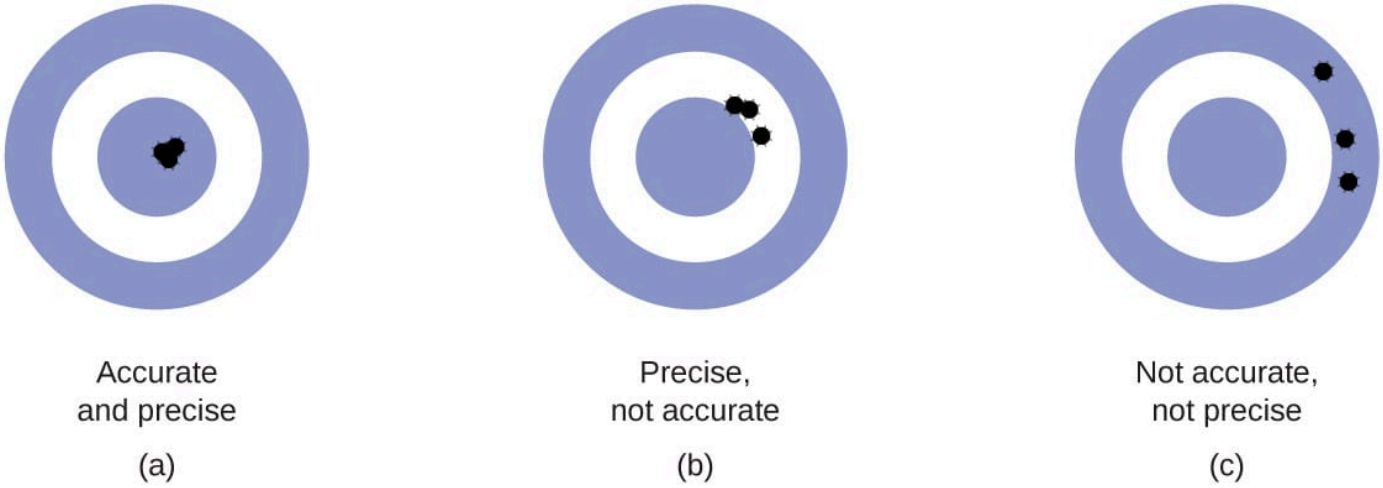


Figure 1.5.2: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Scientific Definitions of Accuracy and Precision

These are the definitions that we will use for evaluating the accuracy and precision of data in General Chemistry. Outside of this class, the bar is actually higher, so don't be surprised if you see other definitions elsewhere.

- Experimental results are **accurate** when the **percent error** is 5% or less OR when the **percent yield** is 95% or higher.
  - Percent error is the difference between a theoretical value and your experimental value. You use it when you measured or calculated an experimental value and want to compare it to something accepted. It is calculated as

$$\text{Percent Error} = \left| \frac{\text{Experimental Value} - \text{Theoretical Value}}{\text{Theoretical Value}} \right| \times 100\% \tag{1.5.1}$$

  - Percent yield is a ratio comparing how much you, personally, got in an experiment versus what you expected to get. It's typically used when you collect a solid, liquid, or gaseous product. It is calculated as

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\% \tag{1.5.2}$$

- Experimental results are **precise** when the **percent relative standard deviation** is 5% or less or the **R^2 value** for a linear fit is 0.95 or higher.
  - Percent relative standard deviation is a ratio comparing the amount of spread in your data (standard deviation) to the average of your experimental values. You will never have to calculate standard deviation by hand - we will teach you to use Microsoft Excel to do this. You use it when you have performed multiple trials of the same experiment. Calculate percent relative standard deviation as

$$\%\text{relative standard deviation} = \frac{standard deviation}{average} \times 100\% \tag{1.5.3}$$

  - R^2 is a measure of how linear a set of experimental values is. If R^2 = 1, that means the data are perfectly linear. If you are using R^2, we will consider a value of 0.95 or higher "linear enough" to be precise.

Applying the Definitions

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in Table 1.5.1.

Table 1.5.1: Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers

Dispenser #1	Dispenser #2	Dispenser #3
279.3	275.3	296.1
279.1	270.2	295.9
278.9	309.0	296.1
279.0	289.8	296.0
279.1	308.0	296.1

Considering these results, she will draw the following conclusions:

- **Dispenser #1** has a standard deviation of 0.15 mL and an average of 279.1 mL. It is precise (percent relative standard deviation of 0.05%) but not accurate (percent error 6%).
- **Dispenser #2** has a standard deviation of 18 mL and an average of 209.5 mL. It is not precise (percent relative standard deviation of 6 %), but it is accurate (percent error 2%)
- **Dispenser #3** has a standard deviation of 0.09 mL and an average of 296.0 mL. It is precise (percent relative standard deviation 0.03%) and accurate (percent error 0.03%). Note that even though the average (296.0 mL) matches the theoretical value of 296 mL, the percent error is not zero. That is because these values are reported according to significant figure rules, but the percent error calculation was performed on unrounded values.

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2: ATOMS MAKE UP IONIC AND COVALENT COMPOUNDS

2.1: Overview and Objectives
2.2: Atomic Structure and Symbolism
2.3: The Periodic Table
2.4: Molecular and Ionic Compounds
2.5: Chemical Nomenclature

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2.1: Overview and Objectives

> "It is useful in this sense to make a clear distinction between the conception of an element as a separate homogenous substance and as a material but invisible part of a compound." (Dimitri Mendeleev)

Mendeleev was not the first person to propose a periodic table of the known chemical elements. It was, though, his periodic table that stuck in our minds and our textbooks, in no small part because Mendeleev was the first person with the audacity to use his periodic table to leave "holes" for what he predicted were yet-to-be-discovered elements. In this chapter, we'll learn about the basics of atomic structure and how this forms the basis for repeating, periodic properties of the elements. We'll also look at how chemical elements come together to form compounds in well-defined, whole-number ratios, and talk about how to name some of those compounds.

Chapter Objectives

- Classify chemical elements by numbers of protons/neutrons/electrons, type (metal, nonmetal, metalloid), or group (alkali metal, alkaline earth metal, halogen, noble gas).
- Determine chemical formulas, names, and molar masses for binary covalent compounds and ionic compounds.

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2.2: Atomic Structure and Symbolism

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Classify chemical elements by numbers of protons/neutrons/electrons, type (metal, nonmetal, metalloid), or group (alkali metal, alkaline earth metal, halogen, noble gas).

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure 2.2.1).

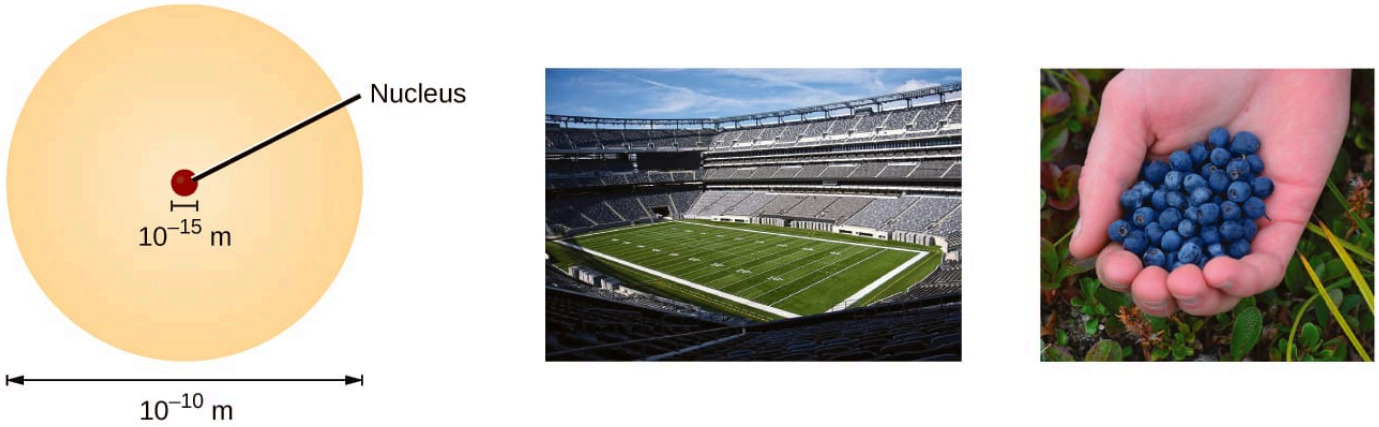


Figure 2.2.1: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber)

Because atoms—and the protons, neutrons, and electrons that compose them—are extremely small, we decribe them with appropriately small units of measure, such as the atomic mass unit (amu) and the fundamental unit of charge (e) The amu is currently defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as "carbon-12" as will be discussed later in this module.) Thus, one amu is exactly $\frac{1}{12}$ of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The **Dalton** (Da) and the **unified atomic mass** unit (u) are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C.

Table 2.2.1 summarizes the location, mass, and charge of each of the subatomic particles. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than 12.00 amu. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table 2.2.1: Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	$-1.602\ 10^{-19}$	1–	0.00055	$0.00091\ 10^{-24}$
proton	nucleus	$1.602\ 10^{-19}$	1+	1.00727	$1.67262\ 10^{-24}$

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
neutron	nucleus	0	0	1.00866	$1.67493\ 10^{-24}$

Classifying Chemical Elements

There are two properties of an element that are important to its description. First, the number of protons in the nucleus of an atom is its **atomic number** (Z). Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. Second, the total number of protons and neutrons in an atom is called its **mass number** (A). The number of neutrons is therefore the difference between the mass number and the atomic number: A – Z = number of neutrons.

$$\begin{aligned} \text{atomic number } (Z) &= \text{ number of protons} \\ \text{mass number } (A) &= \text{ number of protons } + \text{ number of neutrons} \\ A - Z &= \text{ number of neutrons} \end{aligned}$$

Atoms do not have to be electrically neutral (contain the same number of positively charged protons and negatively charged electrons). When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an **ion**. The charge of an atom is defined as follows:

$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

Atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an **anion**. Positively charged atoms called **cations** are formed when an atom loses one or more electrons. For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 – 10 = 1+). A neutral oxygen atom (Z = 8) has eight electrons, and if it gains two electrons it will become an anion with a 2– charge (8 – 10 = 2–).

Example 2.2.1: Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 2.2.2).

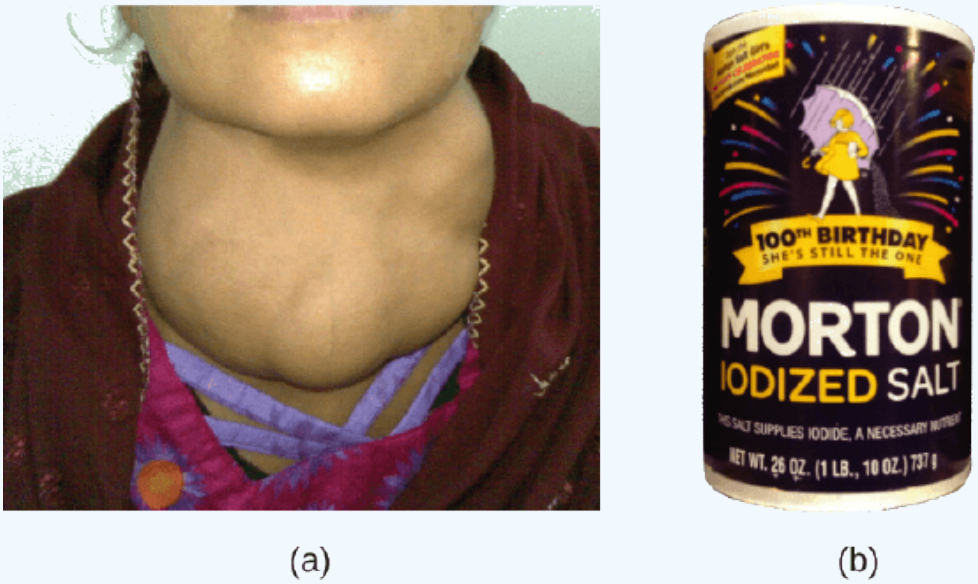


Figure 2.2.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by "Almazi"/Wikimedia Commons; credit b: modification of work by Mike Mozart)

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1– charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 (127 – 53 = 74). Since the iodine is added as a 1– anion, the number of electrons is 54 [53 – (1–) = 54].

Exercise 2.2.1

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

Answer available at the end of this section.

Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure 2.2.3). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).



Figure 2.2.3: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury.

The periodic table (see next section) lists the elements according to their chemical symbols by increasing atomic number. It is important to note that capitalization matters when writing element symbols: tor example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O).

Isotopes

It is possible for two atoms to have the same identity (same atomic number), but to have different numbers of neutrons (different mass number). These are called isotopes. The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure 2.2.4). The atomic number is sometimes written as a subscript preceding

the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ^{25}Mg is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

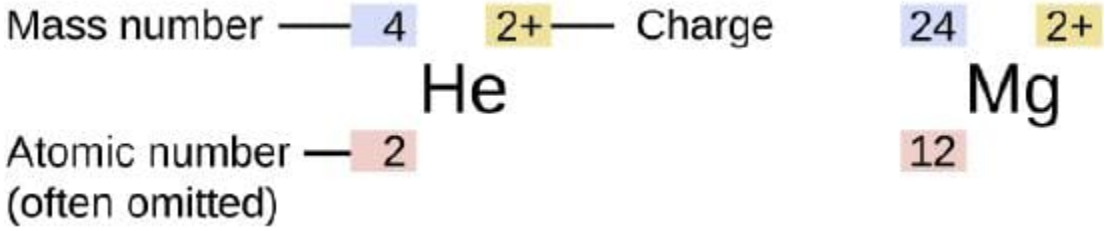


Figure 2.2.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Atomic Mass

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

$$\text{average mass } = \sum_i (\text{ fractional abundance } \times \text{ isotopic mass })_i$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

$$\begin{aligned}\text{boron average mass } &= (0.199 \times 10.0129\,\text{amu}) + (0.801 \times 11.0093\,\text{amu}) \\ &= 1.99\,\text{amu} + 8.82\,\text{amu} \\ &= 10.81\,\text{amu}\end{aligned}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

Example 2.2.2: Calculation of Average Atomic Mass

A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution

$$\begin{aligned}\text{average mass } &= (0.9184 \times 19.9924\,\text{amu}) + (0.0047 \times 20.9940\,\text{amu}) + (0.0769 \times 21.9914\,\text{amu} \\ &= (18.36 + 0.099 + 1.69)\,\text{amu} \\ &= 20.15\,\text{amu}\end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

Exercise 2.2.2

A sample of magnesium is found to contain 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

Answer available at the end of this section.

We can also do variations of this type of calculation, as shown in the next example.

Example 2.2.3: Calculation of Percent Abundance

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

Solution

The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl.

$$\text{average mass } = \left(\text{ fraction of } {}^{35}Cl \times \text{ mass of } {}^{35}Cl\right) + \left(\text{ fraction of } {}^{37}Cl \times \text{ mass of } {}^{37}Cl\right)$$

If we let *x* represent the fraction that is ^{35}Cl, then the fraction that is ^{37}Cl is represented by 1.00 – *x*.

(The fraction that is ^{35}Cl + the fraction that is ^{37}Cl must add up to 1, so the fraction of ^{37}Cl must equal 1.00 – the fraction of ^{35}Cl.)

Substituting this into the average mass equation, we have:

$$\begin{aligned} 35.453amu &= (x \times 34.96885amu) + [(1.00 - x) \times 36.96590amu] \\ 35.453 &= 34.96885x + 36.96590 - 36.96590x \\ 1.99705x &= 1.513 \\ x &= \frac{1.513}{1.99705} = 0.7576 \end{aligned}$$

So solving yields: *x* = 0.7576, which means that 1.00 – 0.7576 = 0.2424. Therefore, chlorine consists of 75.76% ^{35}Cl and 24.24% ^{37}Cl.

Exercise 2.2.3

Naturally occurring copper consists of ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?

Answer available at the end of this section.

Answers

Exercise 2.2.1

78 protons; 117 neutrons; charge is 4+

Exercise 2.2.2

24.31 amu

Exercise 2.2.3

69.15% Cu-63 and 30.85% Cu-65

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2.3: The Periodic Table

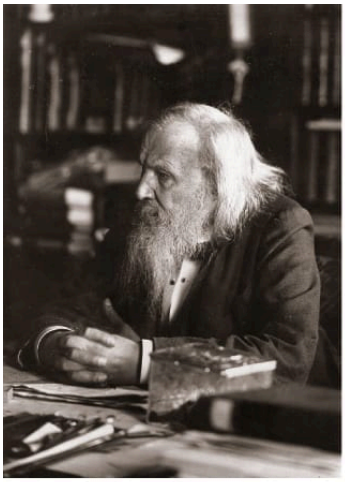
Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Classify chemical elements by numbers of protons/neutrons/electrons, type (metal, nonmetal, metalloid), or group (alkali metal, alkaline earth metal, halogen, noble gas).

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure 2.3.1).



(a)

Reihen	Gruppo I. — R^1O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=86	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(b)

Figure 2.3.1: (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by "Den fjättrade ankan"/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 2.3.2). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called **periods** or **series**, and 18 vertical columns, called **groups**. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are

usually written below the main body of the table.

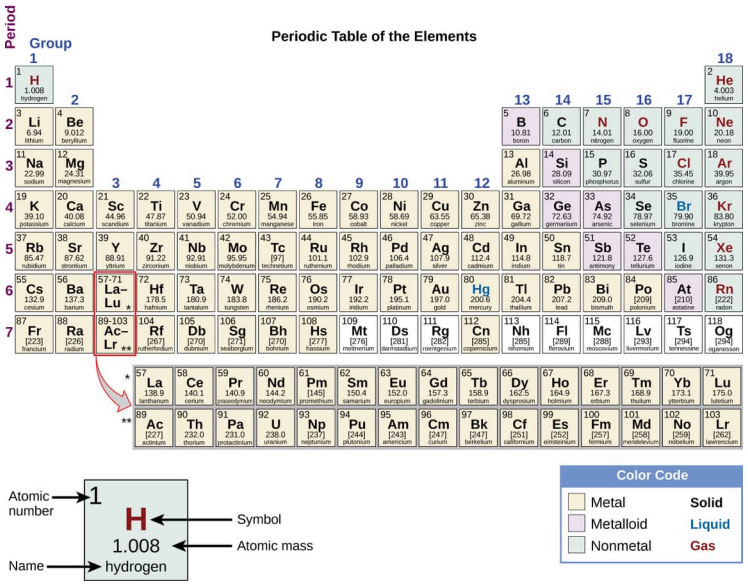


Figure 2.3.2: Elements in the periodic table are organized according to their properties.

Even after the periodic nature of elements and the table itself were widely accepted, gaps remained. Mendeleev had predicted, and others including Henry Moseley had later confirmed, that there should be elements below Manganese in Group 7. German chemists Ida Tacke and Walter Noddack set out to find the elements, a quest being pursued by scientists around the world. Their method was unique in that they did not only consider the properties of manganese, but also the elements horizontally adjacent to the missing elements 43 and 75 on the table. Thus, by investigating ores containing minerals of ruthenium (Ru), tungsten (W), osmium (Os), and so on, they were able to identify naturally occurring elements that helped complete the table. Rhenium, one of their discoveries, was one of the last natural elements to be discovered and is the last stable element to be discovered. (Francium, the last natural element to be discovered, was identified by Marguerite Perey in 1939.)

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: **metals** (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); **nonmetals** (elements that appear dull, poor conductors of heat and electricity—shaded green); and **metalloids** (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the main-group elements (or representative elements) in the columns labeled 1, 2, and 13–18; the transition metals in the columns labeled 3–12[3]; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure 2.3.3). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as **alkali metals**, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called **alkaline earth metals**, with similar properties among members of that group. Other groups with specific names are the **pnictogens** (group 15), **chalcogens** (group 16), halogens (group 17), and the **noble gases** (group 18, also known as inert gases). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

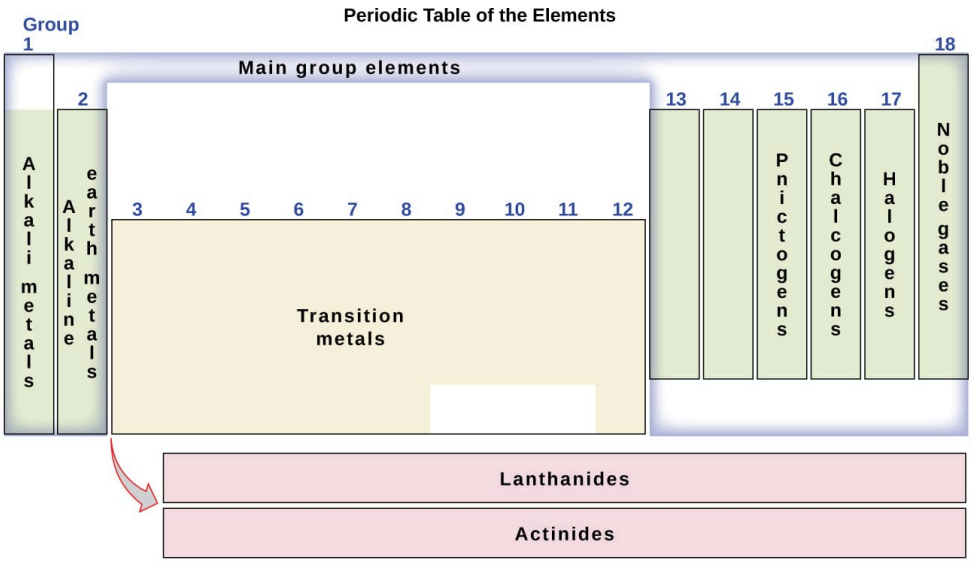


Figure 2.3.3: The periodic table organizes elements with similar properties into groups.

Link to Learning

Click on this link for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element). You may also want to try this one that shows photos of all the elements.

Example 2.3.1: Naming Groups of Elements

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

a. chlorine
b. calcium
c. sodium
d. sulfur

Solution

The family names are as follows:

a. halogen
b. alkaline earth metal
c. alkali metal
d. chalcogen

Exercise 2.3.1

Give the group name for each of the following elements:

a. krypton
b. selenium
c. barium
d. lithium

Answer available at the end of this section.

As you will learn in your further study of chemistry, elements in groups often behave in a somewhat similar manner. This is partly due to the number of electrons in their outer shell and their similar readiness to bond. These shared properties can have far-ranging implications in nature, science, and medicine. For example, when Gertrude Elion and George Hitchens were investigating ways to interrupt cell and virus replication to fight diseases, they utilized the similarity between sulfur and oxygen (both in Group 16) and their capacity to bond in similar ways. Elion focused on purines, which are key components of DNA and which contain oxygen. She found that by introducing sulfur-based compounds (called purine analogues) that mimic the structure of purines, molecules within DNA would bond to the analogues rather than the "regular" DNA purine. With the normal DNA bonding and structure altered, Elion successfully interrupted cell replication. At its core, the strategy worked because of the similarity between sulfur and oxygen. Her discovery led directly to important treatments for leukemia. Overall, Elion's work with George Hitchens not only led to more treatments, but also changed the entire methodology of drug development. By using specific elements and compounds to target specific aspects of tumor cells, viruses, and bacteria, they laid the groundwork for many of today's most common and important medicines, used to help millions of people each year. They were awarded the Nobel Prize in 1988.

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (an approximate atomic mass) of the most stable isotope of that element.

Footnotes

- 3Per the IUPAC definition, group 12 elements are not transition metals, though they are often referred to as such. Additional details on this group's elements are provided in a chapter on transition metals and coordination chemistry.

Answers

Exercise 2.3.1

(a) noble gas; (b) chalcogen; (c) alkaline earth metal; (d) alkali metal

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2.4: Molecular and Ionic Compounds

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Determine chemical formulas, names, and molar masses for binary covalent compounds and ionic compounds.

What are Ions?

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure 2.4.1).

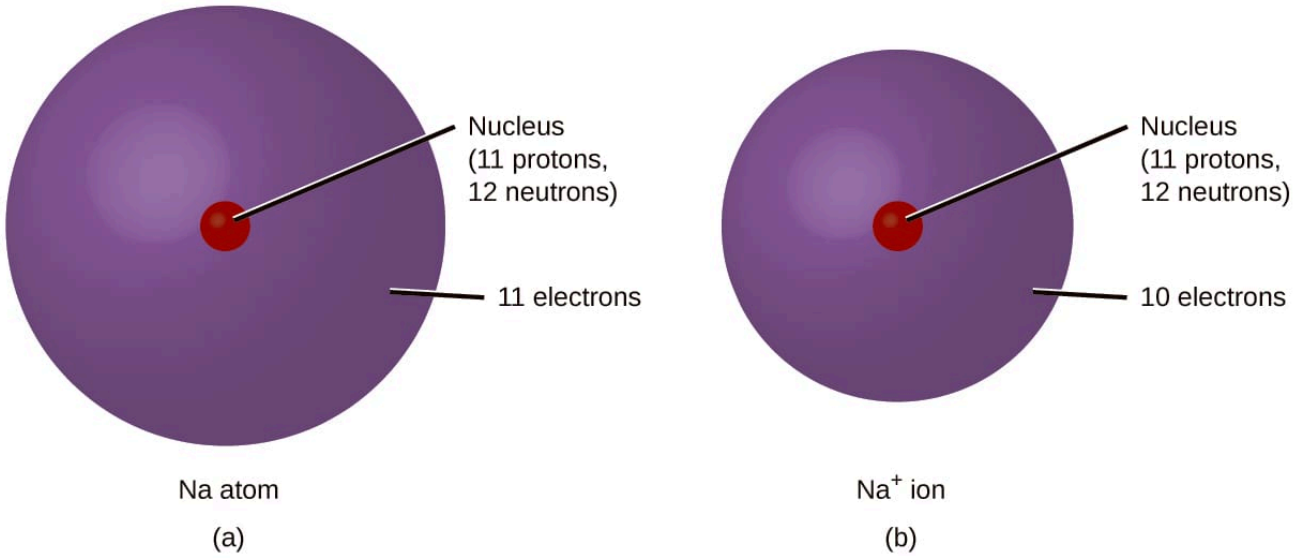


Table 2.4.1: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 2.4.2). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1– ions; group 16 elements (two groups left) form 2– ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

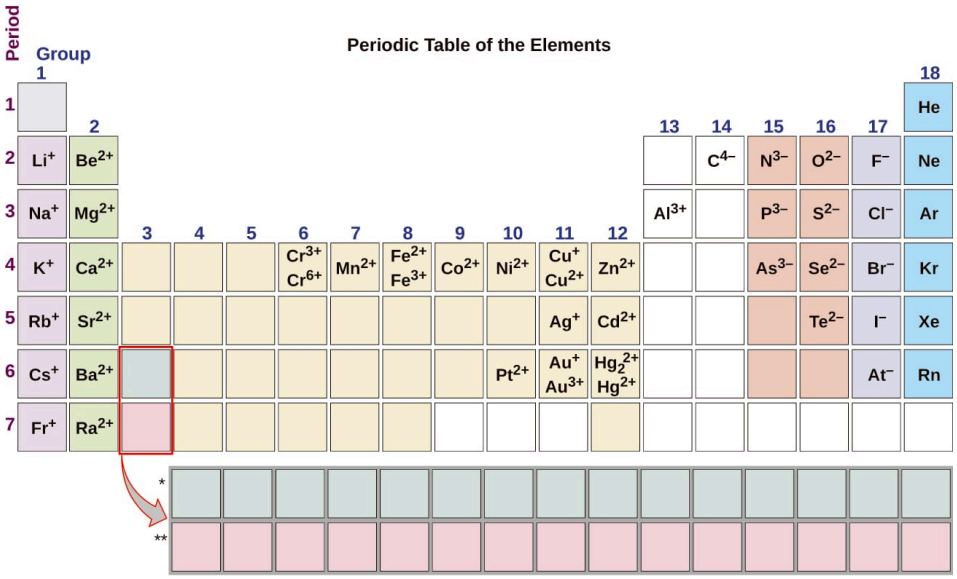


Table 2.4.2: Some elements exhibit a regular pattern of ionic charge when they form ions.

Example 2.4.1: Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al^{3+}.

Exercise 2.4.1

Give the symbol and name for the ion with 34 protons and 36 electrons.

Answer available at the end of this section.

Example 2.4.2: Formation of Ions

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+}, and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3–. The symbol for the ion is N^{3-}, and it is called a nitride ion.

Exercise 2.4.2

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Answer available at the end of this section.

The ions that we have discussed so far are called monatomic ions, that is, they are ions formed from only one atom. We also find many polyatomic ions. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 2.4.1. Oxyanions are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Table 2.4.1: Common Polyatomic Ions to Memorize

Name	Formula
ammonium	NH_4^+
peroxide	O_2^{2-}
hydroxide	OH^-
acetate	CH_3COO^-
cyanide	CN^-
carbonate	CO_3^{2-}
bicarbonate	HCO_3^-
nitrate	NO_3^-
nitrite	NO_2^-
sulfate	SO_{42}^-
sulfite	SO_3^{2-}
phosphate	PO_4^{3-}
perchlorate	ClO_4^-
chlorate	ClO_3^-
chlorite	ClO_2^-
hypochlorite	ClO^-
chromate	CrO_4^{2-}
dichromate	$Cr_2O_7^{2-}$
permanganate	MnO_4^-

Note that there is a system for naming some polyatomic ions; -ate and -ite are suffixes designating polyatomic ions containing more or fewer oxygen atoms. Per- (short for “hyper”) and hypo- (meaning “under”) are prefixes meaning more oxygen atoms than -ate and fewer oxygen atoms than -ite, respectively. For example, perchlorate is ClO_4^-, chlorate is ClO_3^-, chlorite is ClO_2^- and hypochlorite is ClO^-. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is NO_3^- while sulfate is SO_4^{2-}. This will be covered in more detail in the next module on nomenclature.

Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For

example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^-, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form $CaCl_2$, which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

A compound that contains ions and is held together by electrostatic forces of attraction (a.k.a. ionic bonds) is called an ionic compound. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, $AlCl_3$, is not ionic).

Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow ("electricity" is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid (Figure 2.4.3).

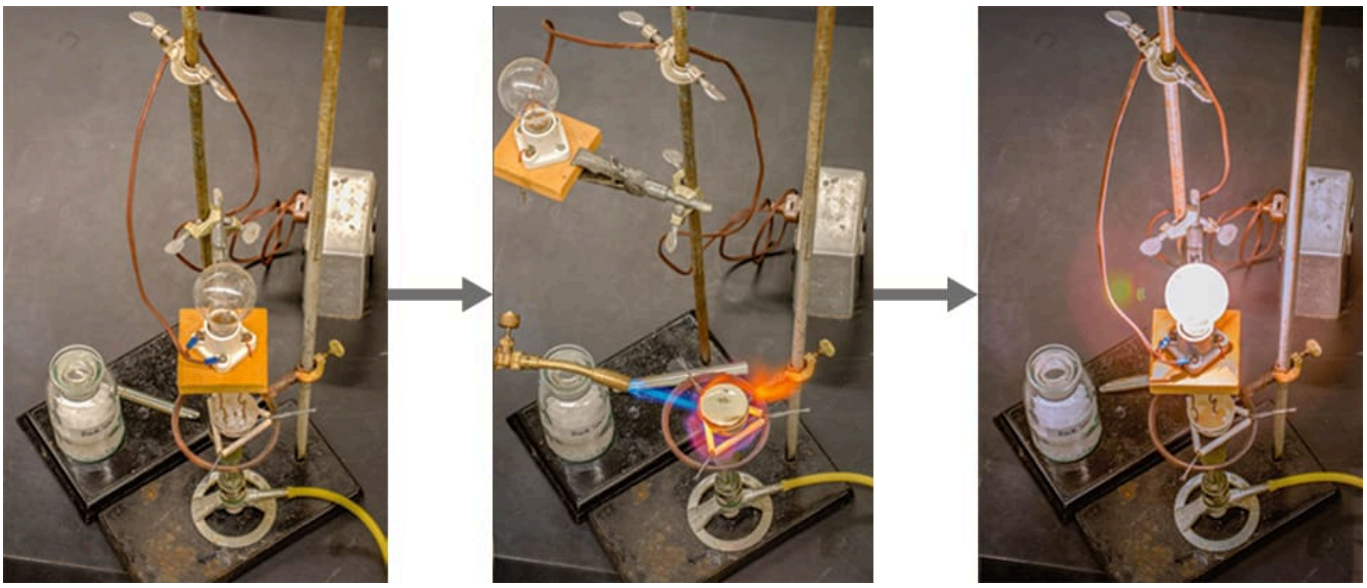


Table 2.4.3: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

Link to Learning

Watch this video to see a mixture of salts melt and conduct electricity.

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Example 2.4.3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 2.4.4) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?



Table 2.4.4: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko via Wikipedia)

Solution

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2–, would give us six negative charges. The formula would be Al_2O_3.

Exercise 2.4.3

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer available at the end of this section.

Many ionic compounds contain polyatomic ions (Table 2.4.1) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate ($PO_4{}^{3-}$) groups. The $PO_4{}^{3-}$ groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3–. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 2.4.4: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $H_2PO_4{}^-$. What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $H_2PO_4{}^-$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

Exercise 2.4.4

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, O_2^{2-} (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Answer available at the end of this section.

Molecular (Covalent) Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These molecular compounds (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

Example 2.4.5: Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

a. KI, the compound used as a source of iodine in table salt
b. H_2O_2, the bleach and disinfectant hydrogen peroxide
c. $CHCl_3$, the anesthetic chloroform
d. Li_2CO_3, a source of lithium in antidepressants

Solution

a. Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
b. Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be molecular.
c. Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; $CHCl_3$ is predicted to be molecular.
d. Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

Exercise 2.4.5

Using the periodic table, predict whether the following compounds are ionic or covalent:

a. SO_2
b. CaF_2
c. N_2H_4
d. $Al_2(SO_4)_3$

Answer available at the end of this section.

Answers

Exercise 2.4.1

Se^{2-}, the selenide ion

Exercise 2.4.2

Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Carbon will form an anion with a charge of 4–: C^{4-}, a carbide ion.

Exercise 2.4.3

Na_2S

Exercise 2.4.4

Li_2O_2

Exercise 2.4.5

a. molecular
b. ionic
c. molecular
d. ionic

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2.5: Chemical Nomenclature

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Determine chemical formulas, names, and molar masses for binary covalent compounds and ionic compounds.

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. The simplest of these are **binary compounds**, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions. We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *–ide*). Some examples are given in Table 2.5.1.

Table 2.5.1: Names of Some Ionic Compounds

NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e. by naming first the cation and then the anion. Examples are shown in Table 2.5.2.

Table 2.5.2: Names of Some Polyatomic Ionic Compounds

$KC_2H_3O_2$, potassium acetate	NH_4Cl, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

Chemistry in Everyday Life: Ionic Compounds in Your Cabinet

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 2.5.3. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table 2.5.3: Everyday Ionic Compounds

Ionic Compound	Use
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to “iodized” salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
$NaHCO_3$, sodium bicarbonate	baking soda; used in cooking (and as antacid)
Na_2CO_3, sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
$CaCO_3$ calcium carbonate	ingredient in antacids
$Mg(OH)_2$, magnesium hydroxide	ingredient in antacids
$Al(OH)_3$, aluminum hydroxide	ingredient in antacids
NaOH, sodium hydroxide	lye; used as drain cleaner
K_3PO_4, potassium phosphate	food additive (many purposes)
$MgSO_4$, magnesium sulfate	added to purified water
Na_2HPO_4, sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3, sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge (Transition Metals)

Most of the transition metals and some main group metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+ (see Figure 2.29), and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table 2.5.4.

Table 2.5.4: Some Ionic Compounds with Variably Charged Metal Ions

Compound	Name
$FeCl_2$	iron(II) chloride
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide

Compound	Name
SnF_2	tin(II) fluoride
SnF_4	tin(IV) fluoride

Out-of-date nomenclature used the suffixes *–ic* and *–ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Molecular (Covalent) Compounds

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table 2.5.5.

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table 2.5.6.

Table 2.5.6: Names of Some Molecular Compounds Composed of Two Elements

Compound	Name	Compound	Name
SO_2	sulfur dioxide	BCl_3	boron trichloride
SO_3	sulfur trioxide	SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide	PF_5	phosphorus pentafluoride
N_2O_4	dinitrogen tetroxide	P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide	IF_7	iodine heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

Example 2.5.2: Naming Covalent Compounds

Name the following covalent compounds:

a. SF_6
b. N_2O_3
c. Cl_2O_7
d. P_4O_6

Solution

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

a. sulfur hexafluoride
b. dinitrogen trioxide
c. dichlorine heptoxide
d. tetraphosphorus hexoxide

Exercise 2.5.2

Write the formulas for the following compounds:

a. phosphorus pentachloride
b. dinitrogen monoxide
c. iodine heptafluoride
d. carbon tetrachloride

Answer available at the end of this section.

Link to Learning

The following website provides practice with naming chemical compounds and writing chemical formulas. You can choose binary, polyatomic, and variable charge ionic compounds, as well as molecular compounds.

Answers

Exercise 2.5.2

(a) PCl_5; (b) N_2O; (c) IF_7; (d) CCl_4

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3: CHEMICAL COMPOSITION INVOLVES FIXED ATOMIC RATIOS

3.1: Overview and Objectives

3.2: Formula Mass and the Mole Concept

3.3: Determining Empirical and Molecular Formulas

3.4: Molarity

3.5: Writing and Balancing Chemical Equations

3.6: Classifying Chemical Reactions

3.7: Reaction Stoichiometry

3.8: Reaction Yields

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3.1: Overview and Objectives

> "We may lay it down as an incontestable axiom, that, in all the operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment; the quality and quantity of the elements remain precisely the same; and nothing takes place beyond changes and modifications in the combination of these elements. Upon this principle the whole art of performing chemical experiments depends: We must always suppose an exact equality between the elements of the body examined and those of the products of its analysis." (Antoine Lavoisier)

When Antoine Lavoisier began his work in the late 18th century, chemistry was barely considered a science. Its prevailing theories came more from commitments to Greek philosophy, especially the four elements of air, water, earth, and fire. In Lavoisier's time, the prevailing theory was that substances that burned lost mass because they were releasing some universal substance, called *phlogiston,* to the air. New experiments were beginning to show, however, that this was not correct - in particular, some showed that certain chemicals *lost* mass when burning (consistent with the phologiston theory), while others *gained* mass (inconsistent with the phologiston theory). Lavoisier's careful work instead showed that air itself was composed of multiple elements, one of which came to be called *oxygen*, and that when substances burned, new substances were produced. What remained the same throughout was the combined *mass* of the starting materials (reactants) and ending materials (products). This law of the conservation of mass is the foundation for our modern understanding of what happens in chemical reactions.

In this chapter, we will learn the basics of *stoichiometry*. This consists of two parts. First, we will learn how to quantitatively describe the composition of mixtures in terms of chemical names, mass (grams), numbers of particles (molecules/ions/moles), or concentration (molarity). Then, we will apply Lavoisier's discovery in the context of chemical reactions, using it to classify chemical reactions by their type and to accurately predict the masses, particle numbers, or concentrations of reactants and products before or after a chemical reaction.

Chapter Objectives

- Describe the composition of a sample before or after a chemical reaction using relevant information (chemical formulas, mass, Avogadro's number, molar mass, concentration, dilution conditions, or balanced chemical equations)
- Write balanced chemical equations and/or net ionic equations for a chemical process from word descriptions.
- Classify chemical reactions as redox or non-redox, and as combustion, synthesis, decomposition, single displacement, double displacement, or acid-base.

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3.2: Formula Mass and the Mole Concept

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Describe the composition of a sample before or after a chemical reaction using relevant information (**chemical formulas, mass, Avogadro's number, molar mass**, concentration, dilution conditions, or balanced chemical equations)

Many argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

Formula Mass

An earlier chapter of this text described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the formula mass of a substance by summing the average atomic masses of all the atoms represented in the substance's formula.

Formula Mass for Covalent Substances

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of tetrafluoroethylene, the building block for the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. Figure $3.2.1$ outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
				Molecular mass	119.37

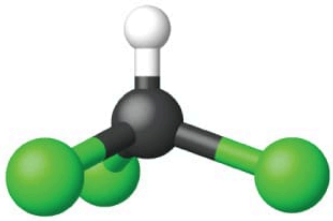


Figure $3.2.1$: The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

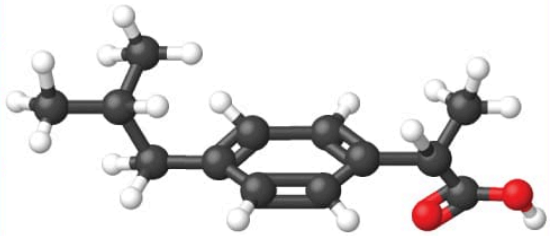
Example $3.2.1$: Computing Molecular Mass for a Covalent Compound

Ibuprofen, $C_{13}H_{18}O_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound?

Solution

Molecules of this compound are composed of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is therefore:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.144
O	2	×	16.00	=	32.00
				Molecular mass	206.27



Formula Mass for Ionic Compounds

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the atoms in the compound's formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the "molecular mass."

As an example, consider sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu (see Figure 3.2.3).

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
				Formula mass	58.44

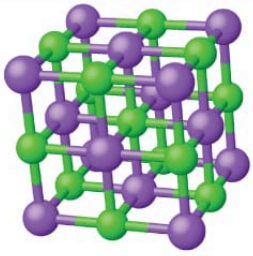


Figure 3.2.3: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

Exercise 3.2.2

Calcium phosphate, $Ca_3(PO_4)_2$, is an ionic compound and a common anti-caking agent added to food products. What is the formula mass (amu) of calcium phosphate?

Answer available at the end of this section.

The Mole

The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion. For example, water, H_2O, and hydrogen peroxide, H_2O_2, are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties.

The *mole* is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of

atoms or molecules in a sample of matter. One Latin connotation for the word “mole” is “large mass” or “bulk,” which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth. A mole of substance is that amount in which there are $6.02214076 \times 10^{23}$.

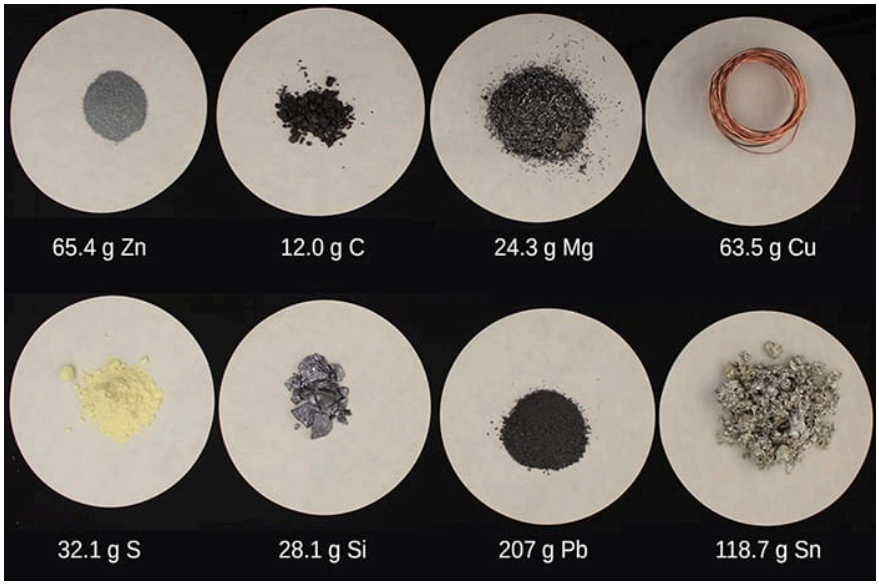


Figure 3.2.4: Each sample contains 6.022 10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott)

The molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). A mole of ^{12}C weighs 12 g (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C. Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (Figure 3.2.5).



Figure 3.2.5: Each sample contains 6.02 10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa)

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	$6.022\ 10^{23}$
H	1.008	1.008	$6.022\ 10^{23}$
O	16.00	16.00	$6.022\ 10^{23}$
Na	22.99	22.99	$6.022\ 10^{23}$
Cl	35.45	35.45	$6.022\ 10^{23}$

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water weighing about 0.03 g (see Figure 3.2.6). Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.



Figure 3.2.6: The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. (credit: "tanakawho"/Wikimedia commons)

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds, as demonstrated in the next several example problems.

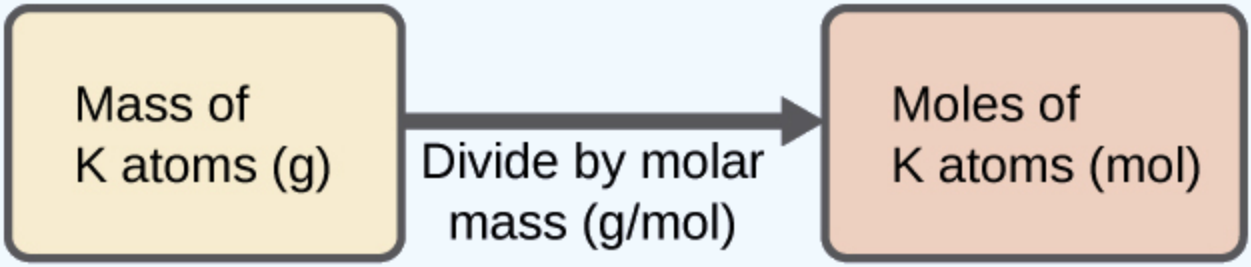
Example 3.2.3: Deriving Moles from Grams for an Element

According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

Solution

The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth the molar mass (39.10 g), so a reasonable "ballpark" estimate of the number of moles would be slightly greater than 0.1 mol.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



The factor-label method supports this mathematical approach since the unit “g” cancels and the answer has units of “mol:”

$$4.7\ \cancel{\text{g K}}\left(\frac{\text{mol K}}{39.10\ \cancel{\text{g K}}}\right) = 0.12\,\text{mol K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol,

Exercise 3.2.3

Beryllium is a light metal used to fabricate transparent X-ray windows for medical imaging instruments. How many moles of Be are in a thin-foil window weighing 3.24 g?

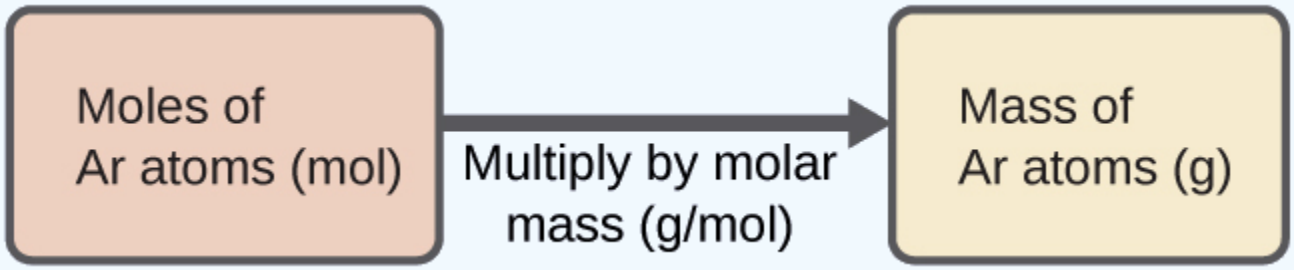
Answer available at the end of this section.

Example 3.2.4: Deriving Grams from Moles for an Element

A liter of air contains $9.2\ 10^{-4}$ mol argon. What is the mass of Ar in a liter of air?

Solution

The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth (~10^{-3}) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass (~0.04 g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

$$9.2 \times 10^{-4}\ \cancel{\text{mol Ar}}\left(\frac{39.95\,\text{g Ar}}{\cancel{\text{mol Ar}}}\right) = 0.037\,\text{g Ar}$$

The result is in agreement with our expectations, around 0.04 g Ar.

Exercise 3.2.1

What is the mass of 2.561 mol of gold?

Answer available at the end of this section.

Example 3.2.5: Deriving Number of Atoms from Mass for an Element

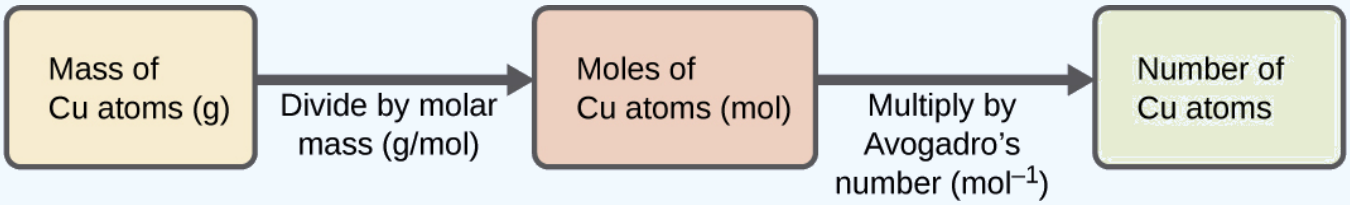
Copper is commonly used to fabricate electrical wire (Figure 3.2.7). How many copper atoms are in 5.00 g of copper wire?



Figure 3.2.7: Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

Solution

The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (N_A) to convert this molar amount to number of Cu atoms:



Considering that the provided sample mass (5.00 g) is a little less than one-tenth the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth N_A, or approximately 10^{22} Cu atoms. Carrying out the two-step computation yields:

$$5.00 \cancel{\text{ g Cu}} \left(\frac{\cancel{\text{mol Cu}}}{63.55 \cancel{\text{ g Cu}}} \right) \left(\frac{6.022 \times 10^{23} \text{Cu atoms}}{\cancel{\text{mol Cu}}} \right) = 4.74 \times 10^{22} \text{ Cu atoms}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

Exercise 3.2.5

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

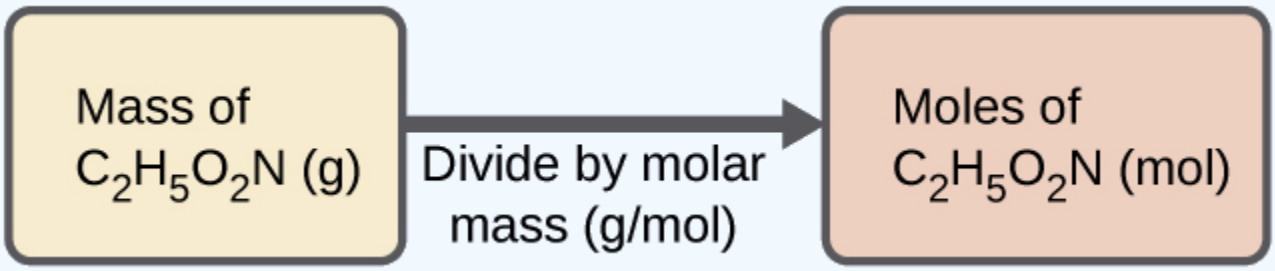
Answer available at the end of this section.

Example 3.2.6: Deriving Moles from Grams for a Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula $C_2H_5O_2N$. How many moles of glycine molecules are contained in 28.35 g of glycine?

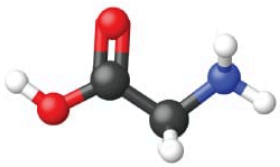
Solution

Derive the number of moles of a compound from its mass following the same procedure used for an element in Example 3.2.3 :



The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine, $C_2H_5O_2N$, contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:

Element	Quantity (mol element/ mol compound)		Molar mass (g/mol element)		Subtotal (g/mol compound)
C	2	×	12.01	=	24.02
H	5	×	1.008	=	5.040
O	2	×	16.00	=	32.00
N	1	×	14.007	=	14.007
Molecular mass (g/mol compound)					75.07



The provided mass of glycine (~28 g) is a bit more than one-third the molar mass (~75 g/mol), so the computed result is expected to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound's mass by its molar mass yields:

$$28.35 \cancel{\text{ g glycine}} \left(\frac{\text{mol glycine}}{75.07 \cancel{\text{ g glycine}}} \right) = 0.378 \,\text{mol glycine}$$

This result is consistent with the rough estimate,

Exercise 3.2.6

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

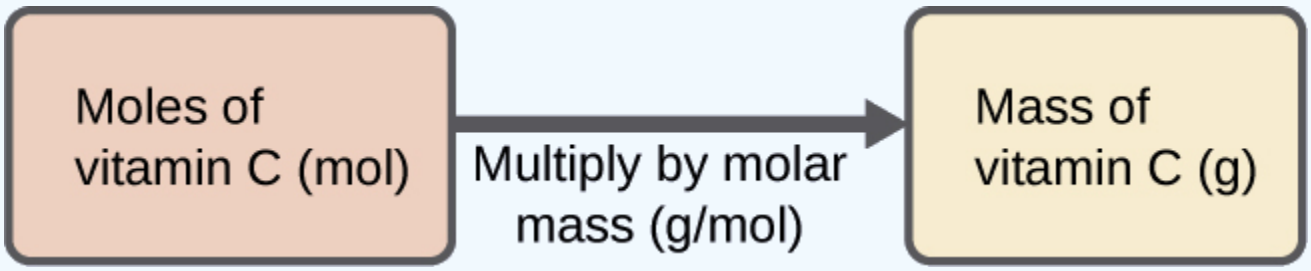
Answer available at the end of this section.

Example 3.2.7: Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula $C_6H_8O_6$. The recommended daily dietary allowance of vitamin C for children aged 4–8 years is $1.42\ 10^{-4}$ mol. What is the mass of this allowance in grams?

Solution

As for elements, the mass of a compound can be derived from its molar amount as shown:



The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole (~10^{-4} or one-ten thousandth); therefore, the corresponding mass is expected to be about one-ten thousandth of the molar mass (~0.02 g). Performing the calculation yields:

$$1.42 \times 10^{-4} \cancel{\text{ mol vitamin C}} \left(\frac{176.124\,\text{g vitamin C}}{\cancel{\text{mol vitamin C}}} \right) = 0.0250\,\text{g vitamin C}$$

This is consistent with the anticipated result.

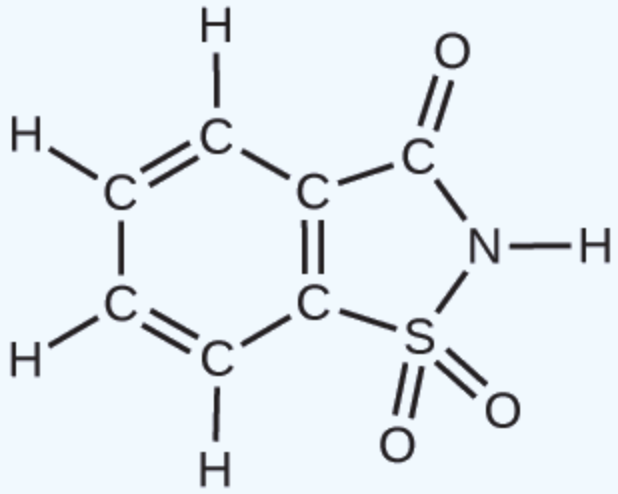
Exercise 3.2.7

What is the mass of 0.443 mol of hydrazine, N_2H_4?

Answer available at the end of this section.

Example 3.2.8: Deriving the Number of Atoms and Molecules from the Mass of a Compound

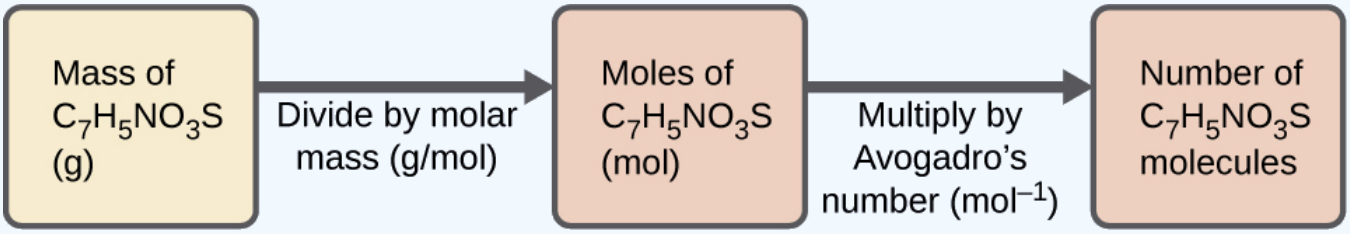
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



Given that saccharin has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0-mg (0.0400-g) sample of saccharin? How many carbon atoms are in the same sample?

Solution

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in Example 3.2.6, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400\ \cancel{\text{g } C_7H_5NO_3S}\left(\frac{\cancel{\text{mol } C_7H_5NO_3S}}{183.18\ \cancel{\text{g } CH_5NO_3S}}\right)\left(\frac{6.022\times10^{23}\ {}_7CH_5NO_3S\text{ molecules}}{1\ \cancel{\text{mol } C_7H_5NO_3S}}\right)$$
$$= 1.31\times10^{20}\ {}_7CH_5NO_3S\text{ molecules}$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

$$1.31\times10^{20}\ {}_7CH_5NO_3S\text{ molecules}\left(\frac{7\text{ C atoms}}{1\ {}_7CH_5NO_3S\text{ molecule}}\right) = 9.17\times10^{20}\text{ C atoms}$$

Exercise 3.2.8

How many C_4H_{10} molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

Answer available at the end of this section.

How Sciences Interconnect: Counting Neurotransmitter Molecules in the Brain

The brain is the control center of the central nervous system (Figure 3.2.8). It sends and receives signals to and from muscles and other internal organs to monitor and control their functions; it processes stimuli detected by sensory organs to guide interactions with the external world; and it houses the complex physiological processes that give rise to our intellect and emotions. The broad field of neuroscience spans all aspects of the structure and function of the central nervous system, including research on the anatomy and physiology of the brain. Great progress has been made in brain research over the past few decades, and the BRAIN Initiative, a federal initiative announced in 2013, aims to accelerate and capitalize on these advances through the concerted efforts of various industrial, academic, and government agencies (more details available at www.whitehouse.gov/share/brain-initiative).

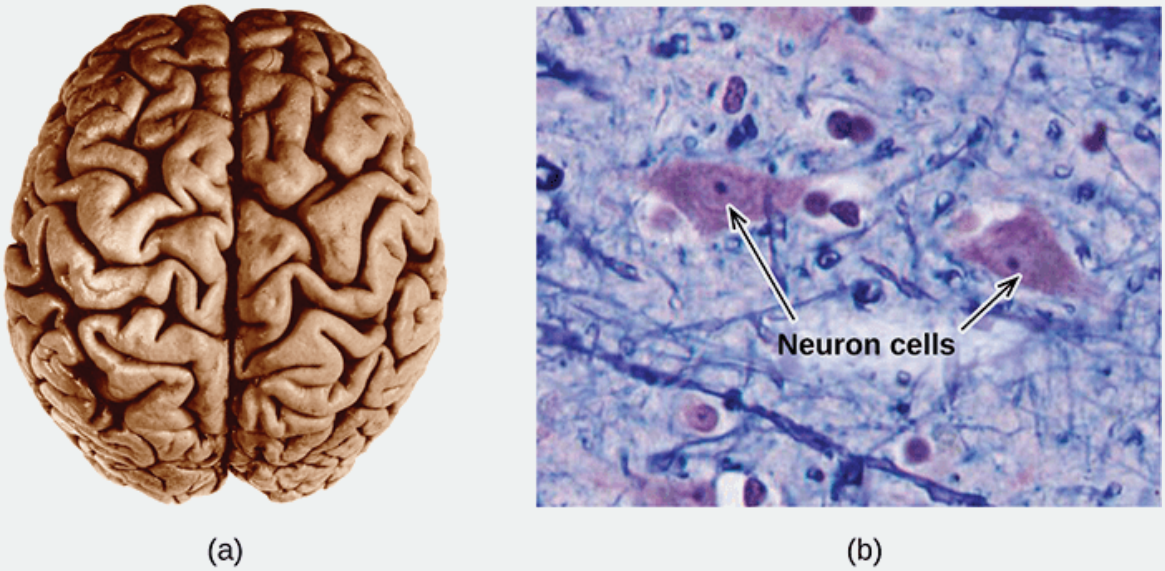


Figure 3.2.8: (a) A typical human brain weighs about 1.5 kg and occupies a volume of roughly 1.1 L. (b) Information is transmitted in brain tissue and throughout the central nervous system by specialized cells called neurons (micrograph shows cells at 1600× magnification).

Specialized cells called neurons transmit information between different parts of the central nervous system by way of electrical and chemical signals. Chemical signaling occurs at the interface between different neurons when one of the cells releases molecules (called neurotransmitters) that diffuse across the small gap between the cells (called the synapse) and bind to the surface of the other cell. These neurotransmitter molecules are stored in small intracellular structures called vesicles that fuse to the cell membrane and then break open to release their contents when the neuron is appropriately stimulated. This process is called exocytosis (see Figure 3.2.9). One neurotransmitter that has been very extensively studied is dopamine, $C_8H_{11}NO_2$. Dopamine is involved in various neurological processes that impact a wide variety of human behaviors. Dysfunctions in the dopamine systems of the brain underlie serious neurological diseases such as Parkinson's and schizophrenia.

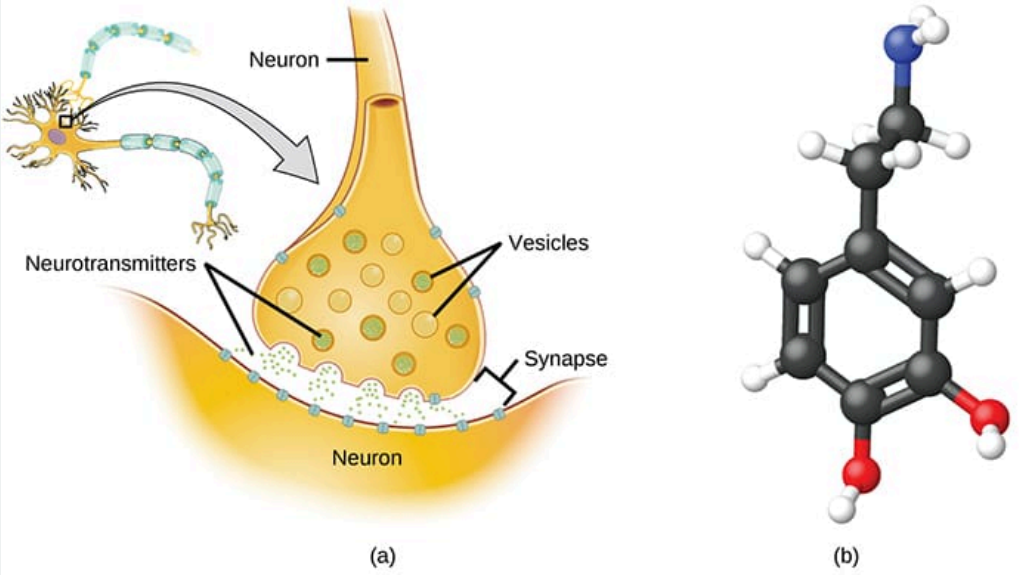


Figure 3.2.9: (a) Chemical signals are transmitted from neurons to other cells by the release of neurotransmitter molecules into the small gaps (synapses) between the cells. (b) Dopamine, $C_8H_{11}NO_2$, is a neurotransmitter involved in a number of neurological processes.

One important aspect of the complex processes related to dopamine signaling is the number of neurotransmitter molecules released during exocytosis. Since this number is a central factor in determining neurological response (and subsequent human thought and action), it is important to know how this number changes with certain controlled stimulations, such as the administration of drugs. It is also important to understand the mechanism responsible for any changes in the number of neurotransmitter molecules released—for example, some dysfunction in exocytosis, a change in the number of vesicles in the neuron, or a change in the number of neurotransmitter molecules in each vesicle.

Significant progress has been made recently in directly measuring the number of dopamine molecules stored in individual vesicles and the amount actually released when the vesicle undergoes exocytosis. Using miniaturized probes that can selectively detect dopamine molecules in very small amounts, scientists have determined that the vesicles of a certain type of mouse brain neuron contain an average of 30,000 dopamine molecules per vesicle (about 5×10^{-20} mol or 50 zmol). Analysis of these neurons from mice subjected to various drug therapies shows significant changes in the average number of dopamine molecules contained in individual vesicles, increasing or decreasing by up to three-fold, depending on the specific drug used. These studies also indicate that not all of the dopamine in a given vesicle is released during exocytosis, suggesting that it may be possible to regulate the fraction released using pharmaceutical therapies.

Footnotes

- 1Omiatek, Donna M., Amanda J. Bressler, Ann-Sofie Cans, Anne M. Andrews, Michael L. Heien, and Andrew G. Ewing. “The Real Catecholamine Content of Secretory Vesicles in the CNS Revealed by Electrochemical Cytometry.” *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

Answers

Exercise 3.2.2
310.18 amu

Exercise 3.2.3
0.360 mol

Exercise 3.2.1
504.4 g

Exercise 3.2.5
4.586×10^{22} Au atoms

Exercise 3.2.6
0.073 mol

Exercise 3.2.7

14.2 g

Exercise 3.2.8

9.545×10^{22} molecules C_4H_{10}

9.545×10^{23} atoms H

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3.3: Determining Empirical and Molecular Formulas

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Describe the composition of a sample before or after a chemical reaction using relevant information (**chemical formulas, mass,** Avogadro's number, **molar mass,** concentration, dilution conditions, or balanced chemical equations)

The previous section discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, one may determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, these same principles will be applied to derive the chemical formulas of unknown substances from experimental mass measurements.

Percent Composition

The elemental makeup of a compound defines its chemical identity, and chemical formulas are the most succinct way of representing this elemental makeup. When a compound's formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally. The results of these measurements permit the calculation of the compound's **percent composition**, defined as the percentage by mass of each element in the compound. For example, consider a gaseous compound composed solely of carbon and hydrogen. The percent composition of this compound could be represented as follows:

$$\%H = \frac{\text{mass } H}{\text{mass compound}} \times 100\%$$
$$\%C = \frac{\text{mass } C}{\text{mass compound}} \times 100\%$$

If analysis of a 10.0-g sample of this gas showed it to contain 2.5 g H and 7.5 g C, the percent composition would be calculated to be 25% H and 75% C:

$$\%H = \frac{2.5gH}{10.0g \text{ compound}} \times 100\% = 25\%$$
$$\%C = \frac{7.5gC}{10.0g \text{ compound}} \times 100\% = 75\%$$

Example 3.3.1: Calculation of Percent Composition

Analysis of a 12.04-g sample of a liquid compound composed of carbon, hydrogen, and nitrogen showed it to contain 7.34 g C, 1.85 g H, and 2.85 g N. What is the percent composition of this compound?

Solution

To calculate percent composition, divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

$$\%C = \frac{7.34gC}{12.04g \text{ compound}} \times 100\% = 61.0\%$$
$$\%H = \frac{1.85gH}{12.04g \text{ compound}} \times 100\% = 15.4\%$$
$$\%N = \frac{2.85gN}{12.04g \text{ compound}} \times 100\% = 23.7\%$$

The analysis results indicate that the compound is 61.0% C, 15.4% H, and 23.7% N by mass.

Exercise 3.3.1

A 24.81-g sample of a gaseous compound containing only carbon, oxygen, and chlorine is determined to contain 3.01 g C, 4.00 g O, and 17.81 g Cl. What is this compound's percent composition?

Answer available at the end of this section.

Determining Percent Composition from Molecular or Empirical Formulas

Percent composition is also useful for evaluating the relative abundance of a given element in different compounds of known formulas. As one example, consider the common nitrogen-containing fertilizers ammonia (NH_3), ammonium nitrate (NH_4NO_3), and urea (CH_4N_2O). The element nitrogen is the active ingredient for agricultural purposes, so the mass percentage of nitrogen in the compound is a practical and economic concern for consumers choosing among these fertilizers. For these sorts of applications, the percent composition of a compound is easily derived from its formula mass and the atomic masses of its constituent elements. A molecule of NH_3 contains one N atom weighing 14.01 amu and three H atoms weighing a total of (3 1.008 amu) = 3.024 amu. The formula mass of ammonia is therefore (14.01 amu + 3.024 amu) = 17.03 amu, and its percent composition is:

$$\%N = \frac{14.01 amu N}{17.03 amu HH} \times 100\% = 82.27\%$$
$$\%H = \frac{3.024 amu H}{17.03 amu H} \times 100\% = 17.76\%$$

This same approach may be taken considering a pair of molecules, a dozen molecules, or a mole of molecules, etc. The latter amount is most convenient and would simply involve the use of molar masses instead of atomic and formula masses, as demonstrated Example 3.3.2. As long as the molecular or empirical formula of the compound in question is known, the percent composition may be derived from the atomic or molar masses of the compound's elements.

Example 3.3.2: Determining Percent Composition from a Molecular Formula

Aspirin is a compound with the molecular formula $C_9H_8O_4$. What is its percent composition?

Solution

To calculate the percent composition, the masses of C, H, and O in a known mass of $C_9H_8O_4$ are needed. It is convenient to consider 1 mol of $C_9H_8O_4$ and use its molar mass (180.159 g/mole, determined from the chemical formula) to calculate the percentages of each of its elements:

$$\%C = \frac{9 mol C \times \text{ molar mass } C}{\text{molar mass } C_9H_8O_4} \times 100 = \frac{9 \times 12.01 g/mol}{180.159 g/mol} \times 100 = \frac{108.09 g/mol}{180.159 g/mol} \times 100$$
$$\%C = 60.00\%C$$

$$\%H = \frac{8 mol H \times \text{ molar mass } H}{\text{molar mass } C_9H_8O_4} \times 100 = \frac{8 \times 1.008 g/mol}{180.159 g/mol} \times 100 = \frac{8.064 g/mol}{180.159 g/mol} \times 100$$
$$\%H = 4.476\%H$$

$$\%O = \frac{4 mol O \times \text{ molar mass}}{\text{molar mass } C_9H_8O_4} \times 100 = \frac{4 \times 16.00 g/mol}{180.159 g/mol} \times 100 = \frac{64.00 g/mol}{180.159 g/mol} \times 100$$
$$\%O = 35.52\%$$

Note that these percentages sum to equal 100.00% when appropriately rounded.

Exercise 3.3.2

To three significant digits, what is the mass percentage of iron in the compound Fe_2O_3?

Answer available at the end of this section.

Determination of Empirical Formulas

As previously mentioned, the most common approach to determining a compound's chemical formula is to first measure the masses of its constituent elements. However, keep in mind that chemical formulas represent the relative *numbers*, not masses, of atoms in the substance. Therefore, any experimentally derived data involving mass must be used to derive the corresponding numbers of atoms in the compound. This is accomplished using molar masses to convert the mass of each element to a number of moles. These molar amounts are used to compute whole-number ratios that can be used to derive the empirical formula of the substance. Consider a sample of compound determined to contain 1.71 g C and 0.287 g H. The corresponding numbers of atoms (in moles) are:

$$1.71gC \times \frac{1molC}{12.01gC} = 0.142molC$$
$$0.287gH \times \frac{1molH}{1.008gH} = 0.284molH$$

Thus, this compound may be represented by the formula $C_{0.142}H_{0.284}$. Per convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

$$C_{\frac{0.142}{0.142}}H_{\frac{0.234}{0.142}} \text{ or } CH_2$$

(Recall that subscripts of "1" are not written but rather assumed if no other number is present.)

The empirical formula for this compound is thus CH_2. This may or may not be the compound's *molecular formula* as well; however, additional information is needed to make that determination (as discussed later in this section).

Consider as another example a sample of compound determined to contain 5.31 g Cl and 8.40 g O. Following the same approach yields a tentative empirical formula of:

$$Cl_{0.150}O_{0.525} = Cl_{\frac{0.150}{0.150}}O_{\frac{0.525}{0.150}} = ClO_{3.5}$$

In this case, dividing by the smallest subscript still leaves us with a decimal subscript in the empirical formula. To convert this into a whole number, multiply each of the subscripts by two, retaining the same atom ratio and yielding Cl_2O_7 as the final empirical formula.

In summary, empirical formulas are derived from experimentally measured element masses by:

1. Deriving the number of moles of each element from its mass
2. Dividing each element's molar amount by the smallest molar amount to yield subscripts for a tentative empirical formula
3. Multiplying all coefficients by an integer, if necessary, to ensure that the smallest whole-number ratio of subscripts is obtained

Figure 3.3.1 outlines this procedure in flow chart fashion for a substance containing elements A and X.

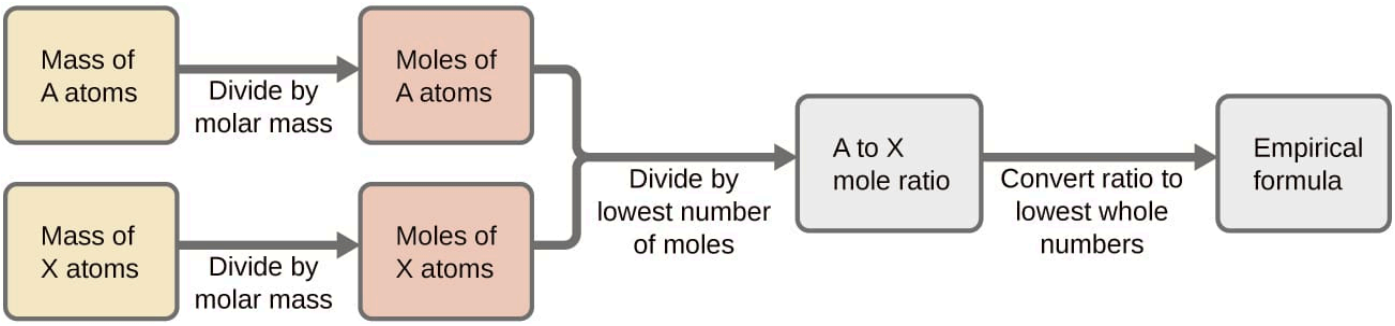


Figure 3.3.1: The empirical formula of a compound can be derived from the masses of all elements in the sample.

Example 3.3.3: Determining a Compound's Empirical Formula from the Masses of Its Elements

A sample of the black mineral hematite (Figure 3.3.2), an oxide of iron found in many iron ores, contains 34.97 g of iron and 15.03 g of oxygen. What is the empirical formula of hematite?



Figure 3.3.2: Hematite is an iron oxide that is used in jewelry. (credit: Mauro Cateb)

Solution

This problem provides the mass in grams of each element. Begin by finding the moles of each:

$$34.97gFe\left(\frac{molFe}{55.85g}\right) = 0.6261molFe$$
$$15.03gO\left(\frac{molO}{16.00g}\right) = 0.9394molO$$

Next, derive the iron-to-oxygen molar ratio by dividing by the lesser number of moles:

$$\frac{0.6261}{0.6261} = 1.000molFe$$
$$\frac{0.9394}{0.6261} = 1.500molO$$

The ratio is 1.000 mol of iron to 1.500 mol of oxygen ($Fe_1O_{1.5}$). Finally, multiply the ratio by two to get the smallest possible whole number subscripts while still maintaining the correct iron-to-oxygen ratio:

$$2\left(Fe_1O_{1.5}\right) = Fe_2O_3$$

The empirical formula is $\mathrm{Fe_2O_3}$.

Exercise 3.3.3

What is the empirical formula of a compound if a sample contains 0.130 g of nitrogen and 0.370 g of oxygen?

Answer available at the end of this section.

Deriving Empirical Formulas from Percent Composition

Finally, with regard to deriving empirical formulas, consider instances in which a compound's percent composition is available rather than the absolute masses of the compound's constituent elements. In such cases, the percent composition can be used to calculate the masses of elements present in any convenient mass of compound; these masses can then be used to derive the empirical formula in the usual fashion.

Example 3.3.4: Determining an Empirical Formula from Percent Composition

The bacterial fermentation of grain to produce ethanol forms a gas with a percent composition of 27.29% C and 72.71% O (Figure 3.3.3). What is the empirical formula for this gas?



Figure 3.3.3: An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: "Dual Freq"/Wikimedia Commons)

Solution

Since the scale for percentages is 100, it is most convenient to calculate the mass of elements present in a sample weighing 100 g. The calculation is "most convenient" because, per the definition for percent composition, the mass of a given element in grams is numerically equivalent to the element's mass percentage. This numerical equivalence results from the definition of the "percentage" unit, whose name is derived from the Latin phrase *per centum* meaning "by the hundred." Considering this definition, the mass percentages provided may be more conveniently expressed as fractions:

$$27.29\%C = \frac{27.29gC}{100g \text{ compound}}$$
$$72.71\%O = \frac{72.71gO}{100g \text{ compound}}$$

The molar amounts of carbon and oxygen in a 100-g sample are calculated by dividing each element's mass by its molar mass:

$$27.29gC\left(\frac{molC}{12.01g}\right)=2.272molC$$
$$72.71gO\left(\frac{molo}{16.00g}\right)=4.544molO$$

Coefficients for the tentative empirical formula are derived by dividing each molar amount by the lesser of the two:

$$\frac{2.272molC}{2.272}=1$$
$$\frac{4.544molO}{2.272}=2$$

Since the resulting ratio is one carbon to two oxygen atoms, the empirical formula is CO_2.

Exercise 3.3.4

What is the empirical formula of a compound containing 40.0% C, 6.71% H, and 53.28% O?

Answer available at the end of this section.

Derivation of Molecular Formulas

Molecular formulas are derived by comparing the compound's molecular or molar mass to its **empirical formula mass**. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If the molecular (or molar) mass of the substance is known, it may be divided by the empirical formula mass to yield the number of empirical formula units per molecule (*n*):

$$\frac{\text{molecular or molar mass (amu or }\frac{\text{g}}{\text{mol}})}{\text{empirical formula mass (amu or }\frac{\text{g}}{\text{mol}}\text{)}}=n\text{ formula units/molecule}$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by *n*, as shown by the generic empirical formula A_xB_y:

$$(A_xB_y)_n=A_{nx}B_{ny}$$

For example, consider a covalent compound whose empirical formula is determined to be CH_2O. The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom). If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

$$\frac{180\,\text{amu / molecule}}{30\,\frac{\text{amu}}{\text{formula unit}}}=6\text{ formula units / molecule}$$

Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:

$$(\text{CH}_2\text{O})_6=\text{C}_6\text{H}_{12}\text{O}_6$$

Note that this same approach may be used when the molar mass (g/mol) instead of the molecular mass (amu) is used. In this case, *one mole* of empirical formula units and molecules is considered, as opposed to single units and molecules.

Example 3.3.5: Determination of the Molecular Formula for Nicotine

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

Solution

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula. Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

$$(74.02gC)\left(\frac{1molC}{12.01gC}\right. = 6.163molC$$
$$(8.710gH)\left(\frac{1molH}{1.008gH}\right. = 8.641molH$$
$$(17.27gN)\left(\frac{1molN}{14.01gN}\right) = 1.233molN$$

Next, calculate the molar ratios of these elements relative to the least abundant element, N.

$$6.163\ \text{mol C}/1.233\ \text{mol N} = 58.641\ \text{mol H}/1.233\ \text{mol N} = 71.233\ \text{mol N}/1.233\ \text{mol N} = 1$$

$$\frac{1.233}{1.233} = 1.000molN$$
$$\frac{6.163}{1.233} = 4.998molC$$
$$\frac{8.624}{1.233} = 6.994molH$$

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is C_5H_7N. The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

Calculate the molar mass for nicotine from the given mass and molar amount of compound:

$$\frac{40.57g\ \text{nicotine}}{0.2500mol\ \text{nicotine}} = \frac{162.3g}{mol}$$

Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

$$\frac{162.3g/mol}{81.13\frac{g}{\text{formula unit}}} = 2\ \text{formula units / molecule}$$

Finally, derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(C_5H_7N)_2 = C_{10}H_{14}N_2$$

Exercise 3.3.1

What is the molecular formula of a compound with a percent composition of 49.47% C, 5.201% H, 28.84% N, and 16.48% O, and a molecular mass of 194.2 amu?

Answer available at the end of this section.

Answers

Exercise 3.3.1

12.1% C, 16.1% O, 71.79% Cl

Exercise 3.3.2

69.9% Fe

Exercise 3.3.3

N_2O_5

Exercise 3.3.4

CH_2O

Exercise 3.3.1

$C_8H_{10}N_4O_2$

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3.4: Molarity

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Describe the composition of a sample before or after a chemical reaction using relevant information (**chemical formulas, mass**, Avogadro's number, **molar mass**, **concentration, dilution conditions**, or balanced chemical equations)

Solutions

A solutions have previously been defined as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology.

The relative amount of a given solution component is known as its **concentration**. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components. This component is called the solvent and may be viewed as the medium in which the other components are dispersed, or **dissolved**. Solutions in which water is the solvent are, of course, very common on our planet. A solution in which water is the solvent is called an **aqueous solution**.

A **solute** is a component of a solution that is typically present at a much lower concentration than the solvent. Solute concentrations are often described with qualitative terms such as **dilute** (of relatively low concentration) and **concentrated** (of relatively high concentration).

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications. **Molarity** (*M*) is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Example 3.4.1: Calculating Molar Concentrations

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.133\,\text{mol}}{355\,\text{mL} \times \frac{1\,\text{L}}{1000\,\text{mL}}} = 0.375M$$

Exercise 3.4.1

A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

Answer available at the end of this section.

Example 3.4.2: Deriving Moles and Volumes from Molar Concentrations

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from Example 3.4.1?

Solution

Rearrange the definition of molarity to isolate the quantity sought, moles of sugar, then substitute the value for molarity derived in Example 3.4.1, 0.375 *M*:

$$\begin{aligned} M &= \frac{\text{mol solute}}{L \text{ solution}} \\ \text{mol solute} &= M \times L \text{ solution} \\ &= 0.375 \frac{\text{mol sugar}}{L} \times \left(10\,\text{mL} \times \frac{1\,\text{L}}{1000\,\text{mL}}\right) \\ &= 0.004\,\text{mol sugar} \end{aligned}$$

Exercise 3.4.2

What volume (mL) of the sweetened tea described in Example 3.4.1 contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer available at the end of this section.

Example 3.4.3: Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure 3.4.2) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?



Figure 3.4.2: Distilled white vinegar is a solution of acetic acid in water.

Solution

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. Since the mass of solute is provided instead of its molar amount, use the solute's molar mass to obtain the amount of solute in moles:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\,\text{g}\,\text{CH}_3\text{CO}_2\text{H} \times \frac{1\,\text{mol}\,\text{CH}_3\text{CO}_2\text{H}}{60.052\,\text{g}\,\text{CH}_3\text{CO}_2\text{H}}}{0.500\,\text{L solution}} = 0.839\,\text{M}$$

Exercise 3.4.3

Calculate the molarity of 6.52 g of $CoCl_2$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Answer available at the end of this section.

Example 3.4.4: Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30-*M* solution?

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in Example 3.4.2:

$$\begin{aligned} M &= \frac{\text{mol solute}}{L\text{ solution}} \\ \text{mol solute} &= M \times L\text{ solution} \\ &= 5.30\frac{\text{mol NaCl}}{\text{L}} \times 0.250L \\ &= 1.325\,\text{mol NaCl} \end{aligned}$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325\,\text{mol NaCl} \times \frac{58.44\,\text{g NaCl}}{1\,\text{mol NaCl}} = 77.4\,\text{g NaCl}$$

Exercise 3.4.4

How many grams of $CaCl_2$ (110.98 g/mol) are contained in 250.0 mL of a 0.200-*M* solution of calcium chloride?

Answer available at the end of this section.

When performing calculations stepwise, as in Example 3.4.4, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In Example 3.4.4, the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If the guard digit had not been retained, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, rounding errors may also be avoided by performing computations in a single step (see Example 3.4.5). This eliminates intermediate steps so that only the final result is rounded.

Example 3.4.5: Determining the Volume of Solution Containing a Given Mass of Solute

In Example 3.4.3, the concentration of acetic acid in white vinegar was determined to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

Combining these two steps into one yields:

$$\text{g solute} \times \left(\frac{\text{mol solute}}{\text{g solute}}\right) \times \left(\frac{\text{L solution}}{\text{mol solute}}\right) = \text{L solution}$$

$$75.6\,\text{g}\,\text{CH}_3\text{CO}_2\text{H}\left(\frac{\text{mol}\,\text{CH}_3\text{CO}_2\text{H}}{60.05\,\text{g}}\right)\left(\frac{\text{L solution}}{0.839\,\text{mol CH 3 CO}_2\text{H}}\right) = 1.50\,\text{L solution}$$

Exercise 3.4.5

What volume of a 1.50-*M* KBr solution contains 66.0 g KBr?

Answer available at the end of this section.

Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure 3.4.3).

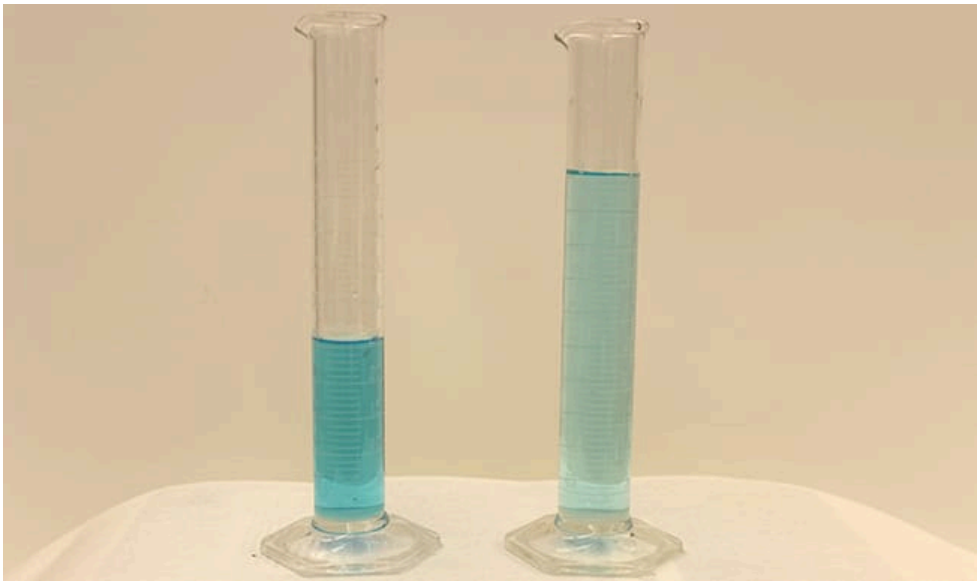


Figure 3.4.3: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott)

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated *stock solution*, a solution of lesser concentration may be prepared. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops, the pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents.

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the number of moles of solute in a solution (*n*) is equal to the product of the solution's molarity (*M*) and its volume in liters (*L*):

$$n = ML$$

Expressions like these may be written for a solution before and after it is diluted:

$$n_1 = M_1 L_1$$
$$n_2 = M_2 L_2$$

where the subscripts "1" and "2" refer to the solution before and after the dilution, respectively. Since the dilution process *does not change the amount of solute in the solution,* $n_1 = n_2$. Thus, these two equations may be set equal to one another:

$$M_1 L_1 = M_2 L_2$$

This relation is commonly referred to as the dilution equation. Although this equation uses molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used as long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

$$C_1 V_1 = C_2 V_2$$

where \(*C*\) and \(*V*\) are concentration and volume, respectively.

Link to Learning

Use the simulation to explore the relations between solute amount, solution volume, and concentration and to confirm the dilution equation.

Example 3.4.6: Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00-*M* solution of copper nitrate, $Cu(NO_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

The stock concentration, C_1, and volume, V_1, are provided as well as the volume of the diluted solution, V_2. Rearrange the dilution equation to isolate the unknown property, the concentration of the diluted solution, C_2:

$$C_1 V_1 = C_2 V_2$$
$$C_2 = \frac{C_1 V_1}{V_2}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), the diluted solution's concentration is expected to be less than one-half 5 *M*. This ballpark estimate will be compared to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

$$C_2 = \frac{0.850 L \times 5.00 \frac{mol}{L}}{1.80 L} = 2.36 M$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 *M*).

Exercise 3.4.6

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-*M* solution of CH_3OH to 500.0 mL?

Answer available at the end of this section.

Example 3.4.7: Volume of a Diluted Solution

What volume of 0.12 *M* HBr can be prepared from 11 mL (0.011 L) of 0.45 *M* HBr?

Solution

Provided are the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. Find the volume of the diluted solution, V_2 by rearranging the dilution equation to isolate V_2:

$$C_1V_1 = C_2V_2$$
$$V_2 = \frac{C_1V_1}{C_2}$$

Since the diluted concentration (0.12 *M*) is slightly more than one-fourth the original concentration (0.45 *M*), the volume of the diluted solution is expected to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

$$V_2 = \frac{(0.45\,\text{M})(0.011\,\text{L})}{(0.12\,\text{M})}$$
$$= 0.041L$$

The volume of the 0.12-*M* solution is 0.041 L (41 mL). The result is reasonable and compares well with the rough estimate.

Exercise 3.4.7

A laboratory experiment calls for 0.125 *M* HNO_3. What volume of 0.125 *M* HNO_3 can be prepared from 0.250 L of 1.88 *M* HNO_3?

Answer available at the end of this section.

Example 3.4.8: Volume of a Concentrated Solution Needed for Dilution

What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?

Solution

Given are the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. Find the volume of the stock solution, V_1 by rearranging the dilution equation to isolate V_1:

$$C_1V_1 = C_2V_2$$
$$V_1 = \frac{C_2V_2}{C_1}$$

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), the volume of the stock solution is expected to be about one-sixteenth that of the diluted solution, or around 0.3 liters. Substituting the given values and solving for the unknown volume yields:

$$V_1 = \frac{(0.100\,\text{M})(5.00\,\text{L})}{1.59\,\text{M}}$$
$$= 0.314\,\text{L}$$

Thus, 0.314 L of the 1.59-*M* solution is needed to prepare the desired solution. This result is consistent with the rough estimate.

Exercise 3.4.8

What volume of a 0.575-*M* solution of glucose ($C_6H_{12}O_6$) can be prepared from 50.00 mL of a 3.00-*M* glucose solution?

Answer available at the end of this section.

Answers

Exercise 3.4.1
0.05 *M*

Exercise 3.4.2
80 mL

Exercise 3.4.3
0.674 *M*

Exercise 3.4.4
5.55 g $CaCl_2$

Exercise 3.4.5
0.370 L

Exercise 3.4.6
0.102 *M* CH_3OH

Exercise 3.4.7
3.76 L

Exercise 3.4.8
0.261 L

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3.5: Writing and Balancing Chemical Equations

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Write balanced chemical equations and/or net ionic equations for a chemical process from word descriptions.

When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of Figure 3.5.1: , with space-filling molecular models shown in the lower half of the figure.

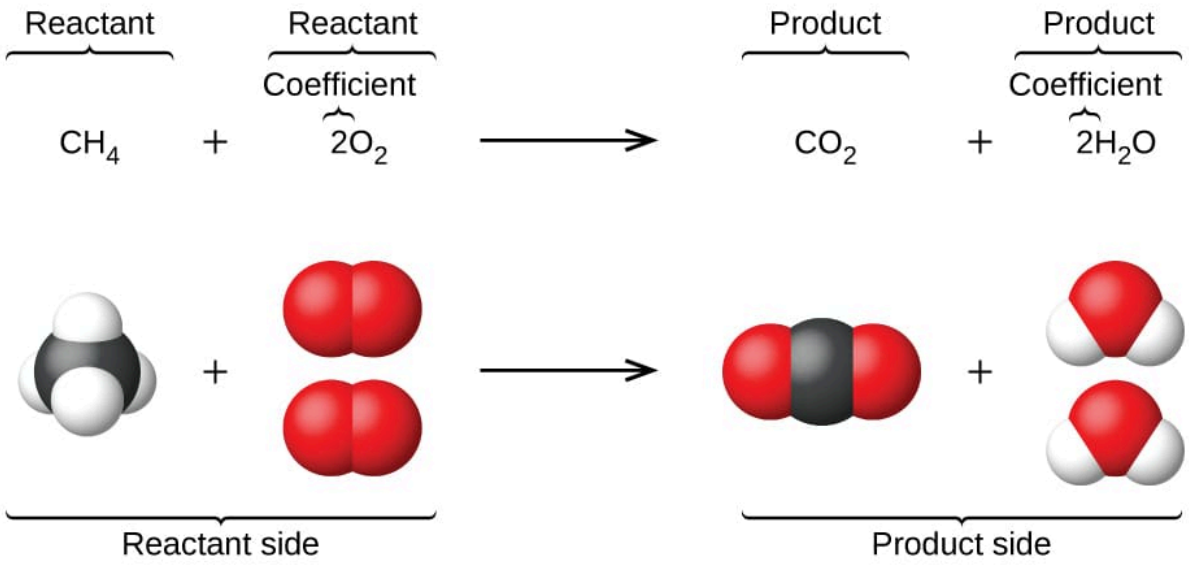


Figure 3.5.1: The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called **reactants,** and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called **products**, and their formulas are placed on the right side of the equation.
3. **Plus signs (+)** separate individual reactant and product formulas, and an **arrow** separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by **coefficients** (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (Figure 3.5.2). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- *One* methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules.
- *One dozen* methane molecules and *two dozen* oxygen molecules react to yield *one dozen* carbon dioxide molecules and *two dozen* water molecules.
- *One mole* of methane molecules and *2 moles* of oxygen molecules react to yield *1 mole* of carbon dioxide molecules and *2 moles* of water molecules.

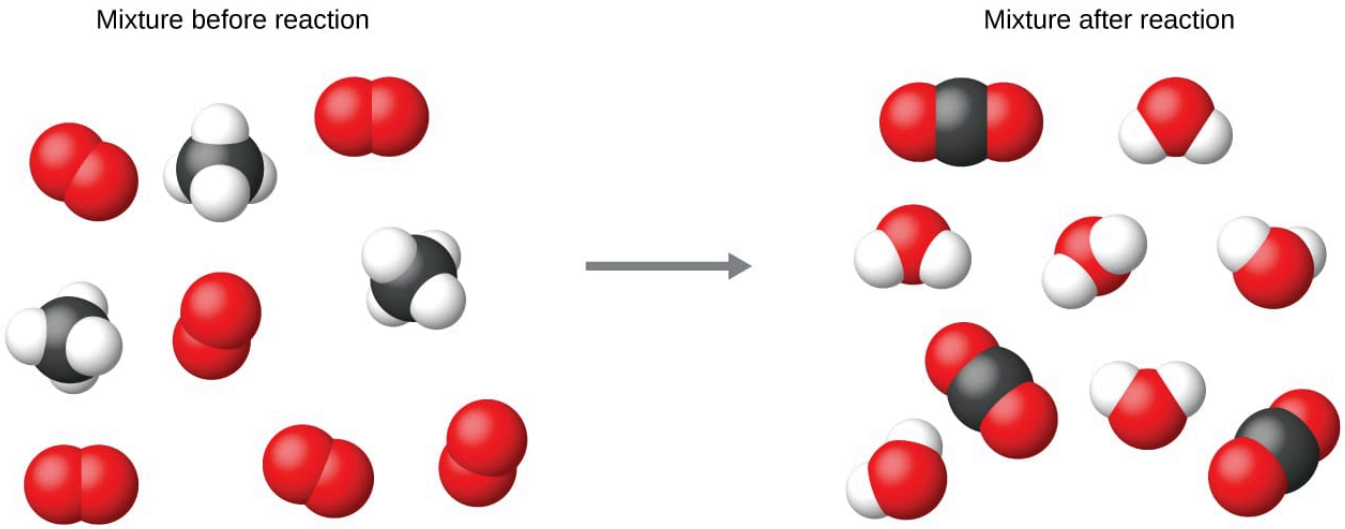


Figure 3.5.2: Regardless of the absolute numbers of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation.

Balancing Equations

The chemical equation described above in Figure 3.5.1 is **balanced**, meaning that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

$$\left(1CO_2 \text{ molecule} \times \frac{2O \text{ atoms}}{CO_2 \text{ molecule}}\right) + \left(2H_2O \text{ molecules} \times \frac{1O \text{ atom}}{H_2O \text{ molecule}}\right) = 4O \text{ atoms}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

$$\mathrm{CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O}$$

Element	Reactants	Products	Balanced?
C	1 × 1 = 1	1 × 1 = 1	1 = 1, yes
H	4 × 1 = 4	2 × 2 = 4	4 = 4, yes
O	2 × 2 = 4	(1 × 2) + (2 × 1) = 4	4 = 4, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

$$\mathrm{H_2O \longrightarrow H_2 + O_2} \qquad \text{(unbalanced)}$$

Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
H	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 1 = 1	1 × 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

$$2\,H_2O \longrightarrow H_2 + O_2 \qquad \text{(unbalanced)}$$

Element	Reactants	Products	Balanced?
H	**2** × 2 = 4	1 × 2 = 2	4 ≠ 2, no
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

$$2\,H_2O \longrightarrow 2\,H_2 + O_2 \qquad \text{(unbalanced)}$$

Element	Reactants	Products	Balanced?
H	2 × 2 = 4	**2** × 2 = 4	4 = 4, yes
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

$$H_2O \longrightarrow H_2 + O_2 \qquad \text{(balanced)}$$

Example 3.5.1: Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

$$N_2 + O_2 \longrightarrow N_2O_5 \qquad \text{(unbalanced)}$$

Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	1 2 = 2	1 2 = 2	2 = 2, yes
O	1 2 = 2	1 5 = 5	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

$$\mathrm{N_2 + 5\,O_2 \longrightarrow 2\,N_2O_5} \quad \text{(unbalanced)}$$

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	**2** × 2 = 4	2 ≠ 4, no
O	**5** × 2 = 10	**2** × 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.

$$\mathrm{2\,N_2 + 5\,O_2 \longrightarrow 2\,N_2O_5} \quad \text{(balanced)}$$

Element	Reactants	Products	Balanced?
N	**2** × 2 = 4	2 × 2 = 4	4 = 4, yes
O	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

Exercise 3.5.1

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Answer available at the end of this section.

Link to Learning

Use this interactive tutorial for additional practice balancing equations.

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

$$\mathrm{2\,Na\,(s) + 2\,H_2O\,(l) \longrightarrow 2\,NaOH\,(aq) + H_2\,(g)}$$

This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

$$\mathrm{CaCO_3\,(s) \xrightarrow{\Delta} CaO\,(s) + CO_2\,(g)}$$

Other examples of these special conditions will be encountered in more depth in later chapters.

Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous

solutions of $CaCl_2$ and $AgNO_3$ are mixed, a reaction takes place producing aqueous $Ca(NO_3)_2$ and solid AgCl:

$$\mathrm{CaCl_2\,(aq) + 2\,AgNO_3\,(aq) \longrightarrow Ca(NO_3)_2\,(aq) + 2\,AgCl\,(s)}$$

This balanced equation, derived in the usual fashion, is called a **molecular equation** because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$\mathrm{CaCl_2\,(aq) \longrightarrow Ca^{2+}\,(aq) + 2\,Cl^-\,(aq)}$$
$$\mathrm{2\,AgNO_3\,(aq) \longrightarrow 2\,Ag^+\,(aq) + 2\,{NO_3}^-\,(aq)}$$
$$\mathrm{Ca(NO_3)_2\,(aq) \longrightarrow Ca^{2+}\,(aq) + 2\,{NO_3}^-\,(aq)}$$

Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, *s*.

Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$\mathrm{Ca^{2+}\,(aq) + 2\,Cl^-\,(aq) + 2\,Ag^+\,(aq) + 2\,{NO_3}^-\,(aq) \longrightarrow Ca^{2+}\,(aq) + 2\,{NO_3}^-\,(aq) + 2\,AgCl\,(s)}$$

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $Ca^{2+}(aq)$ and These spectator ions—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:

$$\cancel{Ca^{2+}(aq)} + \mathrm{2\,Cl^-\,(aq) + 2\,Ag^+\,(aq)} + \cancel{2NO3^-(aq)} \longrightarrow \cancel{Ca^{2+}(aq)} + \cancel{2NO3^-(aq)} + \mathrm{2\,AgCl\,(s)}$$
$$\mathrm{2\,Cl^-\,(aq) + 2\,Ag^+\,(aq) \longrightarrow 2\,AgCl\,(s)}$$

Following the convention of using the smallest possible integers as coefficients, this equation is then written:

$$\mathrm{Cl^-\,(aq) + Ag^+\,(aq) \longrightarrow AgCl\,(s)}$$

This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^- and Ag^+.

Example 3.5.2: Ionic and Molecular Equations

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

$$\mathrm{CO_2\,(aq) + NaOH\,(aq) \longrightarrow Na_2CO_3\,(aq) + H_2O\,(l)} \qquad \text{(unbalanced)}$$

Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

$$\mathrm{CO_2\,(aq) + 2\,NaOH\,(aq) \longrightarrow Na_2CO_3\,(aq) + H_2O\,(l)}$$

The two dissolved ionic compounds, NaOH and $\mathrm{Na_2CO_3}$, can be represented as dissociated ions to yield the complete ionic equation:

$$\mathrm{CO_2\,(aq) + 2\,Na^+\,(aq) + OH^-\,(aq) \longrightarrow 2\,Na^+\,(aq) + {CO_3}^{2-}\,(aq) + H_2O\,(l)}$$

Finally, identify the spectator ion(s), in this case $Na^+(aq)$, and remove it from each side of the equation to generate the net ionic equation:

$$\mathrm{CO_2\,(aq) + \cancel{2Na^+(aq)} + OH^-\,(aq) \longrightarrow \cancel{2Na^+(aq)} + {CO_3}^{2-}\,(aq) + H_2O\,(l)}$$

$$\mathrm{CO_2\,(aq) + OH^-\,(aq) \longrightarrow {CO_3}^{2-}\,(aq) + H_2O\,(l)}$$

Exercise 3.5.2

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

$$\mathrm{NaCl\,(aq) + H_2O\,(l) \xrightarrow{electricity} NaOH\,(aq) + H_2\,(g) + Cl_2\,(g)}$$

Write balanced molecular, complete ionic, and net ionic equations for this process.

Answer available at the end of this section.

Answers

Exercise 3.5.1

$$\mathrm{2\,NH_4NO_3 \longrightarrow 2\,N_2 = O_2 + 4\,H_2O}$$

Exercise 3.5.2

$$\mathrm{2\,NaCl\,(aq) + 2\,H_2O\,(l) \longrightarrow 2\,NaOH\,(aq) + H_2\,(g) + Cl_2\,(g)} \quad \text{(molecular)}$$

$$\mathrm{2\,Na^+\,(aq) + 2\,Cl^-\,(aq) + 2\,H_2O\,(l) \longrightarrow 2\,Na^+\,(aq) + 2\,OH^-\,(aq) + H_2\,(g) + Cl_2\,(g)} \quad \text{(complete ionic)}$$

$$\mathrm{2\,Cl^-\,(aq) + 2\,H_2O\,(l) \longrightarrow 2\,OH^-\,(aq) + H_2\,(g) + Cl_2\,(g)} \quad \text{(net ionic)}$$

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3.6: Classifying Chemical Reactions

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Classify chemical reactions as redox or non-redox, and as combustion, synthesis, decomposition, single displacement, double displacement, or acid-base.

Scientists find it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to three of the most prevalent types of chemical reactions: precipitation, acid-base, and oxidation-reduction.

Precipitation Reactions and Solubility Rules

A precipitation reaction is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and *gravimetric methods* for determining the composition of matter (see the last module of this chapter).

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its solubility, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be soluble. A substance will precipitate when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be insoluble, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in a later chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (Table 3.6.1).

Table 3.6.1

Soluble Ionic Compounds	contain these ions	exceptions
	NH_4^+ group I cations: Li^+ Na^+ K^+ Rb^+ Cs^+	none

	Cl^- Br^- I^-	compounds with Ag^+, Hg_2^{2+}, and Pb^{2+}
	F^-	compounds with group 2 metal cations, Pb^{2+}, and Fe^{3+}
	$C_2H_3O_2^-$ HCO_3^- NO_3^- ClO_3^-	none
	SO_4^{2-}	compounds with Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+} and Sr^{2+}
Insoluble Ionic Compounds	contain these ions	exceptions
	CO_3^{2-} CrO_4^{2-} PO_4^{3-} S^{2-}	compounds with group 1 cations and NH_4^+
	OH^-	compounds with group 1 cations and Ba^{2+}

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

$$2\,\mathrm{KI\,(aq)} + \mathrm{Pb(NO_3)_2\,(aq)} \longrightarrow \mathrm{PbI_2\,(s)} + 2\,\mathrm{KNO_3\,(aq)}$$

This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:

$$\mathrm{Pb^{2+}\,(aq)} + 2\,\mathrm{I^-\,(aq)} \longrightarrow \mathrm{PbI_2\,(s)}$$

Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure $3.6.1$). The properties of pure $\mathrm{PbI_2}$ crystals make them useful for fabrication of X-ray and gamma ray detectors.



Figure 3.6.1: A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

The solubility guidelines in Table 3.6.1 may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium chloride will yield a solution containing Ag^+, NO_3^-, Na^+, and Cl^- ions. Aside from the two ionic compounds originally present in the solutions, $AgNO_3$ and NaCl, two additional ionic compounds may be derived from this collection of ions: $NaNO_3$ and AgCl. The solubility guidelines indicate all nitrate salts are soluble but that AgCl is one of insoluble. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

$$\mathrm{NaCl\,(aq) + AgNO_3\,(aq) \longrightarrow AgCl\,(s) + NaNO_3\,(aq)} \quad \text{(molecular)}$$

$$\mathrm{Ag^+\,(aq) + Cl^-\,(aq) \longrightarrow AgCl\,(s)} \quad \text{(net ionic)}$$

Example 3.6.1: Predicting Precipitation Reactions

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

a. potassium sulfate and barium nitrate
b. lithium chloride and silver acetate
c. lead nitrate and ammonium carbonate

Solution

(a) The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$\mathrm{Ba^{2+}\,(aq) + SO_4{}^{2-}\,(aq) \longrightarrow BaSO_4\,(s)}$$

(b) The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$\mathrm{Ag^+\,(aq) + Cl^-\,(aq) \longrightarrow AgCl\,(s)}$$

(c) The two possible products for this combination are $PbCO_3$ and NH_4NO_3. The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Pb^{2+}(aq) + {CO_3}^{2-}(aq) \longrightarrow PbCO_3(s)$$

Exercise 3.6.1

Which solution could be used to precipitate the barium ion, Ba^{2+}, in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

Answer available at the end of this section.

Acid-Base Neutralization Reactions

An acid-base reaction is one in which a hydrogen ion, H^+, is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text.

For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an **acid** is a substance that has H^+ to donate. You can recognize acids from the H at the front of their chemical formula; for example, HCl or H_2SO_4. Table 3.6.2 shows some more common acids.

Table 3.6.2: Common Strong Acids

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydroiodic acid
HNO_3	nitric acid
$HClO_4$	perchloric acid
H_2SO_4	sulfuric acid

A base is a substance that will dissolve in water to yield hydroxide ions, OH^-. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion—for example, NaOH and $Ca(OH)_2$. Unlike the acid compounds discussed previously, these compounds do not react chemically with water; instead they dissolve and dissociate, releasing hydroxide ions directly into the solution. For example, KOH and $Ba(OH)_2$ dissolve in water and dissociate completely to produce cations (K^+ and Ba^{2+}, respectively) and hydroxide ions, OH^-. These bases, along with other hydroxides that completely dissociate in water, are considered **strong bases**.

A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base (but not water), and the products are often a salt and water

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid $Mg(OH)_2$) is ingested to ease symptoms associated with excess stomach acid (HCl):

$$Mg(OH)_2(s) + 2\,HCl(aq) \longrightarrow MgCl_2(aq) + 2\,H_2O(l)$$

Note that in addition to water, this reaction produces a salt, magnesium chloride.

Example 3.6.2: Writing Equations for Acid-Base Reactions

Write balanced chemical equations for the acid-base reactions described here:

a. the weak acid hydrogen hypochlorite reacts with water
b. a solution of barium hydroxide is neutralized with a solution of nitric acid

Solution

(a) The two reactants are provided, HOCl and H_2O. Since the substance is reported to be an acid, its reaction with water will involve the transfer of H^+ from HOCl to H_2O to generate hydronium ions, H_3O^+ and hypochlorite ions, OCl^-.

$$\mathrm{HOCl\,(aq) + H_2O\,(l) \rightleftharpoons OCl^-\,(aq) + H_3O^+\,(aq)}$$

A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion

$$\mathrm{Ba(OH)_2\,(aq) + 2\,HNO_3\,(aq) \longrightarrow Ba(NO_3)_2\,(aq) + 2\,H_2O\,(l)}$$

Exercise 3.6.2

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

Answer available at the end of this section.

Oxidation-Reduction (Redox) Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term **oxidation** was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$\mathrm{2\,Na\,(s) + Cl_2\,(g) \longrightarrow 2\,NaCl\,(s)}$$

In this reaction, then, sodium goes from a 0 to a +1 charge, which is *oxidation* and chlorine goes from a 0 charge to a -1 charge, which is *reduction*.

Some redox processes do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound were ionic*. We will look at this sub-class of reactions in much greater detail at a later date. For now, if you see neutral elements becoming ions or vice versa, know that you are seeing an o**xidation-reduction (redox) reaction**.

Several subclasses of redox reactions are recognized:

- **combustion reactions** in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$\begin{aligned} \text{oxidation} &= \text{increase in oxidation number} \\ \text{reduction} &= \text{decrease in oxidation number} \end{aligned}$$

Link to Learning

Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

- **Single-displacement (replacement) reactions** are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)}$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$\mathrm{Cu\,(s) + 2\,AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,Ag\,(s)}$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color (Figure 3.6.6).

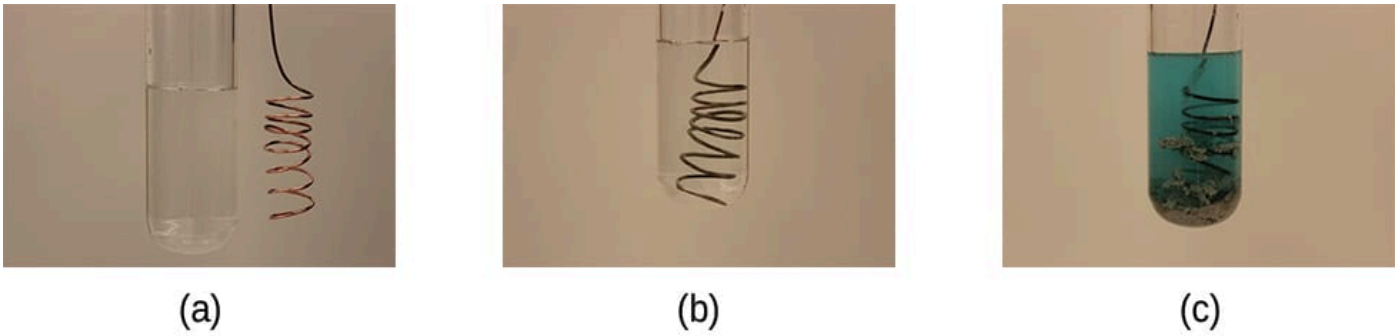


Figure 3.6.6: (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

Example 3.6.4: Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

a. $\mathrm{ZnCO_3\,(s) \longrightarrow ZnO\ (s)^+\ CO_2\,(g)}$
b. $\mathrm{2\,Ga\,(l) + 3\,Br_2\,(l) \longrightarrow 2\,GaBr_3\,(s)}$
c. $\mathrm{2\,H_2O_2\,(aq) \longrightarrow 2\,H_2O\,(l) + O_2\,(g)}$
d. $\mathrm{BaCl_2\,(aq) + K_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + 2\,KCl\,(aq)}$
e. $\mathrm{C_2H_4\,(g) + 3\,O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(l)}$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

a. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
b. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(l) to +3 in $GaBr_3$(s). The reducing agent is Ga(l). Bromine is reduced, its oxidation number decreasing from 0 in Br_2(l) to –1 in $GaBr_3$(s). The oxidizing agent is Br_2(l).
c. This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from –1 in H_2O_2(aq) to 0 in O_2(g). Oxygen is also reduced, its oxidation number decreasing from –1 in H_2O_2(aq) to –2 in H_2O(l). For disproportionation reactions, the same substance functions as an oxidant and a reductant.
d. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
e. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from –2 in C_2H_4(g) to +4 in CO_2(g). The reducing agent (fuel) is C_2H_4(g). Oxygen is reduced, its oxidation number decreasing from 0 in O_2(g) to –2 in H_2O(l). The oxidizing agent is O_2(g).

Exercise 3.6.4

This equation describes the production of tin(II) chloride:

$$\mathrm{Sn\,(s) + 2\,HCl\,(g) \longrightarrow SnCl_2\,(s) + H_2\,(g)}$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Answer available at the end of this section.

Footnotes

- 1The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.

Answers

Exercise 3.6.1

sodium sulfate, $\mathrm{BaSO_4}$

Exercise 3.6.2

$$\mathrm{H_3O^+\,(aq) + OH^-\,(aq) \longrightarrow 2\,H_2O\,(l)}$$

Exercise 3.6.4

Yes, a single-replacement reaction. $\mathrm{Sn\,(s)}$ is the reductant and $\mathrm{HCl\,(g)}$ is the oxidant.

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3.7: Reaction Stoichiometry

Learning Objectives

By the end of this section, you will have background informtion that will help you be able to:

- Describe the composition of a sample before or after a chemical reaction using relevant information (**chemical formulas, mass,** Avogadro's number, **molar mass, concentration,** dilution conditions, or **balanced chemical equations**)

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's **stoichiometry**, a term derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure"). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

Food preparation, for example, offers an appropriate macroscopic comparison to microscopic stoichiometry. A recipe for making eight pancakes calls for 1 cup pancake mix, cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

$$1 \text{ cup mix } + \frac{3}{4} \text{ cup milk } + 1 \text{ egg } \longrightarrow 8 \text{ pancakes}$$

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24 \cancel{\text{ pancakes}} \times \frac{1 \text{ egg}}{8 \cancel{\text{ pancakes}}} = 3 \text{ eggs}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive **stoichiometric factors** that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g)}$$

This equation shows ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2 \text{ NH}_3 \text{ molecules}}{3 \text{ H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ doz NH}_3 \text{ molecules}}{3 \text{ doz H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ mol NH}_3 \text{ molecules}}{3 \text{ mol H}_2 \text{ molecules}}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Example 3.7.1: Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation (see Figure 3.7.1)?

$$\mathrm{2\,Al + 3\,I_2 \longrightarrow 2\,AlI_3}$$

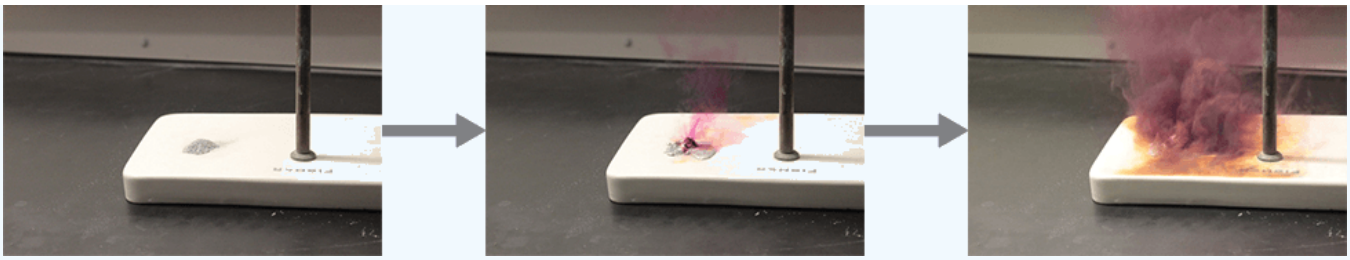
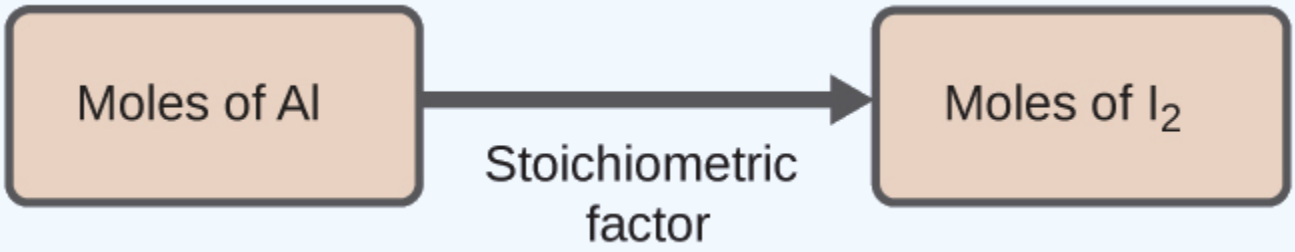


Figure 3.7.1: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\begin{aligned} mol\,\mathrm{I_2} &= 0.429\,\mathrm{mol\,Al} \times \frac{3\,\mathrm{mol\,I_2}}{2\,\mathrm{mol\,Al}} \\ &= 0.644\,\mathrm{mol\,I_2} \end{aligned}$$

Exercise 3.7.1

How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation

Answer available at the end of this section.

Example 3.7.2: Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

$$\mathrm{C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O}$$

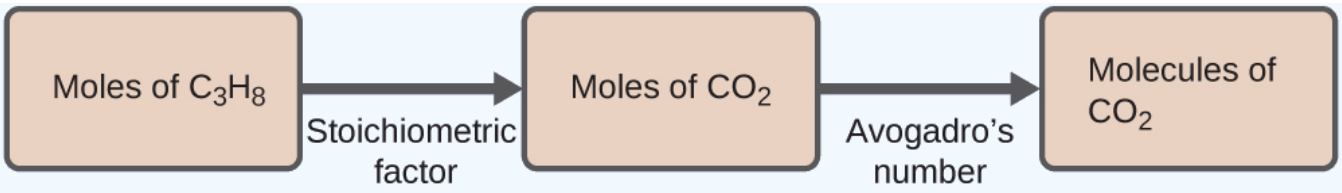
Solution

The approach here is the same as for Example 3.7.1, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

$$\frac{3\,\mathrm{mol\,CO_2}}{1\,\mathrm{mol\,C_3H_8}}$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75 mol\ {}_3CH_8 \times \frac{3 mol CO_2}{1 mol\ C_3H_8} \times \frac{6.022 \times 10^{23}\ CO_2\ \text{molecules}}{mol\ CO_2} = 1.4 \times 10^{24}\ CO_2\ \text{molecules}$$

Exercise 3.7.2

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow 2\,NH_3 + CaSO_4 + 2\,H_2O$$

Answer available at the end of this section.

These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

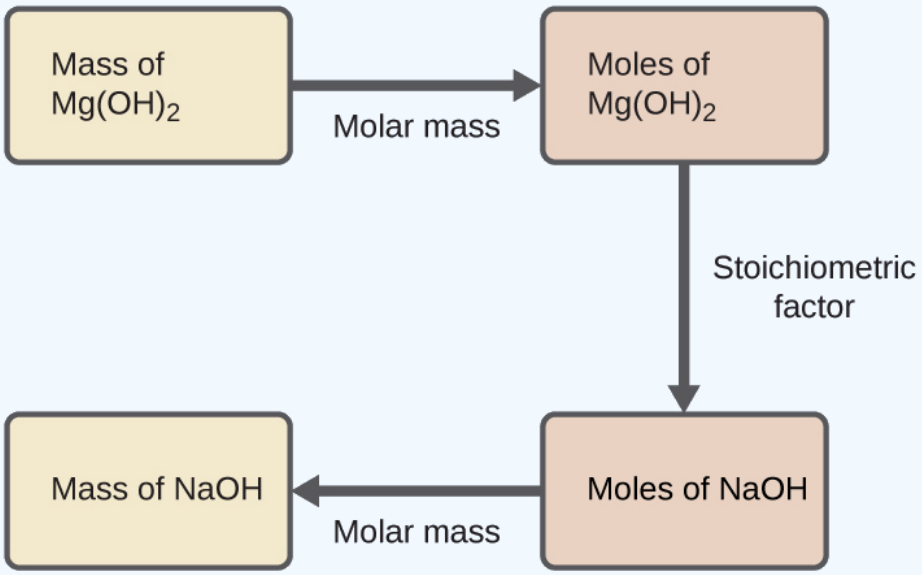
Example 3.7.3: Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $Mg(OH)_2$] by the following reaction?

$$MgCl_2\,(aq) + 2\,NaOH\,(aq) \longrightarrow Mg(OH)_2\,(s) + 2\,NaCl\,(aq)$$

Solution

The approach used previously in Example 3.7.1 and Example 3.7.2 is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



$$16 g \mathrm{Mg(OH)_2} \times \frac{1 mol \mathrm{Mg(OH)_2}}{58.3 g \mathrm{Mg(OH)_2}} \times \frac{2 \mathrm{mol\ NaOH}}{1\ \mathrm{mol\ Mg(OH)_2}} \times \frac{40.0\ \mathrm{g\ NaOH}}{\mathrm{mol\ NaOH}} = 22\ \mathrm{g\ NaOH}$$

Exercise 3.7.3

What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is:

$$4\ \mathrm{Ga} + 3\ \mathrm{O_2} \longrightarrow 2\ \mathrm{Ga_2O_3}$$

Answer available at the end of this section.

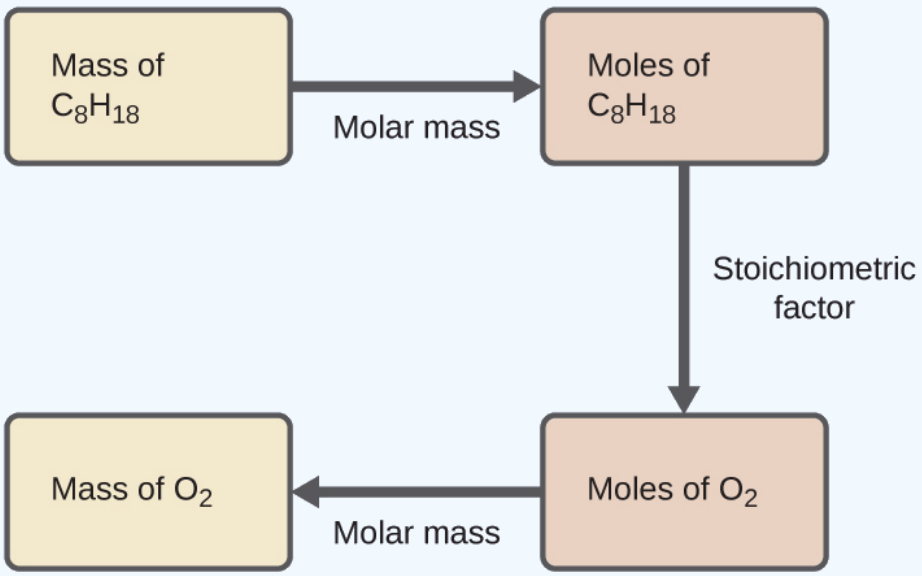
Example 3.7.4: Relating Masses of Reactants

What mass of oxygen gas, O_2, from the air is consumed in the combustion of 702 g of octane, C_8H_{18}, one of the principal components of gasoline?

$$2\ \mathrm{C_8H_{18}} + 25\ \mathrm{O_2} \longrightarrow 16\ \mathrm{CO_2} + 18\ \mathrm{H_2O}$$

Solution

The approach required here is the same as for the Example 3.7.3, differing only in that the provided and requested masses are both for reactant species.



$$702 g C_8H_{18} \times \frac{1 mol C_8H_{18}}{114.23 g G_8H_{18}} \times \frac{25 mol O_2}{2 mol C_8H_{18}} \times \frac{32.00 g O_2}{mol O_2} = 2.46 \times 10^3 g O_2$$

Exercise 3.7.4

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $\mathrm{Fe_2O_3} + 3\ \mathrm{CO} \longrightarrow 2\ \mathrm{Fe} + 3\ \mathrm{CO_2}$?

Answer available at the end of this section.

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the

use of stoichiometric factors derived from balanced chemical equations. Figure 3.7.2: provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

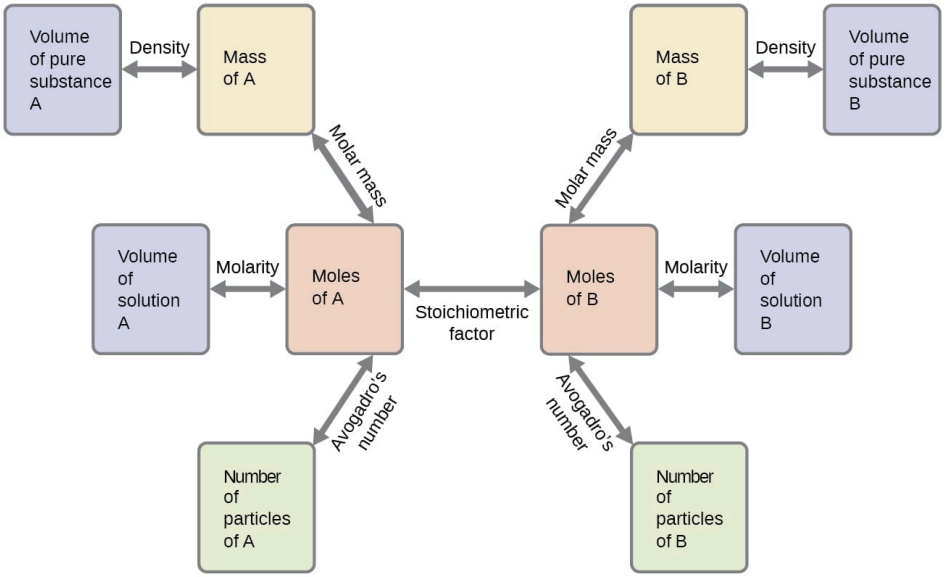


Figure 3.7.2: The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

Chemistry in Everyday Life: Airbags

Airbags (Figure 3.7.3) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\,\mathrm{NaN_3\,(s)} \longrightarrow 3\,\mathrm{N_2\,(g)} + 2\,\mathrm{Na\,(s)}$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.



Figure 3.7.3: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Answers

Exercise 3.7.1

2.04 mol

Exercise 3.7.2

4.8 10^{24} NH_3 molecules

Exercise 3.7.3

39.0 g

Exercise 3.7.4

13.22 g

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3.8: Reaction Yields

Learning Objectives

By the end of this section, you will be able to:

- Describe the composition of a sample before or after a chemical reaction using relevant information (**chemical formulas, mass,** Avogadro's number, **molar mass, concentration,** dilution conditions, or **balanced chemical equations**)

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*. All the exercises of the preceding module involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered, in which reactants are not present in stoichiometric amounts.

Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure 3.8.1):

$$1 \text{ slice of cheese } + 2 \text{ slices of bread } \longrightarrow 1 \text{ sandwich}$$

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

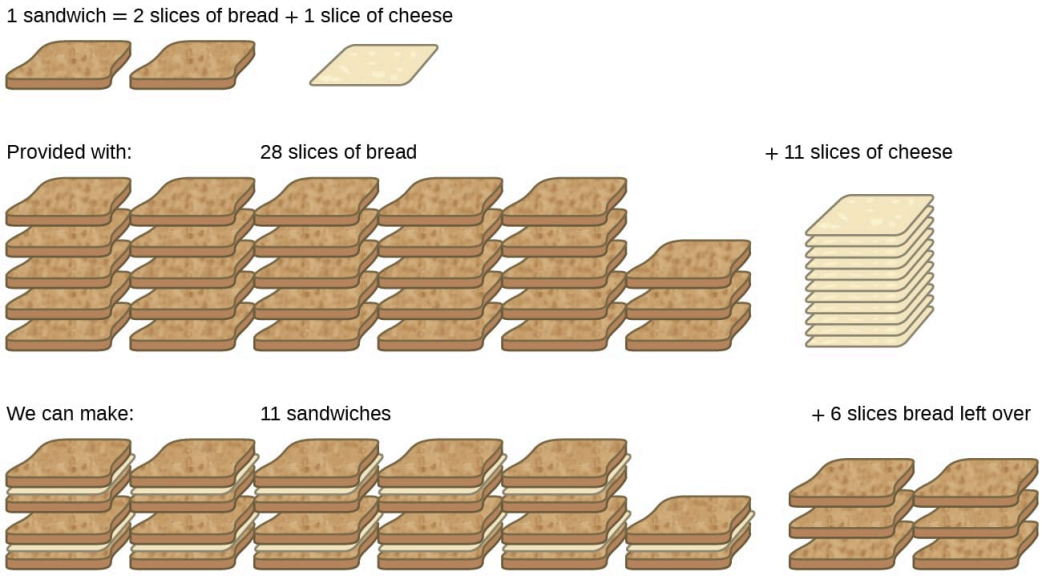


Figure 3.8.1: Sandwich making can illustrate the concepts of limiting and excess reactants.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be

generated. This substance is the **limiting reactant**, and the other substance(s) is the **excess reactant**. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of H_2 and 2 moles of Cl_2. This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen unreacted.

An alternative approach to identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant. For the example in the previous paragraph, complete reaction of the hydrogen would yield

$$\text{mol HCl produced} = 3\,\text{mol H}_2 \times \frac{2\,\text{mol HCl}}{1\,\text{mol H}_2} = 6\,\text{mol HCl}$$

Complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 2\,\text{mol Cl}_2 \times \frac{2\,\text{mol HCl}}{1\,\text{mol Cl}_2} = 4\,\text{mol HCl}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be unreacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure 3.8.2).

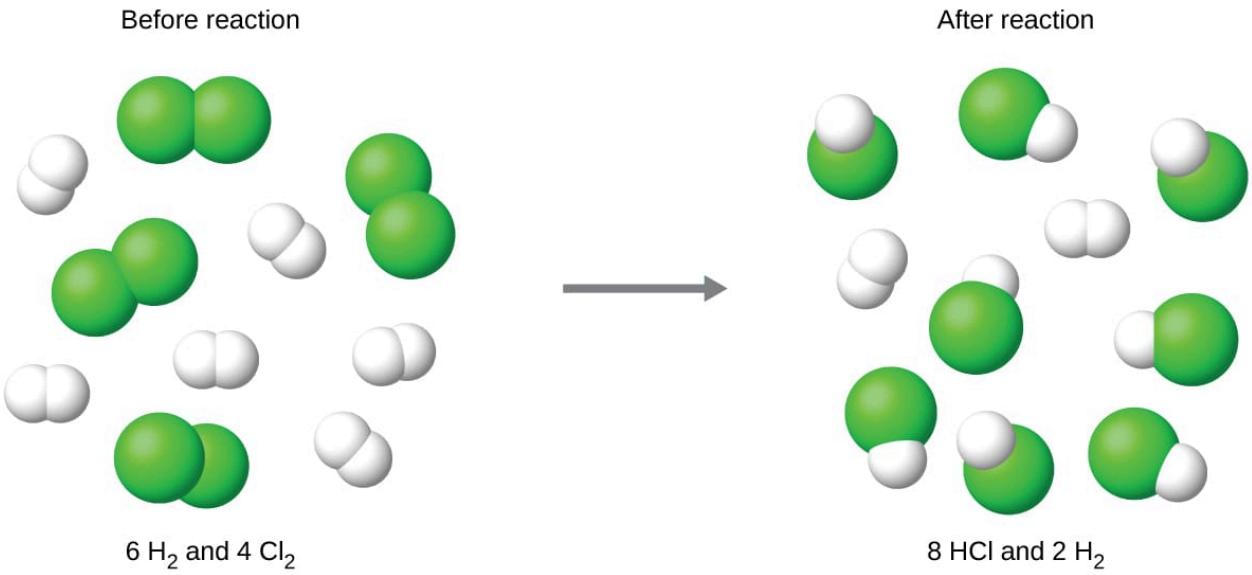


Figure 3.8.2: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

Link to Learning

View this interactive simulation illustrating the concepts of limiting and excess reactants.

Example 3.8.1: Identifying the Limiting Reactant

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3Si(s) + 2N_2(g) \longrightarrow Si_3N_4(s)$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of N_2 react?

Solution

Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant.

$$molSi = 2.00gSi \times \frac{1molSi}{28.09gSi} = 0.0712molSi$$

$$molSi = 2.00gSi \times \frac{1molSi}{28.09gSi} = 0.0712molSi$$

The provided Si:N_2 molar ratio is:

$$\frac{0.0712molSi}{0.0535molN_2} = \frac{1.33molSi}{1molN_2}$$

The stoichiometric Si:N_2 ratio is:

$$\frac{3molSi}{2molN_2} = \frac{1.5molSi}{1molN_2}$$

Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant.

Alternatively, compute the amount of product expected for complete reaction of each of the provided reactants. The 0.0712 moles of silicon would yield

$$molSi_3N_4 \text{ produced } = 0.0712molSi \times \frac{1molSi_3N_4}{3molSi^2} = 0.0237molSi_3N_4$$

while the 0.0535 moles of nitrogen would produce

$$\text{mol Si } N_4 \text{ produced } = 0.0535molN \times \frac{1molSi_3N_4}{2molN_2} = 0.0268molSi_3N_4$$

Since silicon yields the lesser amount of product, it is the limiting reactant.

Exercise 3.8.1

Which is the limiting reactant when 5.00 g of H_2 and 10.0 g of O_2 react and form water?

Answer available at the end of this section.

Percent Yield

The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the **theoretical yield** of the reaction. In practice, the amount of product obtained is called the **actual yield**, and it is often less than the theoretical yield for a number of reasons. Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products. Others are, by nature, incomplete (consider the partial reactions of weak acids and bases discussed earlier in this chapter). Some products are difficult to collect without some loss, and so less than perfect recovery will reduce the actual yield. The extent to which a reaction's theoretical yield is achieved is commonly expressed as its **percent yield**:

$$\text{percent yield } = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{3.8.1}$$

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if

the product is a gas). As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated.

Example 3.8.2: Calculation of Percent Yield

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$\mathrm{CuSO_4\,(aq) + Zn\,(s) \longrightarrow Cu\,(s) + ZnSO_4\,(aq)}$$

What is the percent yield?

Solution

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

$$1.274\,\mathrm{g\,CuSO_4} \times \frac{1\,\mathrm{mol\,CuSO_4}}{159.62\,\mathrm{g\,CuSO_4}} \times \frac{1\,\mathrm{mol\,Cu}}{1\,\mathrm{mol\,CuSO_4}} \times \frac{63.55\,\mathrm{g\,Cu}}{1\,\mathrm{mol\,Cu}} = 0.5072\,\mathrm{g\,Cu}$$

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated (via Equation 3.8.1 to be

$$\begin{aligned}\text{percent yield} &= \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100\% \\ &= \left(\frac{0.392\,\mathrm{g\,Cu}}{0.5072\,\mathrm{g\,Cu_2}}\right) \times 100\% \\ &= 77.3\%\end{aligned}$$

Exercise 3.8.2

What is the percent yield of a reaction that produces 12.5 g of the gas Freon CF_2Cl_2 from 32.9 g of CCl_4 and excess HF?

$$\mathrm{CCl_4 + 2\,HF \longrightarrow CF_2Cl_2 + 2\,HCl}$$

Answer available at the end of this section.

How Sciences Interconnect: Green Chemistry and Atom Economy

The purposeful design of chemical products and processes that minimize the use of environmentally hazardous substances and the generation of waste is known as *green chemistry*. Green chemistry is a philosophical approach that is being applied to many areas of science and technology, and its practice is summarized by guidelines known as the "Twelve Principles of Green Chemistry" (see details at this website). One of the 12 principles is aimed specifically at maximizing the efficiency of processes for synthesizing chemical products. The *atom economy* of a process is a measure of this efficiency, defined as the percentage by mass of the final product of a synthesis relative to the masses of *all* the reactants used:

$$\text{atom economy} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100\%$$

Though the definition of atom economy at first glance appears very similar to that for percent yield, be aware that this property represents a difference in the *theoretical* efficiencies of *different* chemical processes. The percent yield of a given chemical process, on the other hand, evaluates the efficiency of a process by comparing the yield of product actually obtained to the maximum yield predicted by stoichiometry.

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (Figure 3.8.3). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process

was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.

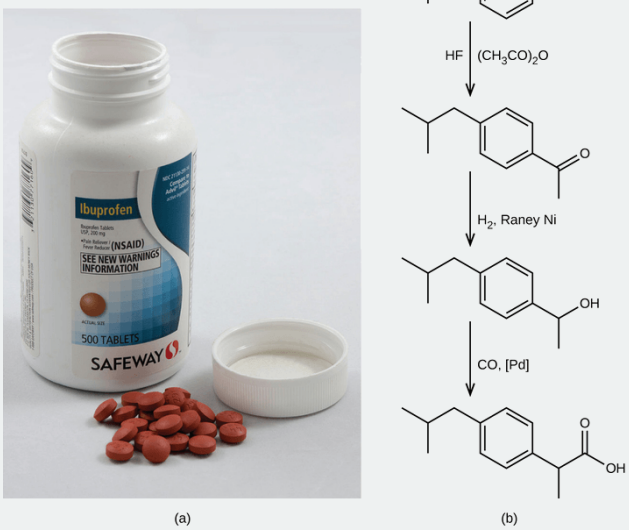


Figure 3.8.3: (a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)

Answers

Exercise 3.8.1

O_2

Exercise 3.8.2

48.3%

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4: QUANTUM MECHANICS DESCRIBES ATOMIC STRUCTURE

4.1: Overview and Objectives

4.2: Electromagnetic Energy

4.3: Coulomb's Law and the Electrostatic Potential

4.3.1: Coulomb's Law and the Electrostatic Potential (Problems)

4.4: The Bohr Model

4.5: Development of Quantum Theory

4.6: Electronic Structure of Atoms (Electron Configurations)

4.7: Periodic Variations in Element Properties

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4.1: Overview and Objectives

> "*We must be clear that when it comes to atoms, language can be used only as in poetry. The poet, too, is not nearly so concerned with describing facts as with creating images and establishing mental connections.*" *(Niels Bohr)*

We humans mostly work with physics in the realm of the "medium sized." This means things that are roughly the same size, mass, or speed as us, give or take a few factors of 10. At this size scale, the laws of what is called classical physics very well for predicting behavior. However, when an object gets "too small" (roughly 1 nm or less), "too fast" (approaching the speed of light), or "too light/too heavy" (think atoms on one end and planets on the other), classical physics breaks down and we need different descriptors of behavior. This is very relevant to chemistry, where atoms and molecules are very small and very light, which makes their behavior very weird as compared to the expectations of classical physics. In this chapter, we will look at some of the experiments that illuminated (pun intended) the odd behaviors of light, subatomic particles, atoms, and molecules. We'll then learn the basics of the physics of very small objects, which we call *quantum mechanics,* and we'll apply those basics as an explanation for certain properties of elements and the structure of the modern periodic table.

From the outset, it's important to recognize that those rules look very different than the rules we are used to. Most importantly, the principle of wave-particle duality is operative and responsible for some pretty odd behaviors. You will have trouble visualizing what that might look like. You're supposed to - just look at what Danish physicist Niels Bohr, one of the fathers of quantum mechanics, said above. Small things do not behave in ways that we can visualize. The images you'll get for what these objects are doing are incomplete and metaphorical. They are not exact descriptions of atoms or molecules, because we simply lack the language to do that. As you read, take the time to stop and marvel at how very strange, and how very interesting, our world truly is.

Chapter Objectives

- Convert between wavelength/frequency/energy/mass or compute electronic transition wavelengths in the hydrogen atom.
- Compare and contrast quantum mechanical models of atomic structure (Bohr model and shell model).
- In accordance with the shell model, write electron configurations, draw orbital diagrams, identify core and valence electrons, and predict magnetic properties for ground state or excited atoms or ions.
- Rank atoms and ions by their radius, first ionization energy, electronegativity, and metallicity.

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4.2: Electromagnetic Energy

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- **Convert between wavelength/frequency/energy/mass** or compute electronic transition wavelengths in the hydrogen atom.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave-they all stay in or above their seats.

All waves, including forms of electromagnetic radiation, are characterized by, a **wavelength** (denoted by λ, the lowercase Greek letter lambda), a **frequency** (denoted by ν, the lowercase Greek letter nu), and an **amplitude**. As can be seen in Figure $4.2.1$, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^{3} m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the **hertz** (Hz). Common multiples of this unit are megahertz, ($1\ \mathrm{MHz} = 1 \times 10^{6}\ \mathrm{Hz}$) and gigahertz ($1\ \mathrm{GHz} = 1 \times 10^{9}\ \mathrm{Hz}$). The amplitude corresponds to the magnitude of the wave's displacement and so, in Figure $4.2.1$, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

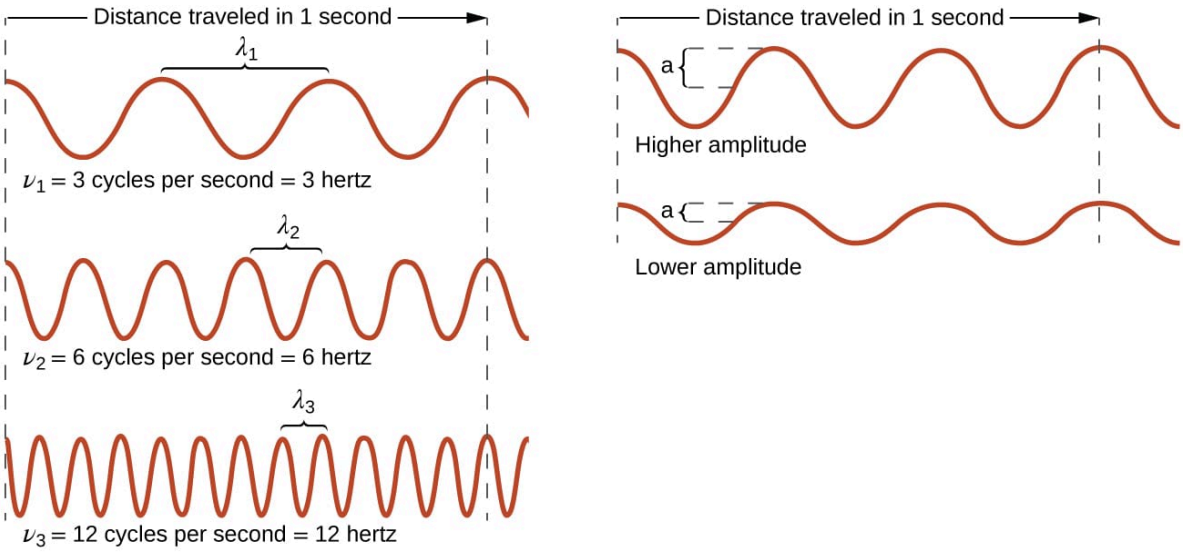


Figure 4.2.1: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum, speed is equal to the fundamental constant, c as shown below. **This is an equation you must memorize.**

$$c = 2.998 \times 10^8 ms^{-1} = \lambda\nu$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure 4.2.2. This figure also shows the electromagnetic spectrum, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

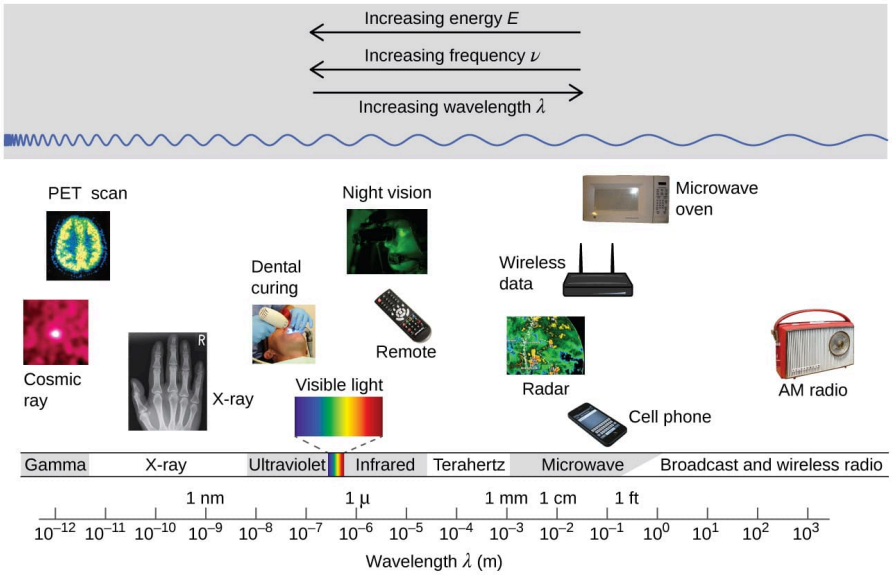


Figure 4.2.2: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. (credit “Cosmic ray": modification of work by NASA; credit “PET scan": modification of work by the National Institute of Health; credit “X-ray": modification of work by Dr. Jochen Lengerke; credit “Dental curing": modification of work by the Department of the Navy; credit “Night vision": modification of work by the Department of the Army; credit “Remote": modification of work by Emilian Robert Vicol; credit “Cell phone": modification of work by Brett Jordan; credit “Microwave oven": modification of work by Billy Mabray; credit “Ultrasound": modification of work by Jane Whitney; credit “AM radio": modification of work by Dave Clausen)

Example 4.2.1: Determining the Frequency and Wavelength of Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm (1 nm = 1×10^{-9} m). What is the frequency of this light?

Solution

We can rearrange the Equation $c = \lambda\nu$ to solve for the frequency:

$$\nu = \frac{c}{\lambda}$$

Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = \left(\frac{2.998 \times 10^{8} ms^{-1}}{589 nm}\right)\left(\frac{1 \times 10^{9} nm}{1 m}\right) = 5.09 \times 10^{14} s^{-1}$$

Exercise 4.2.1

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

Answer available at the end of this section.

Chemistry in Everyday Life: Wireless Communication



Figure 4.2.3: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 4.2.4). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.

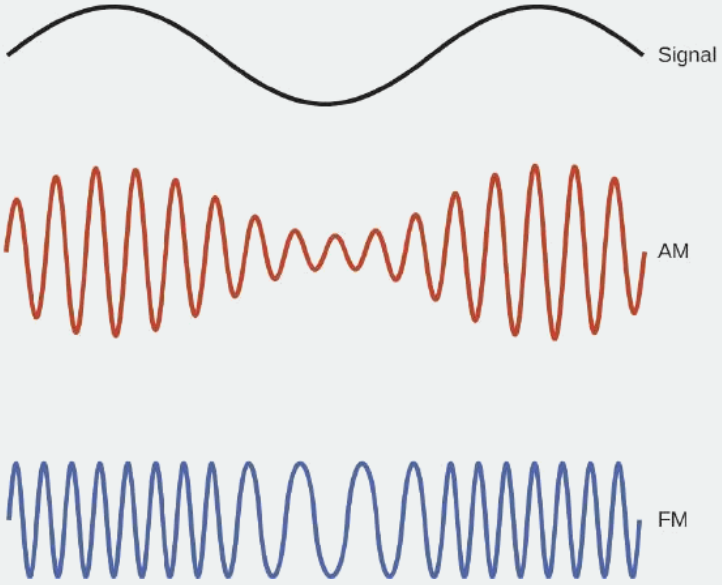


Figure 4.2.4: This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 4.2.5 shows the interference patterns that arise when light passes through narrow slits closely spaced about a wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in Figure 4.2.5 correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference patterns cannot be explained by particles moving according to the laws of classical mechanics.



Figure 4.2.5: Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

Portrait of a Chemist: Dorothy Crowfoot Hodgkin

X-rays exhibit wavelengths of approximately 0.01–10 nm. Since these wavelengths are comparable to the spaces between atoms in a crystalline solid, X-rays are scattered when they pass through crystals. The scattered rays undergo constructive and destructive interference that creates a specific diffraction pattern that may be measured and used to precisely determine the positions of atoms within the crystal. This phenomenon of X-ray diffraction is the basis for very powerful techniques enabling the determination of molecular structure. One of the pioneers who applied this powerful technology to important biochemical substances was Dorothy Crowfoot Hodgkin.

Born in Cairo, Egypt, in 1910 to British parents, Dorothy's fascination with chemistry was fostered early in her life. At age 11 she was enrolled in a prestigious English grammar school where she was one of just two girls allowed to study chemistry. On her 16th birthday, her mother, Molly, gifted her a book on X-ray crystallography, which had a profound impact on the trajectory of her career. She studied chemistry at Oxford University, graduating with first-class honors in 1932 and directly entering Cambridge University to pursue a doctoral degree. At Cambridge, Dorothy recognized the promise of X-ray crystallography for protein structure determinations, conducting research that earned her a PhD in 1937. Over the course of a very productive career, Dr. Hodgkin was credited with determining structures for several important biomolecules, including cholesterol iodide, penicillin, and vitamin B12. In recognition of her achievements in the use of X-ray techniques to elucidate the structures of biochemical substances, she was awarded the 1964 Nobel Prize in Chemistry. In 1969, she led a team of scientists who deduced the structure of insulin, facilitating the mass production of this hormone and greatly advancing the treatment of diabetic patients worldwide. Dr. Hodgkin continued working with the international scientific community, earning numerous distinctions and awards prior to her death in 1993.

Blackbody Radiation and the Ultraviolet Catastrophe

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a **continuous spectrum**. Figure 4.2.8 shows the wavelength distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light, and more slowly for longer wavelength infrared (IR) light.

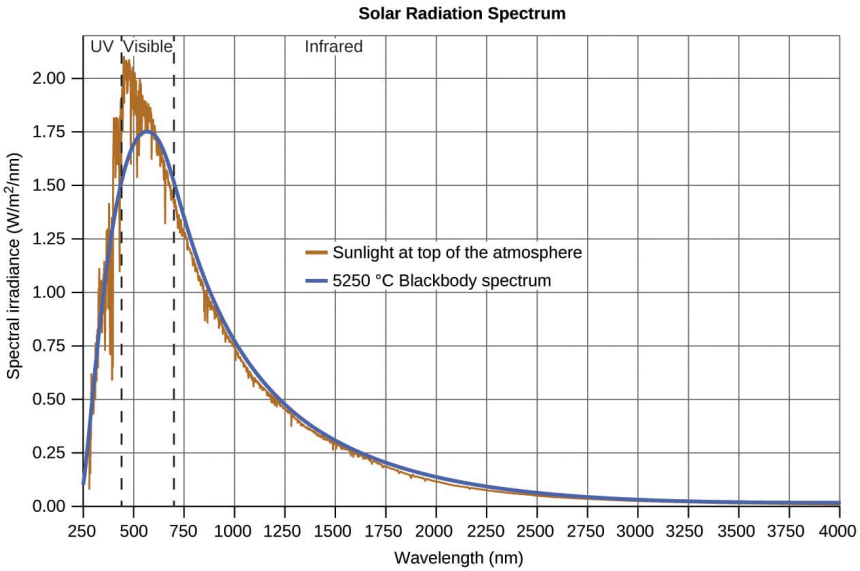


Figure 4.2.8: The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)

In Figure 4.2.8, the solar distribution is compared to a representative distribution, called a **blackbody spectrum**, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A blackbody is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is “ideal” in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. Figure 4.2.9 shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves, λ_{max}, shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the “ultraviolet catastrophe” because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region. **This is an equation that applies in many contexts and that you must memorize.**

$$E = nh\nu, n = 1, 2, 3, ... \tag{4.2.1}$$

The quantity h is a constant now known as **Planck's constant**, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies, which he was unable to explain. The value of Planck's constant is very small, 6.626×10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.

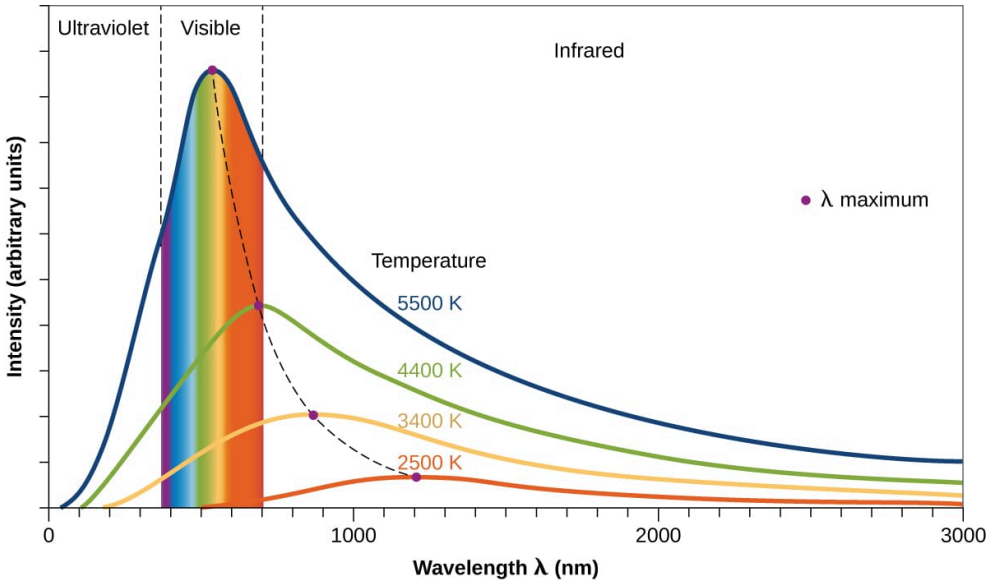


Figure 4.2.9: Blackbody spectral distribution curves are shown for some representative temperatures.

The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (Figure 4.2.10). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within in a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

The observed phenomenon (not discovered by Einstein) was that electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

$$E = h\nu$$

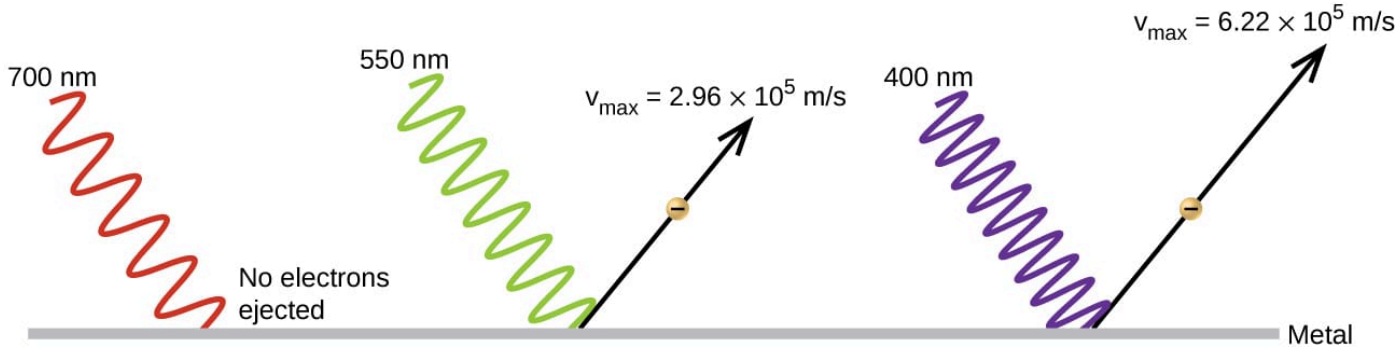


Figure 4.2.10: Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called **photons**) whose energy depended on their frequency, according to Planck's formula (Equation 4.2.1), $E = h\nu$. Einstein showed that you can combine this equation with the earlier relationship between wavelength, frequency, and the speed of light, $c = \nu\lambda$, to yield

$$E = \frac{hc}{\lambda})$$

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as **wave-particle duality**.

Example 4.2.2: Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, λ, and convert units of nanometers to meters so that the units of λ and c are the same.

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= \frac{\left(6.626 \times 10^{-34}\ \text{J}\cdot\cancel{\text{s}}\right)\left(2.998 \times 10^{8}\ \cancel{\text{m}}\ \cancel{\text{s}}^{-1}\right)}{\left(640\ \cancel{\text{nm}}\right)\left(\frac{1\ \cancel{\text{m}}}{10^{9}\ \cancel{\text{nm}}}\right)} \\ &= 3.10 \times 10^{-19} J \end{aligned}$$

Exercise 4.2.2

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven-they do not contain water molecules.) This frequency is about 3 10^9 Hz. What is the energy of one photon in these microwaves?

Answer available at the end of this section.

Link to Learning

Use this simulation program to experiment with the photoelectric effect to see how intensity, frequency, type of metal, and other factors influence the ejected photons.

Example 4.2.3: Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

a. Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
b. Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
c. Increasing the brightness of incoming light *increases* the number of ejected electrons.
d. Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Solution

a. False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.
b. False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
c. True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.
d. True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

Exercise 4.2.3

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is 9.87 10^{14} Hz.

Answer available at the end of this section.

Line Spectra

Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in Figure 4.2.8: , sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in Figure 4.2.9.

In contrast to continuous spectra, light can also occur as discrete or **line spectra** having very narrow line widths interspersed throughout the spectral regions such as those shown in Figure 4.2.12. Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way (Figure 4.2.11). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



Figure 4.2.11: Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in Figure 4.2.12.

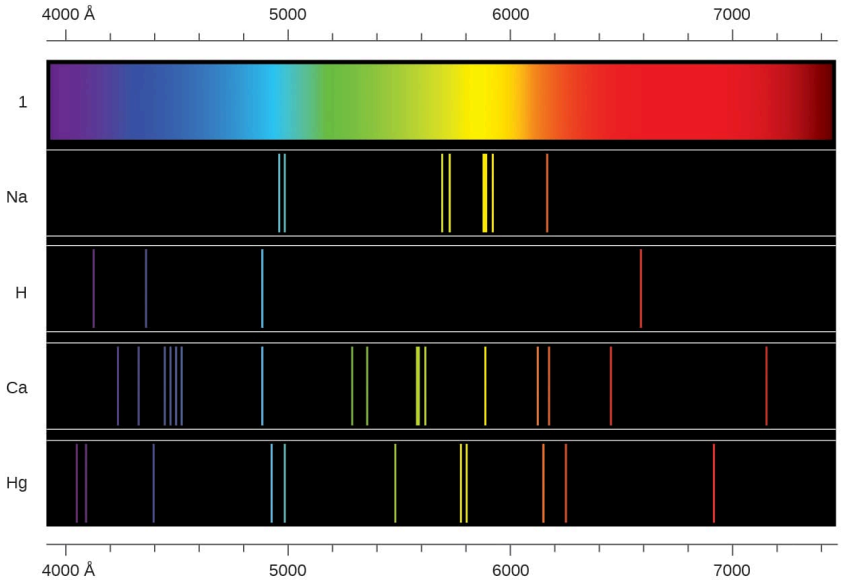


Figure 4.2.12: Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which *k* is a constant:

$$\frac{1}{\lambda} = k\left(\frac{1}{4} - \frac{1}{n^2}\right), \quad n = 3, 4, 5, 6$$

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range,

where n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the **Rydberg constant** (1.097 10^7 m^{-1}). **You do not have to memorize this equation, but you do need to know what the variables are and how to use them.**

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

Answers

Exercise 4.2.1

0.353 m = 35.3 cm

Exercise 4.2.2

2 10^{-24} J

Exercise 4.2.3

394 kJ/mol

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4.3: Coulomb's Law and the Electrostatic Potential

Skills to Develop

- Use Coulomb's Law to explain electrostatic potential and bonding

Through the work of scientists in the late 18th century, the main features of the **electrostatic force**—the existence of two types of charge, the observation that like charges repel, unlike charges attract, and the decrease of force with distance—were eventually refined, and expressed as a mathematical formula. The mathematical formula for the electrostatic force is called **Coulomb's law** after the French physicist Charles Coulomb (1736–1806), who performed experiments and first proposed a formula to calculate it.



Figure $4.3.1$***:*** *This NASA image of Arp 87 shows the result of a strong gravitational attraction between two galaxies. In contrast, at the subatomic level, the electrostatic attraction between two objects, such as an electron and a proton, is far greater than their mutual attraction due to gravity. (credit: NASA/HST)*

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles, based on Coulomb's Law:

$$F_{gravity} = G\frac{m_1 m_2}{r^2} \tag{4.3.1}$$

with

- G is a gravitational constant
- m_1 and m_2 are the masses of particle 1 and 2, respectively
- r is the distance between the two particles

The electrostatic force has the same form as the gravitational force between two mass particles except that the electrostatic force depends on the magnitudes of the charges on the particles (+1 for the proton and –1 for the electron) instead of the magnitudes of the particle masses that govern the gravitational force.

$$F_{electrostatic} = k\frac{m_1 m_2}{r^2} \tag{4.3.2}$$

with

- k is a constant
- m_1 and m_2 are the masses of particle 1 and 2, respectively
- r is the distance between the two particles

The electrostatic force is a vector quantity and is expressed in units of newtons. The force is understood to be along the line joining the two charges. (Figure $4.3.2$)

Although the formula for Coulomb's law is simple, it was no mean task to prove it. The experiments Coulomb did, with the primitive equipment then available, were difficult. Modern experiments have verified Coulomb's law to great precision. For example, it has been shown that the force is inversely proportional to distance between two objects squared $(F \propto 1/r^2)$ to an accuracy of 1 part in 10^{16}. No exceptions have ever been found, even at the small distances within the atom.

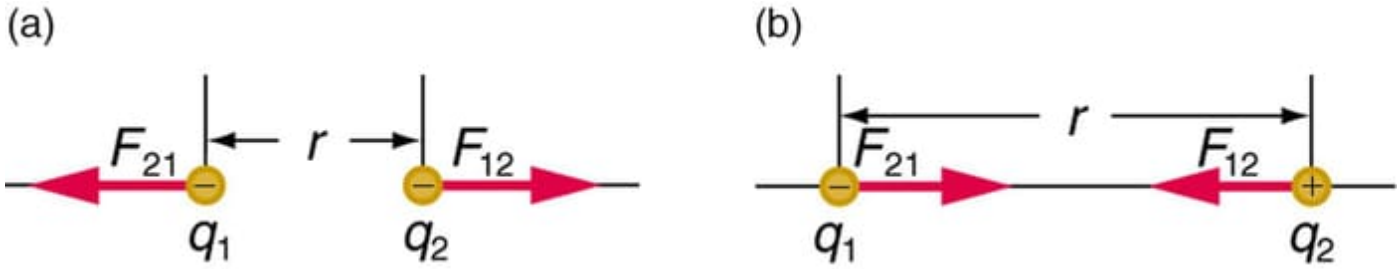


Figure $4.3.2$***:*** *The magnitude of the electrostatic force* F *between point charges* q_1 *and* q_2 *separated by a distance* r *is given by Coulomb's law. Note that Newton's third law (every force exerted creates an equal and opposite force) applies as usual—the force on* q_1 *is equal in magnitude and opposite in direction to the force it exerts on* q_2*. (a) Like charges. (b) Unlike charges.*

Since forces can be derived from potentials, it is convenient to work with potentials instead, since they are forms of energy. The electrostatic potential is also called the *Coulomb potential*. Because the electrostatic potential has the same form as the gravitational potential, according to classical mechanics, the equations of motion should be similar, with the electron moving around the nucleus in circular or elliptical orbits (hence the label "planetary" model of the atom). Potentials of the form *V*(*r*) that depend only on the radial distance r are known as central potentials. Central potentials have spherical symmetry, and so rather than specifying the position of the electron in the usual Cartesian coordinates (*x*, *y*, *z*), it is more convenient to use polar spherical coordinates centered at the nucleus, consisting of a linear coordinate *r* and two angular coordinates, usually specified by the Greek letters theta (θ) and phi (*Φ*). These coordinates are similar to the ones used in GPS devices and most smart phones that track positions on our (nearly) spherical earth, with the two angular coordinates specified by the latitude and longitude, and the linear coordinate specified by sea-level elevation. Because of the spherical symmetry of central potentials, the energy and angular momentum of the classical hydrogen atom are constants, and the orbits are constrained to lie in a plane like the planets orbiting the sun. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron's orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

visualize coulomb's law with this simulation!

PhET Simulation

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Summary

YouTube Video

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Video $4.3.1$***:*** *A review of Coulomb's Law.*

Frenchman Charles Coulomb was the first to publish the mathematical equation that describes the electrostatic force between two objects. Coulomb's law gives the magnitude of the force between point charges. It is $F = k\frac{|q_1 q_2|}{r^2}$, where q_1 and q_2 are two point charges separated by a distance r, and $k \approx 8.99 \times 10^9 N \cdot m^2/C^2$. This Coulomb force is extremely basic, since most charges are due to point-like particles. It is responsible for all electrostatic effects and underlies most macroscopic forces. The Coulomb force is extraordinarily strong compared with the gravitational force, another basic force—but unlike gravitational force it can cancel, since it can be either attractive or repulsive. The electrostatic force between two subatomic particles is far greater than the gravitational force between the same two particles.

Glossary

Coulomb's law
: the mathematical equation calculating the electrostatic force vector between two charged particles

Coulomb force
: another term for the electrostatic force

electrostatic force
: the amount and direction of attraction or repulsion between two charged bodies

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4.3.1: Coulomb's Law and the Electrostatic Potential (Problems)

PROBLEM 4.3.1.1

Would you expect two like charges close together to have a relative potential energy above or below 0?

Answer

Like charges should have energies above 0.

PROBLEM 4.3.1.2

Would you expect two like charges far apart to have a relative potential energy above or below 0?

Answer

Like charges should have energies above 0.

PROBLEM 4.3.1.3

Would you expect two opposite charges far apart to have a relative potential energy above or below 0?

Answer

opposite charges should have energies below 0.

PROBLEM 4.3.1.4

Rank the following scenarios from HIGHEST (most positive) to LOWEST (most negative) relative potential energy.

a. +3, -2 charges, 100 angstroms apart

b. +1, -1 charges, 200 angstroms apart

c. +1, +1 charges, 200 angstroms apart

d. -3, -3 charges, 100 angstroms apart

Answer

d, c, b, a

Click here for a video of the solution

YouTube Video

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Feedback

Think one of the answers above is wrong? Let us know here.

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4.4: The Bohr Model

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Convert between wavelength/frequency/energy/mass or **compute electronic transition wavelengths in the hydrogen atom.**
- Compare and contrast quantum mechanical models of atomic structure (Bohr model and shell model).

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron's orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism's prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom Planck's ideas of quantization and Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. His theoretical description matched the experimentally-determined Rydberg equation from the previous section:

$$R_\infty = \frac{k}{hc}$$

When Bohr calculated his theoretical value for the Rydberg constant, R_∞, and compared it with the experimentally accepted value, he got excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that Bohr's model was taken seriously, despite the many assumptions that Bohr needed to derive it.

One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the n = 1 orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its ground electronic state (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher n value and the atom is now in an excited electronic state (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (Figure $4.4.2$).

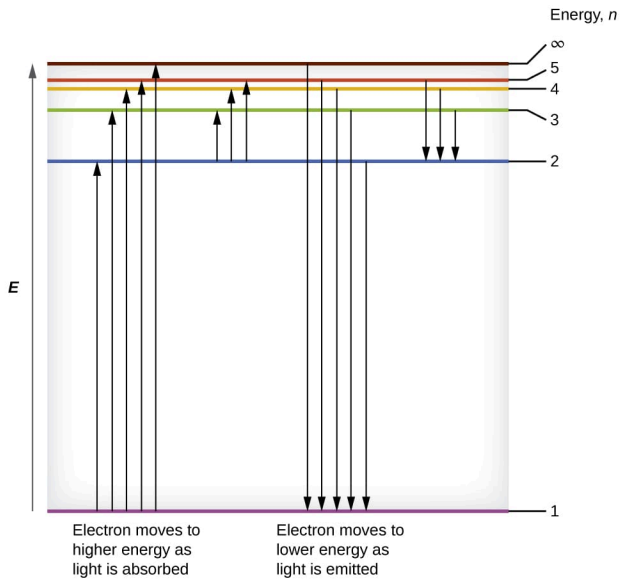


Figure 4.4.2: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Since Bohr's model involved only a single electron, it could also be applied to the single electron ions He^{+}, Li^{2+}, Be^{3+}, and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as hydrogen-like atoms. The energy expression for hydrogen-like atoms is a generalization of the hydrogen atom energy, in which Z is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on) and k has a value of 2.179 10^{-18} J.

$$E_n = -\frac{kZ^2}{n^2} \tag{4.4.1}$$

Example 4.4.1: Calculating the Energy of an Electron in a Bohr Orbit

Early researchers were very excited when they were able to predict the energy of an electron at a particular distance from the nucleus in a hydrogen atom. If a spark promotes the electron in a hydrogen atom into an orbit with n = 3, what is the calculated energy, in joules, of the electron?

Solution

The energy of the electron is given by Equation 4.4.1:

$$E = \frac{-kZ^2}{n^2}$$

The atomic number, Z, of hydrogen is 1; k = 2.179 10^{-18} J; and the electron is characterized by an \(n\) value of 3. Thus,

$$E = \frac{-\left(2.179 \times 10^{-18} J\right) \times (1)^2}{(3)^2} = -2.421 \times 10^{-19} J$$

Exercise 4.4.1

The electron in Figure 4.4.2 is promoted even further to an orbit with $n = 6$. What is its new energy?

Answer available at the end of this section.

Example 4.4.2: Calculating the Energy and Wavelength of Electron Transitions in a One-electron (Bohr) System

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with $n = 4$ to the orbit with $n = 6$? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

$$\begin{aligned}\Delta E &= E_1 - E_2 \\ &= 2.179 \times 10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \\ &= 2.179 \times 10^{-18}\left(\frac{1}{4^2} - \frac{1}{6^2}\right) J \\ &= 2.179 \times 10^{-18}\left(\frac{1}{16} - \frac{1}{36}\right) J \\ &= 7.566 \times 10^{-20} J\end{aligned}$$

This energy difference is positive, indicating a photon enters the system (is absorbed) to excite the electron from the *n* = 4 orbit up to the *n* = 6 orbit. The wavelength of a photon with this energy is found by the expression $E = \frac{hc}{\lambda}$. Rearrangement gives:

$$\begin{aligned}\lambda &= \frac{hc}{E} \\ &= \left(6.626 \times 10^{-34}\ \cancel{\text{J} \cdot \text{s}}\right) \times \frac{2.998 \times 10^{8}\ \text{m}\,\cancel{s^{-1}}}{7.566 \times 10^{-20}\ \cancel{J}} \\ &= 2.626 \times 10^{-6}\ \text{m}\end{aligned}$$

From the illustration of the electromagnetic spectrum in Electromagnetic Energy, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

Exercise 4.4.2

What is the energy in joules and the wavelength in meters of the photon produced when an electron falls from the *n* = 5 to the *n* = 3 level in a He^+ ion (*Z* = 2 for He^+)?

Answer available at the end of this section.

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by quantum numbers: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions. Unfortunately, although this was a remarkable achievement, Bohr was unable to extend his theory to the next simplest atom, He, which only has two electrons.

Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

Answers

Exercise 4.4.1

-6.053×10^{-20} J

Exercise 4.4.2

6.198×10^{-19} J; 3.205×10^{-7} m

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4.5: Development of Quantum Theory

Learning Objectives

By the end of this section, you will be able to:

- **Convert between wavelength/frequency/energy/mass** or compute electronic transition wavelengths in the hydrogen atom.
- Compare and contrast quantum mechanical models of atomic structure (Bohr model and shell model).

Bohr's model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number n = 1, 2, 3, and so on, but never in between? Why did the model work so well describing hydrogen and one-electron ions, but could not correctly predict the emission spectrum for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

Wave-Particle Duality Applies to Matter

As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

One of the first people to pay attention to the special behavior of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass m and velocity v (that is, with linear momentum p) should also exhibit the behavior of a wave with a wavelength value λ, given by this expression in which h is the familiar Planck's constant. **You do not need to memorize this equation, but you do need to know what the variables mean and how to use it.**

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

This is called the **de Broglie wavelength**. Unlike the other values of λ discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [v, m/s], not frequency [ν, Hz]. Although these two symbols appear nearly identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure $4.5.2$).

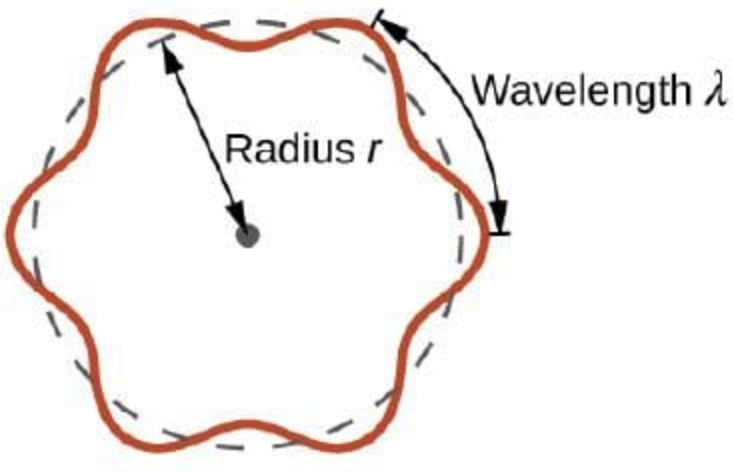


Figure 4.5.2: If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.

For a circular orbit of radius r, the circumference is $2\pi r$, and so de Broglie's condition is:

$$2\pi r = n\lambda, \qquad n = 1, 2, 3, ...$$

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. It is strikingly similar to the interference patterns for light shown in Electromagnetic Energy for light passing through two closely spaced, narrow slits. Thus the wave–particle duality first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.

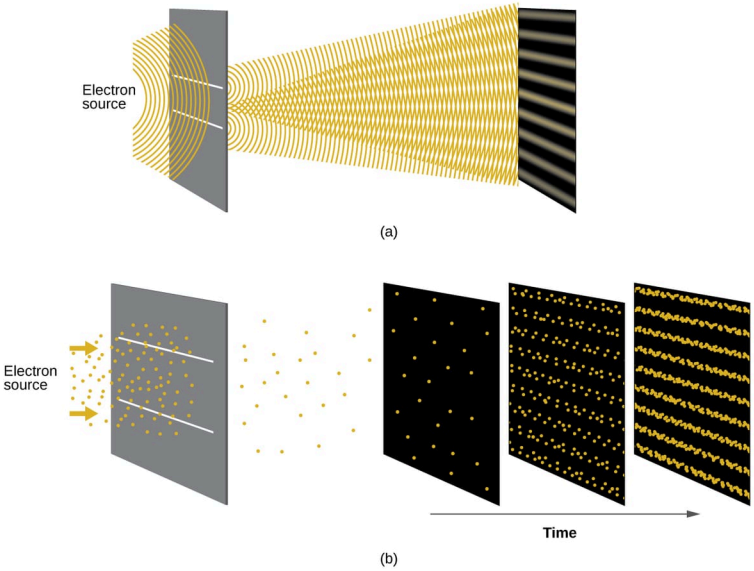


Figure 4.5.3: (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons.

Link to Learning

View the Dr. Quantum – Double Slit Experiment cartoon for an easy-to-understand description of wave–particle duality and the associated experiments.

Example 4.5.1: Calculating the Wavelength of a Particle

If an electron travels at a velocity of $1.000 \times 10^7\ \text{m s}^{-1}$ and has a mass of $9.109 \times 10^{-28}\ \text{g}$, what is its wavelength?

Solution

We can use de Broglie's equation to solve this problem, but we first must do a unit conversion of Planck's constant. You learned earlier that $1\ \text{J} = 1\text{kg m}^2/\text{s}^2$. Thus, we can write $h = 6.626 \times 10^{-34}\ \text{J} \cdot \text{s}$ as $6.626 \times 10^{-34}\ \text{kg m}^2/\text{s}$.

$$\begin{aligned}\lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34}\,\text{kg m}^2/\text{s}}{\left(9.109 \times 10^{-31}\,\text{kg}\right)\left(1.000 \times 10^7\,\text{m/s}\right)} \\ &= 7.274 \times 10^{-11} m\end{aligned}$$

This is a small value, but it is significantly larger than the size of an electron in the classical (particle) view. This size is the same order of magnitude as the size of an atom. This means that electron wavelike behavior is going to be noticeable in an atom.

Exercise 4.5.1

Calculate the wavelength of a softball with a mass of 100 g traveling at a velocity of 35 m s^{-1}, assuming that it can be modeled as a single particle.

Answer available at the end of this section.

Wave-particle duality also implies uncertainty. Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the Heisenberg uncertainty principle: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle*. For a particle of mass \(*m*\) moving with velocity v_x in the x direction (or equivalently with momentum p_x), the product of the uncertainty in the position, Δx, and the uncertainty in the momentum, Δp_x, must be greater than or equal to $\hbar/2$ (where $\hbar = h/2$, the value of Planck's constant divided by 2π).

$$\Delta x \times \Delta p_x = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2}$$

This equation allows us to calculate the limit to how precisely we can know both the simultaneous position of an object and its momentum.

The Quantum-Mechanical Model of an Atom

Erwin Schrödinger extended de Broglie's work by deriving what is today known as the Schrödinger equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra. Schrödinger described electrons as three-dimensional stationary waves, or **wavefunctions**, represented by the Greek letter psi, ψ. A few years later, Max Born proposed an interpretation of the wavefunction ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

$$\hat{H}\psi = E\psi$$

$\hat{H}$ is the Hamiltonian operator, a set of mathematical operations representing the total energy of the quantum particle (such as

an electron in an atom), ψ is the wavefunction of this particle that can be used to find the special distribution of the probability of finding the particle, and E is the actual value of the total energy of the particle.

Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as **quantum mechanics**.

Link to Learning

You may also have heard of Schrödinger because of his famous thought experiment. This story explains the concepts of superposition and entanglement as related to a cat in a box with poison.

Quantum Theory of Electrons in Atoms - The Shell Model

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding to these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an n value, where $n = 1, 2, 3, \ldots$. Generally speaking, the energy of an electron in an atom is greater for greater values of n. This number, *n*, is referred to as the principal quantum number or shell number. The principal quantum number defines the location of the energy level. It is essentially the same concept as the *n* in the Bohr atom description. The shells of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (Figure $4.5.4$). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.

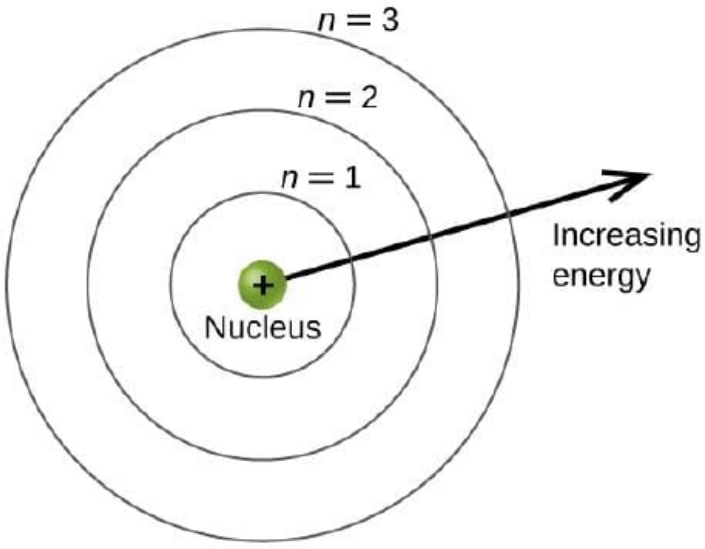


Figure $4.5.4$: Different shells are numbered by principal quantum numbers.

The principal quantum number is the first of three quantum numbers used to characterize an orbital. An **atomic orbital** is a general region in an atom within which an electron is most probable to reside. Another quantum number is l, the **secondary (angular momentum) quantum number**. It is an integer that may take the values, $l = 0, 1, 2, \ldots, n–1$. This means that an orbital with $n = 1$ can have only one value of l, $l = 0$, whereas $n = 2$ permits $l = 0$ and $l = 1$, and so on. Whereas the principal quantum number, n, defines the general size and energy of the orbital, the secondary quantum number l specifies the shape of the orbital.

Orbitals with the same value of l define a **subshell**.

Orbitals with $l = 0$ are called s orbitals and they make up the s subshells. The value $l = 1$ corresponds to the p orbitals. For a given n, p orbitals constitute a p subshell (e.g., 3p if n = 3). The orbitals with $l = 2$ are called the **d orbitals**, followed by the *f-, g-, and h*-orbitals for l = 3, 4, and 5.

The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.

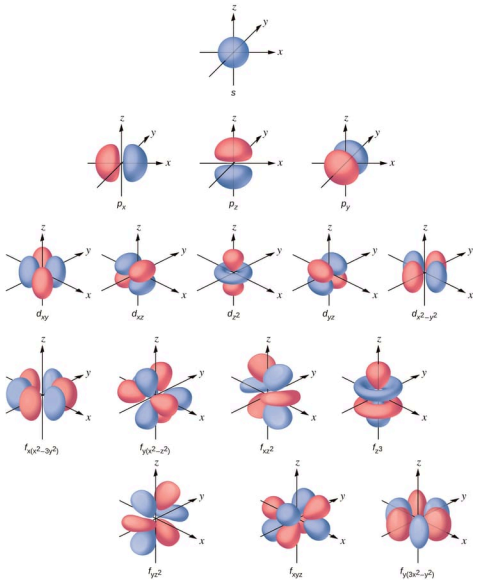


Figure $4.5.6$: Shapes of s, *p*, *d*, and *f* orbitals.

The third quantum number for describin atomic orbitals is the **magnetic quantum number**, m_l. It specifies the relative spatial orientation of a particular orbital. Generally speaking, m_l are rangeed from $-l$ to $+l$, i.e.

$$-l, -(l-1), \ldots, 0, \ldots, (l-1), l\backslash).$$

The total number of possible orbitals with the same value of l (that is, in the same subshell) is $2l + 1$. Thus, there is one s-orbital in an s subshell ($l = 0$), there are three p-orbitals in a p subshell ($l = 1$), five d-orbitals in a d subshell (l = 2), seven f-orbitals in an f subshell ($l = 3$), and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in Figure $4.5.6$.

Figure $4.5.7$ illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, n. The letter in the orbital name defines the subshell with a specific angular momentum quantum number *l* = 0 for s orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^{+}, Li^{2+}, and so on), energies of all the orbitals with the same n are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, n, are called degenerate orbitals. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies, as shown on Figure $4.5.7$. Orbitals within the same subshell are still degenerate and have the same energy.

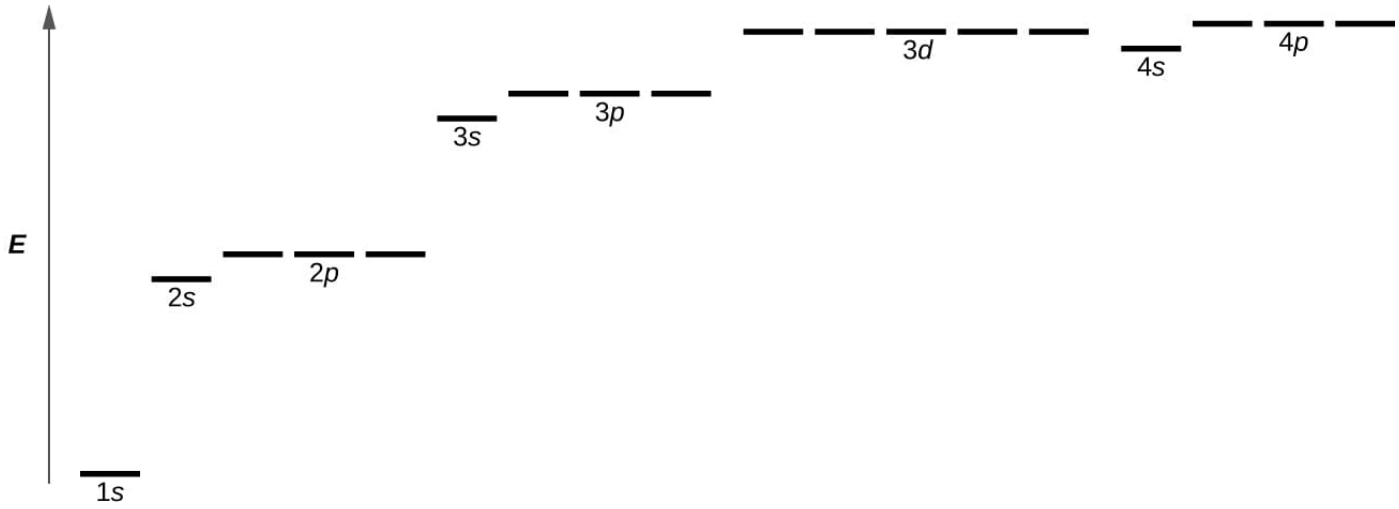


Figure 4.5.7: The chart shows the energies of electron orbitals in a multi-electron atom.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the **spin quantum number**, or m_s. Spin is a property of individual electrons that is independent of their atomic orbital description. Atomic orbitals define a region of space where an electron is most likely to be located. On the other hand, spin cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian *x*, *y*, and *z*). It is something wholly different with no spatial analogue.

The magnitude of the overall electron spin can only have one value, and an electron can only "spin" in one of two quantized states. One is termed the α state, with the z component of the spin being in the positive direction of the z axis. This corresponds to the spin quantum number $m_s = +1/2$. The other is called the $\beta state$, with the z component of the spin being negative and $m_s = -1/2$. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $m_s = +1/2$ and $m_s = -1/2$ are different if an external magnetic field is applied.

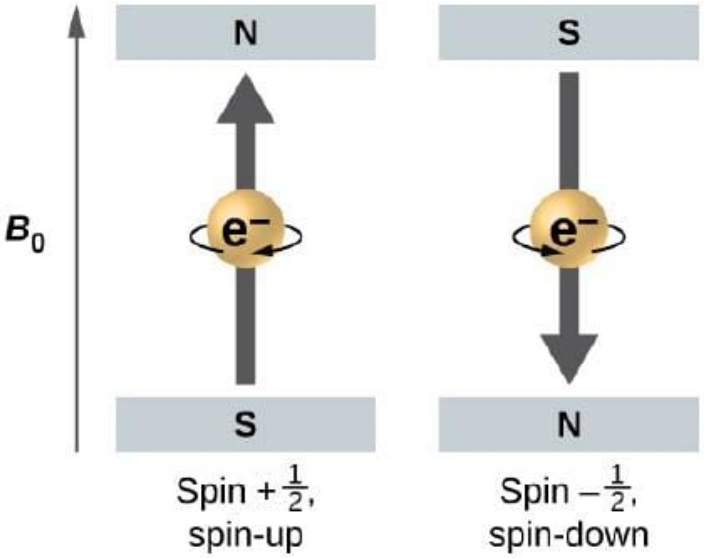


Figure 4.5.8: Electrons with spin values in an external magnetic field.

Figure 4.5.8 illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the *z* axis) for the $m_s = +1/2$ spin quantum number and down (in the negative z direction) for the spin quantum number of

$m_s = -1/2$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron on Figure 4.5.8) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $m_s = +1/2$ has a slightly lower energy in an external field in the positive z direction, and an electron with $m_s = -1/2$ has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: n, l, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. One formulation of his **Pauli exclusion principle** is: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that two electrons can share the same orbital (the same set of the quantum numbers *n*, *l*, and m_l) only if their spin quantum numbers m_s have different values. Therefore, any atomic orbital can be populated by only zero, one, or two electrons. The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table 4.5.1.

Table 4.5.1: Quantum Numbers, Their Properties, and Significance

Name	Symbol	Allowed values	Physical meaning
principal quantum number	n	1, 2, 3, 4, ...	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	l	$0 \le l \le n–1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$–l \le m_l \le l$	orientation of the orbital
spin quantum number	m_s	$+\frac{1}{2}$ and $-\frac{1}{2}$	direction of the intrinsic quantum “spinning” of the electron

Example 4.5.2: Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the $n = 4$ shell of an atom.

Solution

For $n = 4$, l can have values of 0, 1, 2, and 3. Thus, s, p, d, and f subshells are found in the n = 4 shell of an atom. For $l = 0$ (the s subshell), m_l can only be 0. Thus, there is only one 4s orbital. For $l = 1$ (p-type orbitals), m can have values of –1, 0, +1, so we find three 4p orbitals. For l = 2 (d-type orbitals), m_l can have values of –2, –1, 0, +1, +2, so we have five 4d orbitals. When $l = 3$ (f-type orbitals), m_l can have values of –3, –2, –1, 0, +1, +2, +3, and we can have seven 4f orbitals. Thus, we find a total of 16 orbitals in the $n = 4$ shell of an atom.

Exercise 4.5.2

Identify the subshell in which electrons with the following quantum numbers are found:

a. *n* = 3, l = 1
b. n = 5, l = 3
c. n = 2, l = 0

Answer available at the end of this section.

Example 4.5.3: Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) *n* = 2, (b) *n* = 5, and (c) *n* as a variable. Note you are only looking at the orbitals with the specified *n* value, not those at lower energies.

Solution

a. When $n = 2$, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.
b. When $n = 2$, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.
When $n = 5$, there are five subshells of orbitals that we need to sum:

$$\begin{aligned} &1 \text{ orbital labeled 5s} \\ &3 \text{ orbitals labeled 5p} \\ &5 \text{ orbitals labeled 5d} \\ &7 \text{ orbitals labeled 5f} \\ +\ &9 \text{ orbitals labeled 5g} \\ &25 \text{ orbitals total} \end{aligned}$$

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.
c. The number of orbitals in any shell n will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$.

Exercise 4.5.3

If a shell contains a maximum of 32 electrons, what is the principal quantum number, n?

Answer available at the end of this section.

Example 4.5.4: Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	n	l	m_l degeneracy	Radial nodes (#)
4*f*				
	4	1		
	7		7	3
5*d*				

Solution

The table can be completed using the following rules:

- The orbital designation is nl, where $l = 0, 1, 2, 3, 4, 5, \ldots$ is mapped to the letter sequence s, p, d, f, g, h, ...,
- The m_l degeneracy is the number of orbitals within an l subshell, and so is $2l + 1$ (there is one s orbital, three p orbitals, five d orbitals, seven f orbitals, and so forth).
- The number of radial nodes is equal to n–l–1.

Orbital	n	l	m_l degeneracy	Radial nodes (#)
4*f*	4	3	7	0

Orbital	n	l	m_l degeneracy	Radial nodes (#)
4*p*	4	1	3	2
7*f*	7	3	7	3
5*d*	5	2	5	2

Exercise 4.5.1

How many orbitals have $l = 2$ and $n = 3$?

Answer available at the end of this section.

Answers

Exercise 4.5.1

1.9×10^{-34} m.

We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Exercise 4.5.2

a. 3*p*
b. 5*f*
c. 2s

Exercise 4.5.3

$n = 4$

Exercise 4.5.1

The five degenerate 3*d* orbitals

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4.6: Electronic Structure of Atoms (Electron Configurations)

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- In accordance with the shell model, write electron configurations, draw orbital diagrams, identify core and valence electrons, and predict magnetic properties for ground state or excited atoms or ions.

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, *n*, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of *l* differ so that the energy of the orbitals increases within a shell in the order *s* < *p* < *d* < *f*. Figure 4.6.1: depicts how these two trends in increasing energy relate. The 1s orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3s, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4s orbital. Such overlaps continue to occur frequently as we move up the chart.

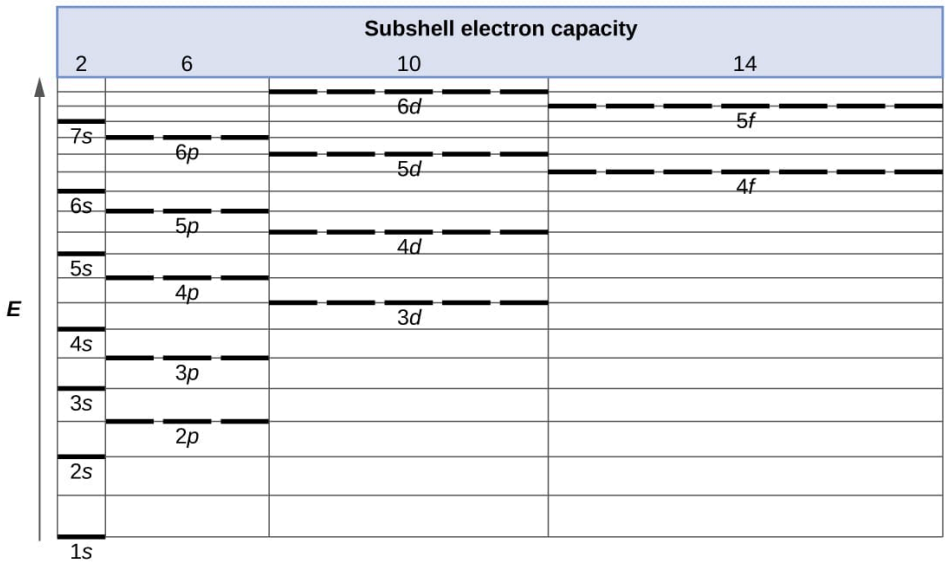


Figure 4.6.1: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6s. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order *s* > *p* > *d* > *f*. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have –1 charges, but nuclei have +*Z* charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1s through 3*p*), the increase in energy

due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure $4.6.2$):

1. The number of the principal quantum shell, n,
2. The letter that designates the orbital type (the subshell, l), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

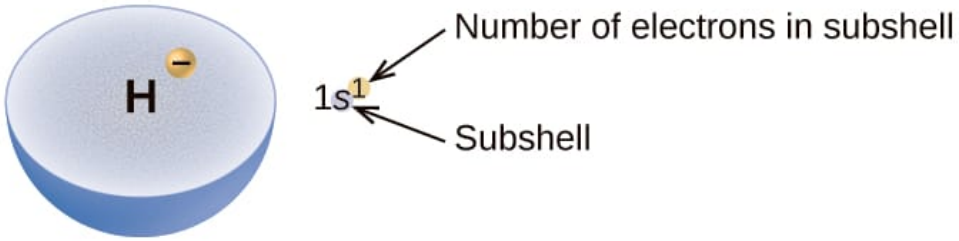


Figure $4.6.2$: The diagram of an electron configuration specifies the subshell (*n* and *l* value, with letter symbol) and superscript number of electrons.

The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure $4.6.1$), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure $4.6.3$ illustrates the traditional way to remember the filling order for atomic orbitals.

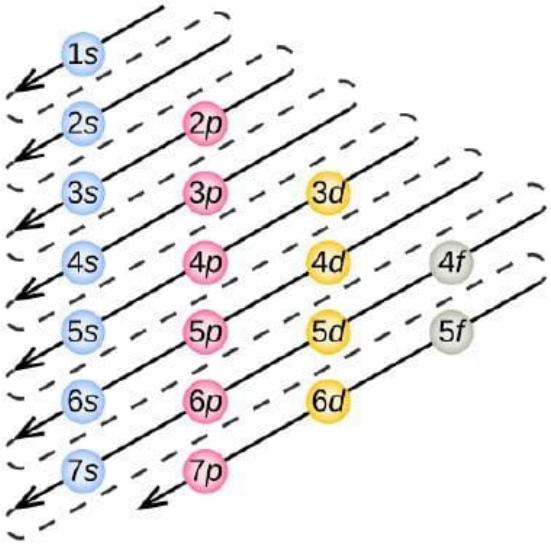


Figure $4.6.3$: This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.

Since the arrangement of the periodic table is based on the electron configurations, Figure $4.6.4$ provides an alternative method

for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3*d* orbitals.

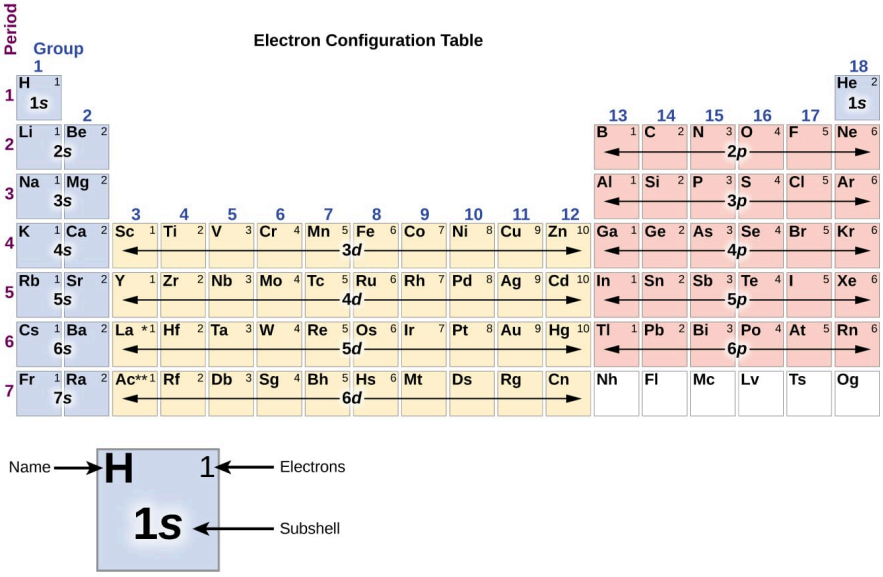
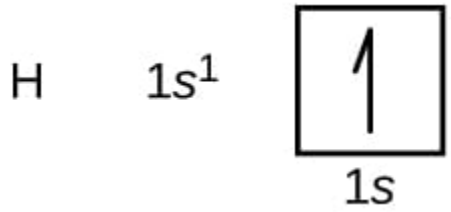
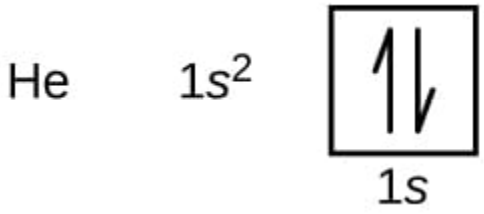


Figure 4.6.4: This partial periodic table shows electron configurations for the valence subshells of atoms. By "building up" from hydrogen, this table can be used to determine the electron configuration for atoms of most elements in the periodic table. (Electron configurations of the lanthanides and actinides are not accurately predicted by this simple approach. See Figure 4.6.6:

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. **Orbital diagrams** are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure 4.6.3 or Figure 4.6.4, we would expect to find the electron in the 1s orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:

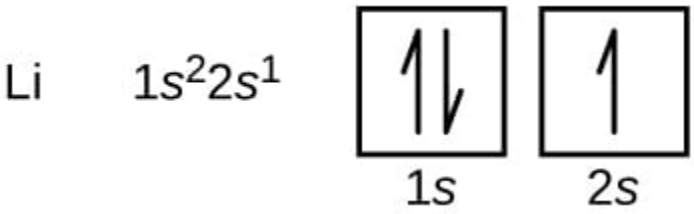


Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (\(*n* = 1\), \(*l* = 0\), \(*m_l* = 0\), $m_s = +\frac{1}{2}$. The second electron also goes into the 1s orbital and fills that orbital. The second electron has the same n, l, and ml quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

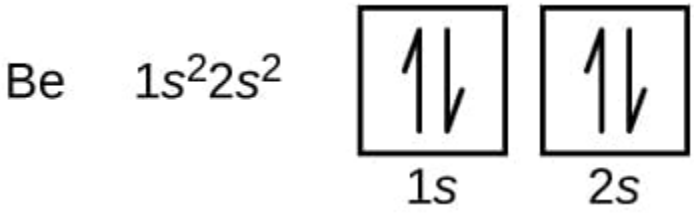


The $n = 1$ shell is completely filled in a helium atom.

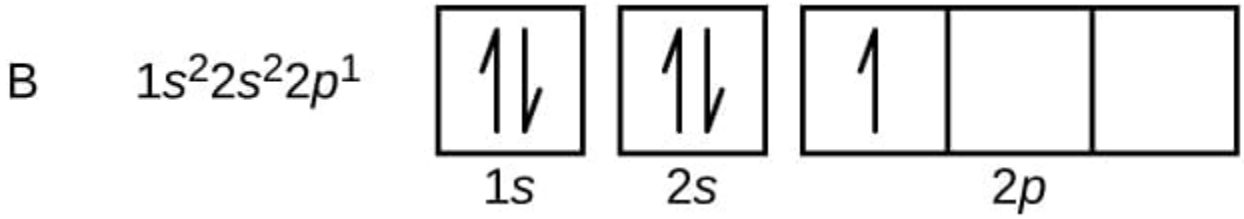
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1s orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2s orbital (Figure $4.6.3$ or Figure $4.6.4$). Thus, the electron configuration and orbital diagram of lithium are:



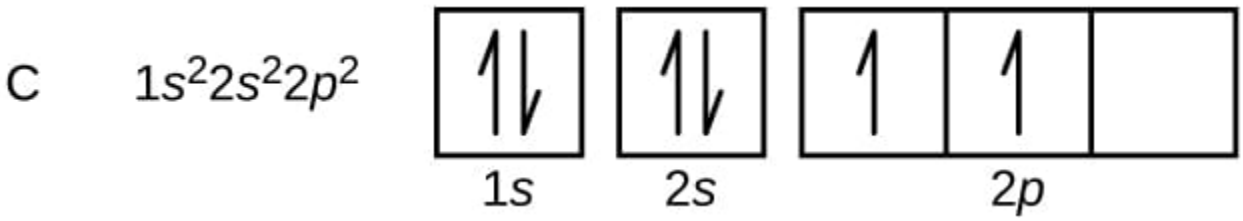
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2s orbital.



An atom of boron (atomic number 5) contains five electrons. The n = 1 shell is filled with two electrons and three electrons will occupy the n = 2 shell. Because any s subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals (m_l = –1, 0, +1) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

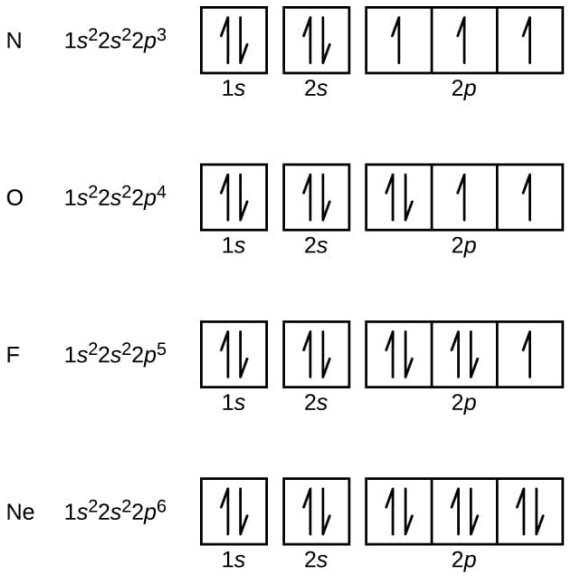


Carbon (atomic number 6) has six electrons. Four of them fill the 1s and 2s orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical n, l, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:



Nitrogen (atomic number 7) fills the 1s and 2s subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p*

orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:



The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** (Figure 4.6.5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is $[Ne]3s^1$.

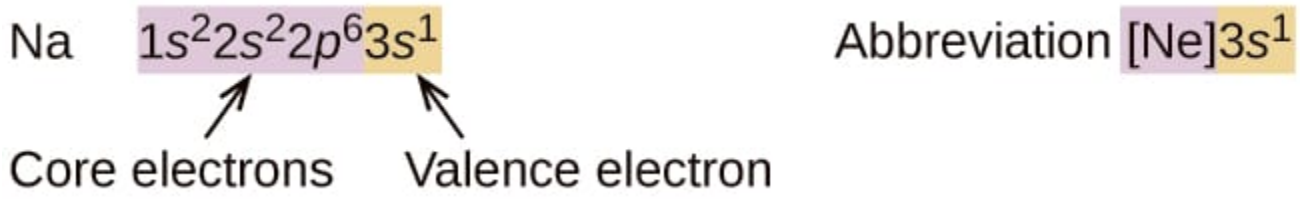


Figure 4.6.5: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as $[He]2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence s subshell outside a filled set of inner shells.

$$Li : [He]2s^1$$
$$Na : [Ne]3s^1$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a $[Ne]3s^2$ configuration, is analogous to its family member beryllium, $[He]2s^2$. Both atoms have a filled s subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration $[Ne]3s^2 3p^1$, is analogous to its family member boron, $[He]2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and

argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure 4.6.6: shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

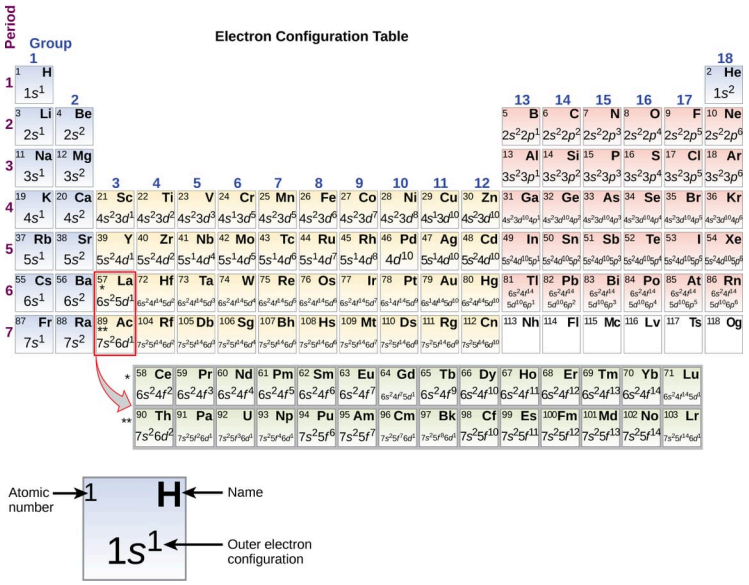


Figure 4.6.6: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure 4.6.6). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4s, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of $[Ar]4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

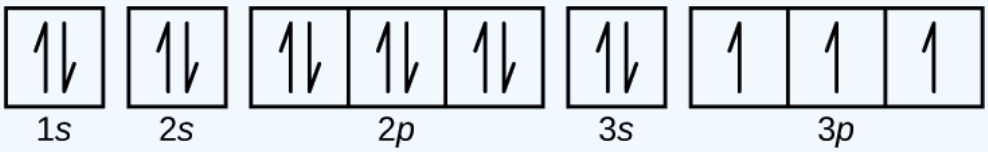
Example 4.6.1: Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1s, 2s, 2*p*, 3s, 3*p*, 4s, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

P $1s^2 2s^2 2p^6 3s^2 3p^3$



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$

Exercise 4.6.1

Identify the atoms from the electron configurations given:

a. $[Ar]4s^2 3d^5$
b. $[Kr]5s^2 4d^{10} 5p^6$

Answer available at the end of this section.

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 4.6.3: or Figure 4.6.4. For instance, the electron configurations (shown in Figure 4.6.6) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4s into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[Kr]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[Kr]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5s orbital are larger than the gap in energy between the 5s and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 4.6.6), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 4.6.6: , which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure 4.6.6: show the three categories of elements classified by

the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the **valence shell**, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an s or a *p* orbital in the outermost shell, shown in blue and red in Figure 4.6.6. This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration [Ar]$\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and (*n* – 1) *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 4.6.6) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure 4.6.6), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 4.6.6. The valence shells of the inner transition elements consist of the (*n* – 2)*f,* the (*n* – 1)*d*, and the *ns* subshells. There are two inner transition series:
   a. The lanthanide series: lanthanum (La) through lutetium (Lu)
   b. The actinide series: actinium (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

Electron Configurations of Ions

Ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *ns* electrons are lost, and then the (*n* – 1)*d* or (*n* – 2)*f* electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example 4.6.2: Predicting Electron Configurations of Ions

What is the electron configuration of:

a. Na^+
b. P^{3-}
c. Al^{2+}
d. Fe^{2+}
e. Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

a. Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so Na^+: $1s^2 2s^2 2p^6 3s^1$ = Na^+: $1s^2 2s^2 2p^6$.
b. P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$.

c. Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^1 = Al^{2+}$: $1s^2 2s^2 2p^6 3s^1$.
d. Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4s orbital Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.
e. Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium trication loses three electrons. The first two will be lost from the 6s orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

Exercise 4.6.21

Which ion with a +2 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^5$? Which ion with a +3 charge has this configuration?

Answer available at the end of this section.

Answers

Exercise 4.6.1

a. Mn
b. Xe

Exercise 4.6.21

Tc^{2+}, Ru^{3+}

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4.7: Periodic Variations in Element Properties

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Rank atoms and ions by their radius, first ionization energy, electronegativity, and metallicity.

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

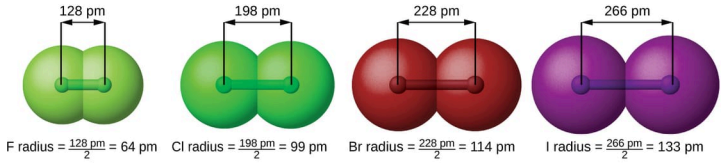
As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Link to Learning

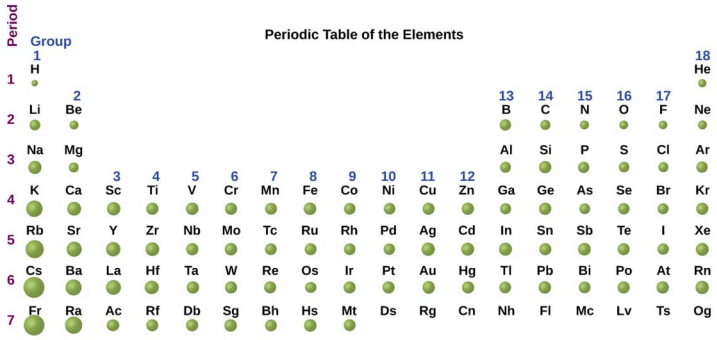
Explore visualizations of the periodic trends discussed in this section (and many more trends). With just a few clicks, you can create three-dimensional versions of the periodic table showing atomic size or graphs of ionization energies from all measured elements.

Variation in Covalent Radius

There are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure $4.7.1$), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table $4.7.1$ and Figure $4.7.1$. The trends for the entire periodic table can be seen in Figure $4.7.2$.



(a)



(b)

Figure 4.7.1: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as *n* increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

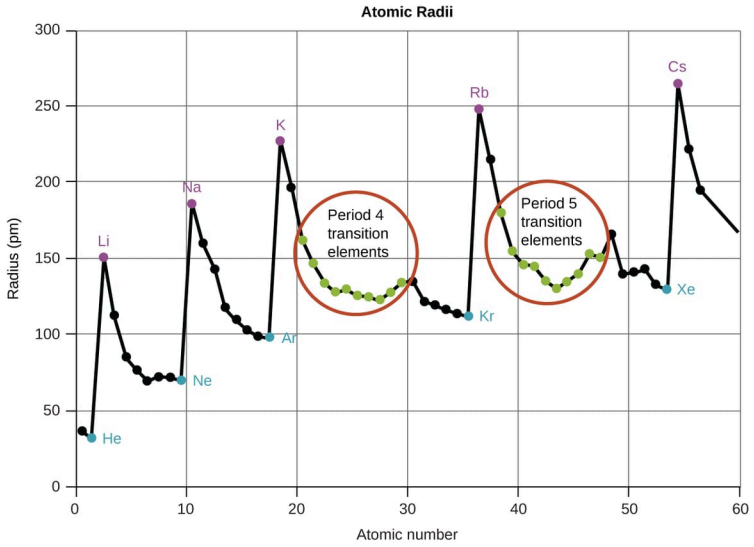


Figure 4.7.2: Within each period, the trend in atomic radius decreases as *Z* increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as *Z* increases.

As shown in Figure 4.7.2, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge**, Z_{eff}. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - \text{ shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the $(n - 1)d$ electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

Example 4.7.1: Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

Exercise 4.7.1

Give an example of an atom whose size is smaller than fluorine.

Answer available at the end of this section.

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 4.7.3). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.



Figure 4.7.3: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, *n*.

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 4.7.3). For example, a sulfur atom ($[Ne]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} ($1s^2 2s^2 2p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+} ($[Ne]3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first **ionization energy** (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$\mathrm{X\,(g)} \longrightarrow \mathrm{X^{+}\,(g)} + \mathrm{e^{-}} \qquad IE_1$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\mathrm{X^{+}\,(g)} \longrightarrow \mathrm{X^{2+}\,(g)} + \mathrm{e^{-}} \qquad IE_2$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

Figure 4.7.4 graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in Figure 4.7.5. Within a period, the IE_1 generally increases with increasing *Z*. Down a group, the IE_1 value generally decreases with increasing *Z*. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as *l* increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the *s* electrons are lower in energy than the *p* electrons. This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of beryllium ([He]$2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ([He]$2s^2 2p^1$) is a *p* electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

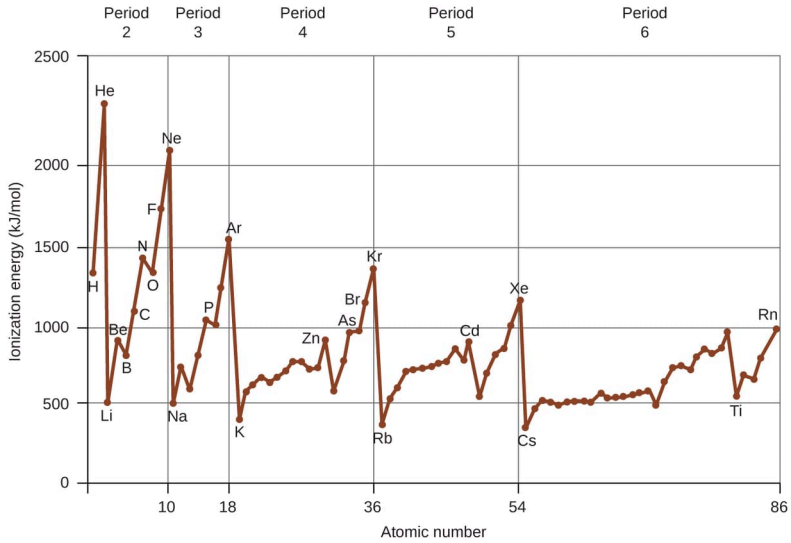


Figure 4.7.4: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

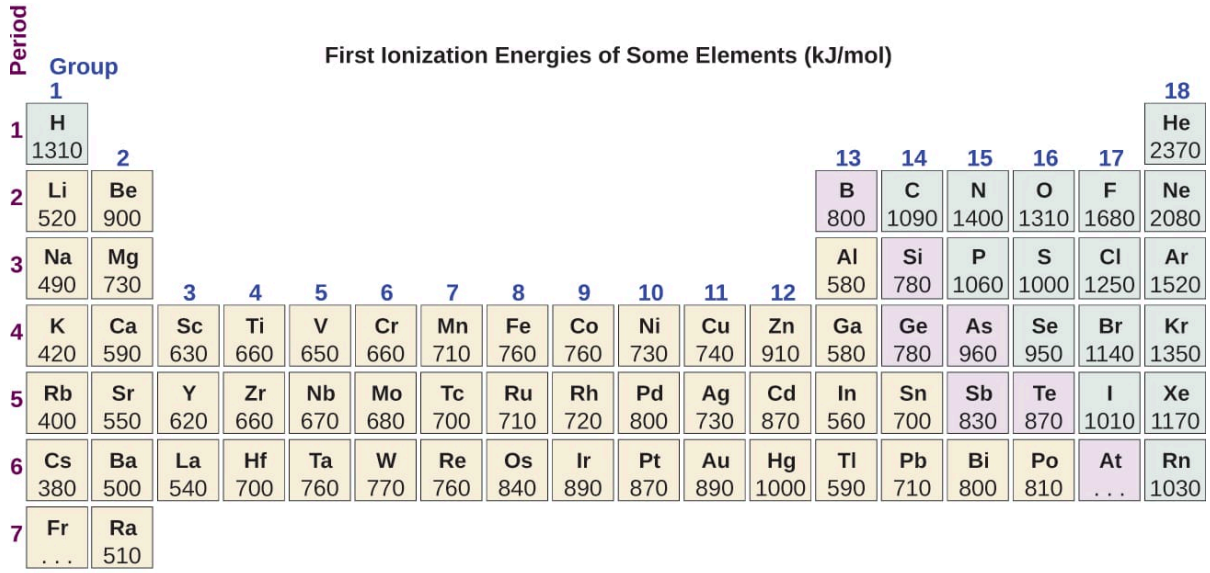
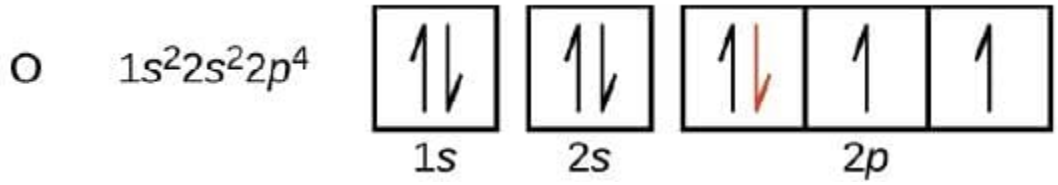


Figure 4.7.5: This version of the periodic table shows the first ionization energy (IE_1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the *2p* orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 4.7.5).



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 4.7.2, there is a large increase in the ionization energies for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 4.7.2: Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Example 4.7.2: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher *n* orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from Al ($Al^{2+} \longrightarrow Al^{3+} + e^-$) requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain: $IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na)$.

Exercise 4.7.2

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer available at the end of this section.

Variation in Electron Affinities

The **electron affinity** (EA) is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

$$X(g) + e^- \longrightarrow X^-(g) \quad EA_1$$

This process can be either endothermic (positive EA) or exothermic (negative EA), as shown for some of the elements in Figure 4.7.6. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We will replace this idea with the theoretical concept of electronegativity (EN) in class.

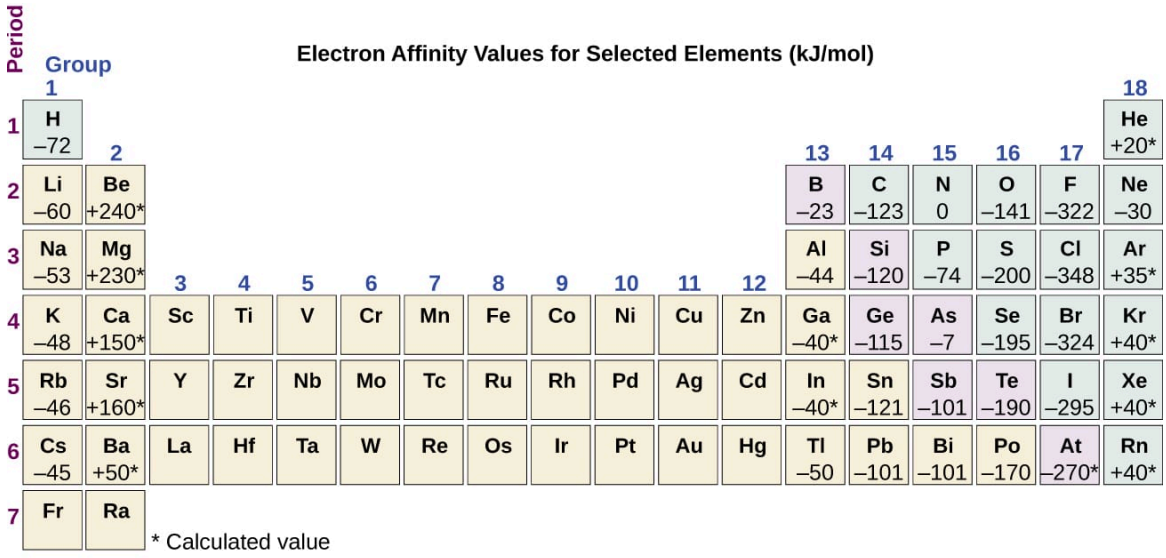


Figure 4.7.6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Answers

Exercise 4.7.1

Ne or He

Exercise 4.7.2

Ba

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5: MODELS FOR CHEMICAL BONDING AND SHAPE

5.1: Overview and Objectives

5.2: Ionic Bonding

5.3: Metallic Bonding

5.4: Covalent Bonding

5.5: Lewis Symbols and Structures

5.6: Strengths of Ionic and Covalent Bonds

5.7: VSEPR Theory Predicts Molecular Structure and Shape

5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity

5.9: Valence Bond Theory Describes Bonds as Overlapping Atomic Orbitals

5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals

5.11: Valence Bond Treatment of Multiple Bonds

5.12: Molecular Orbital Theory Resolves Issues in Other Bonding Theories

5.13: Coordinate Covalent Bonding is Different

5.14: Spectroscopic and Magnetic Properties of Coordination Compounds

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5.1: Overview and Objectives

> *"Even the sense of taste and odor are based upon molecular configuration rather than upon ordinary chemical properties. A molecule that has the same shape as a camphor molecule will smell like camphor even though it may be quite unrelated to camphor chemically." (Linus Pauling)*

Pauling was pointing out the relationship between a molecule's *structure* (the nature and arrangement of chemical bonds) and its *function* (how it interacts with other entities - in this case, the molecular receptors in our noses and mouths that are responsible for our sense of smell). This suggests that there are rules underlying chemical structure that control molecular function. There certainly are; and these rules come from quantum mechanics. In this chapter, we'll establish models for ionic, covalent, and metallic bonding. We'll look at covalent bonding in great detail, extending those quantum mechanical models to describe molecular shape and polarity. Lastly, we'll turn to one implication of polarity (structure) for how some molecules interact with water (function).

Chapter Objectives

- Identify bonding types in chemical compounds (ionic, covalent, or metallic).
- Compare and contrast major theories of chemical bonding (Lewis, Valence-Shell-Electron-Pair Repulsion, Valence Bond Theory, Molecular Orbital Theory)
- Draw Lewis structures, predict molecular geometry, and describe orbital hybridization according to accepted models of chemical bonding.
- Order covalent bonds by length, strength, energy, and polarity.
- Predict whether a molecule/region of a molecule will be polar/nonpolar or hydrophobic/hydrophilic.
- Predict the oxidation state, coordination number, spin state, magnetic properties, or color of a coordinate covalent complex.

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5.2: Ionic Bonding

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Identify bonding types in chemical compounds (ionic, covalent, or metallic).

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell. As we read in previous sections, these compounds tend to be brittle, have high melting points, and are conductive when dissolved in water due to the production of ions.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure 5.2.1). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure 5.2.1: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons)

Ionic Compounds

The total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3, indicates that this ionic

compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, (2 +3) + (3 –2) = 0].

It is important to note, however, that the formula for an ionic compound only represents the lowest whole number ratio of elements in the compound. It does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure 5.2.2).

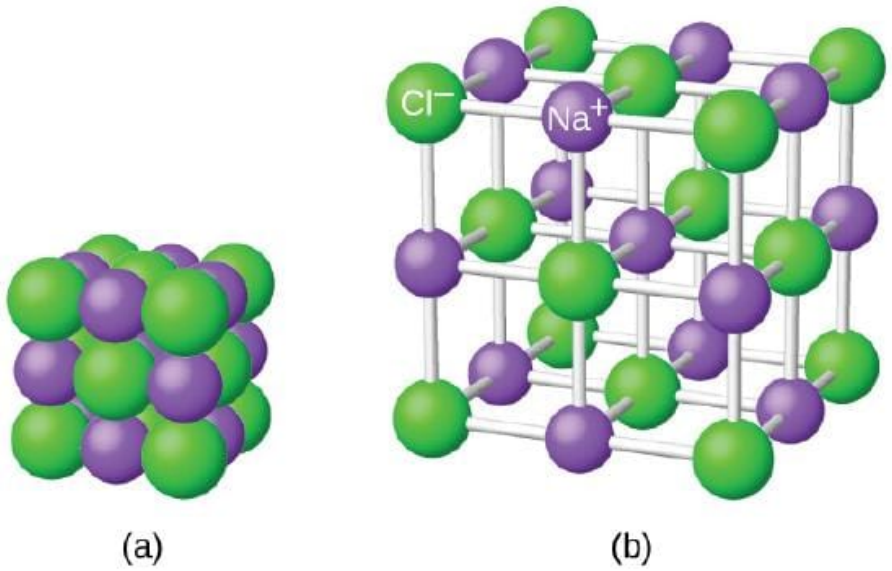


Figure 5.2.2: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl\,(s)} \longrightarrow \mathrm{Na^+\,(g) + Cl^-\,(g)} \qquad \Delta H = 769\,\mathrm{kJ}$$

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5.3: Metallic Bonding

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Identify bonding types in chemical compounds (ionic, covalent, or metallic).

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 5.3.4. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a "sea" of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.

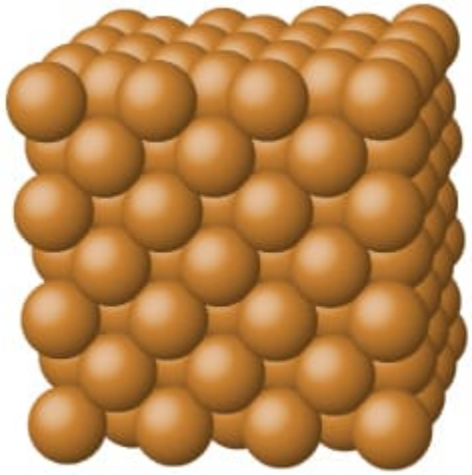


Figure 5.3.4: Copper is a metallic solid.

Properties of Solids

A crystalline solid, like those listed in Table 5.3.1, has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Table 5.3.1: Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
molecular (covalent)	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

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5.4: Covalent Bonding

Learning Objectives

By the end of this section, you will be able to:

- Identify bonding types in chemical compounds (ionic, covalent, or metallic).

Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. It is typically associated with elements that are vastly different in electronegativity (a difference of around 2.0 or greater).

A different type of bonding results from the mutual attraction of atoms for a "shared" pair of electrons. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar electronegativities (differences much closer to 0).

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure $5.4.1$ illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1s) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

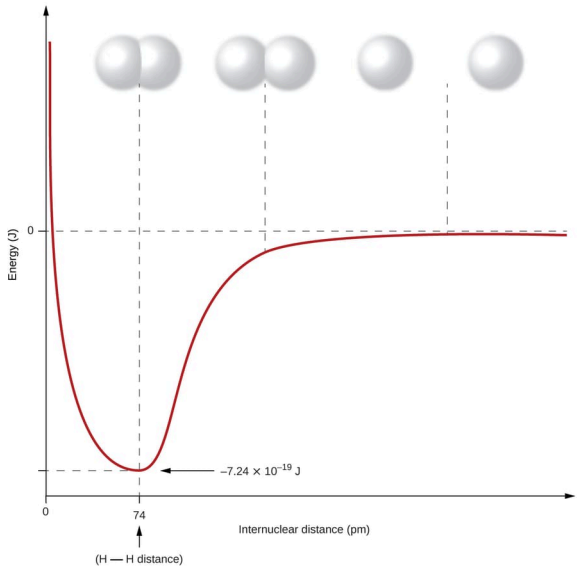


Figure 5.4.1: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2\,(g)} \longrightarrow \mathrm{2\,H\,(g)} \quad \Delta H = 436\,\mathrm{kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$\mathrm{2\,H\,(g)} \longrightarrow \mathrm{H_2\,(g)} \quad \Delta H = -436\,\mathrm{kJ}$$

Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl + Cl} \longrightarrow \mathrm{Cl_2}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 5.4.2 shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure 5.4.1, which shows the even distribution of electrons in the H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,” δ, with

a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure 5.4.2.

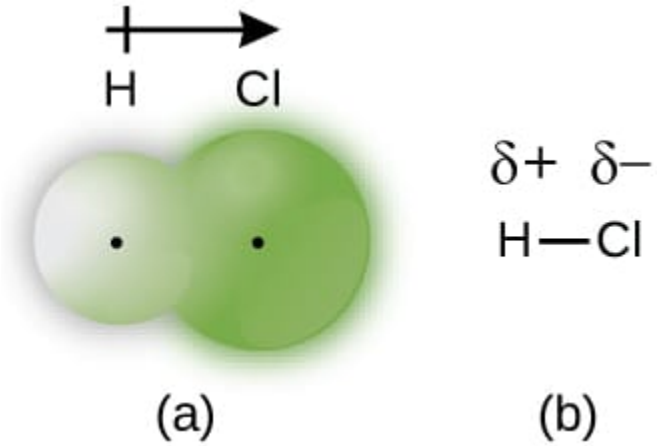


Figure 5.4.2: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by differences in electronegativity between the elements in the bond. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 5.4.3 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure 5.4.4). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

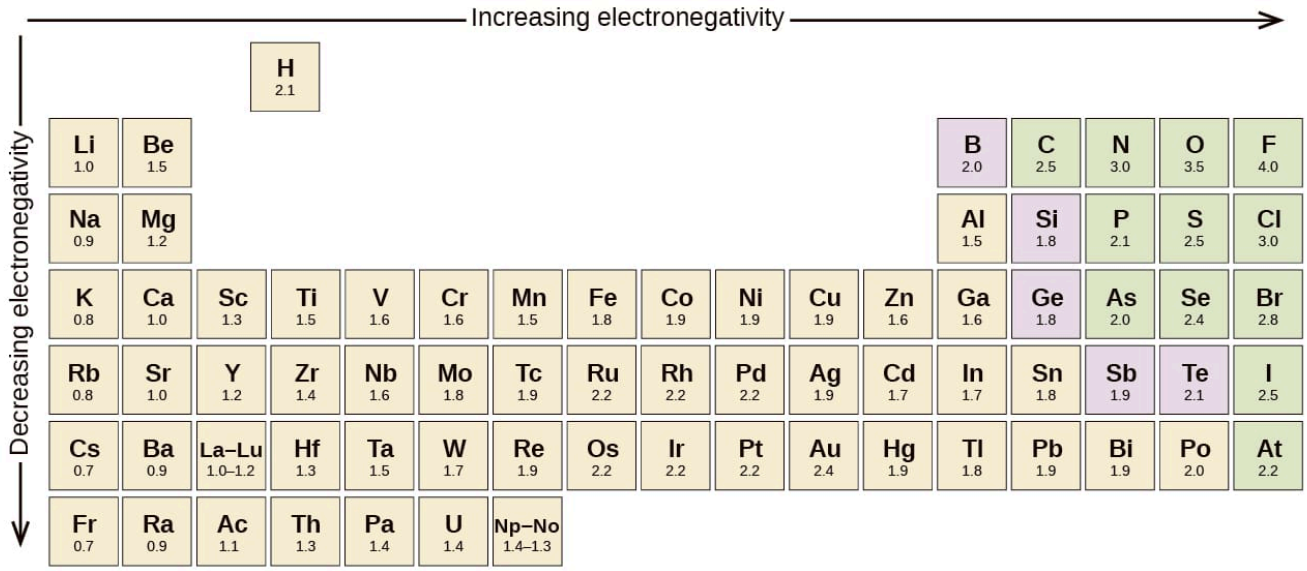


Figure 5.4.3: The electronegativity values derived by Pauling follow predictable periodic trends, with the higher electronegativities toward the upper right of the periodic table.

Portrait of a Chemist: Linus Pauling

Linus Pauling, shown in Figure 5.4.4, is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.

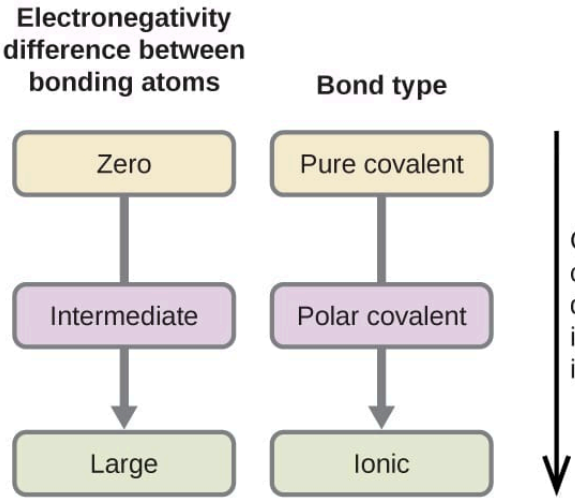


Figure 5.4.4: Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 5.4.5 shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 5.4.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 5.4.5. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, and are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and as well as covalent between the nitrogen and oxygen atoms in

Example 5.4.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Figure 5.4.3, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 5.4.1 shows these bonds in order of increasing polarity.

Table 5.4.1: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	
S–H	0.4	
C–N	0.5	
N–H	0.9	
C–O	1.0	
O–H	1.4	

Exercise 5.4.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 5.4.3, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer available at the end of this section.

Answers

Exercise 5.4.1

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	
Si–C	0.7	
Si–O	1.7	

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5.5: Lewis Symbols and Structures

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Compare and contrast major theories of chemical bonding (**Lewis**, Valence-Shell-Electron-Pair Repulsion, Valence Bond Theory, Molecular Orbital Theory)
- **Draw Lewis structures,** predict molecular geometry, and describe orbital hybridization according to accepted models of chemical bonding.

In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A Lewis symbol consists of an elemental symbol surrounded by one dot for each of its valence electrons:



Figure 5.5.1: shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na•
magnesium	$[Ne]3s^2$	•Mg•
aluminum	$[Ne]3s^23p^1$	•Al•
silicon	$[Ne]3s^23p^2$	•Si•
phosphorus	$[Ne]3s^23p^3$	•P•
sulfur	$[Ne]3s^23p^4$	:S•
chlorine	$[Ne]3s^23p^5$	:Cl•
argon	$[Ne]3s^23p^6$	:Ar:

Figure 5.5.1: Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:

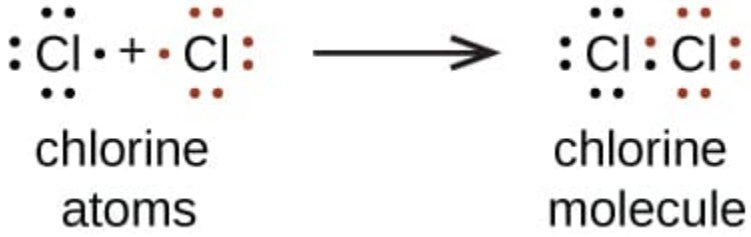


Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

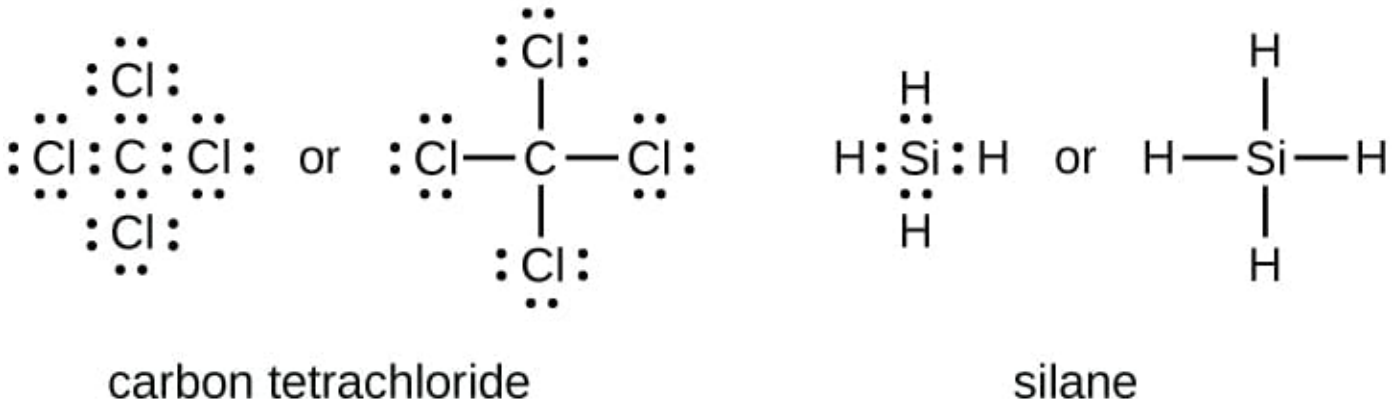


A single shared pair of electrons is called a single bond. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

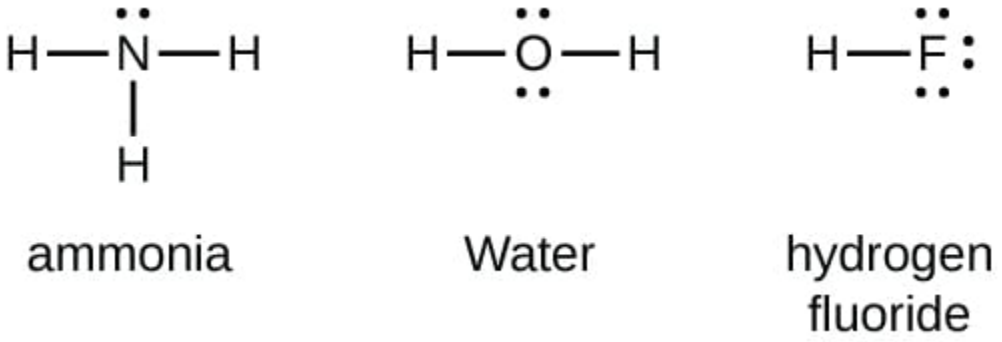
The Octet Rule

The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:

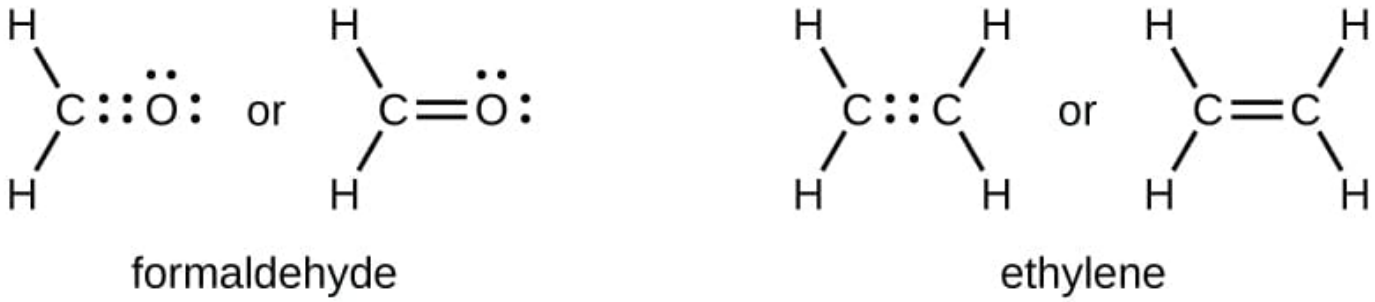


Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):

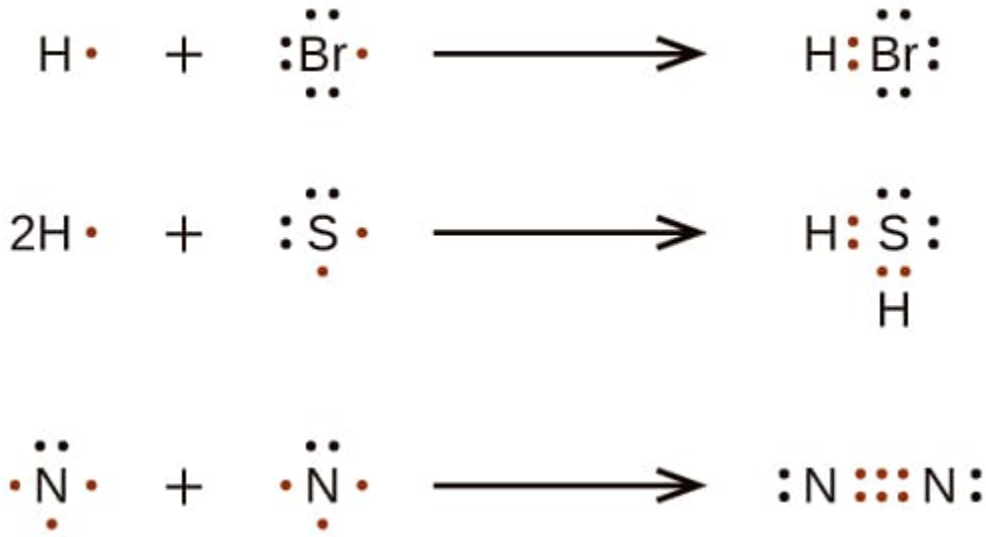


A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here.

Writing Lewis Structures

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of $\mathrm{SiH_4}$, $\mathrm{CHO_2^-}$, $\mathrm{NO^+}$, and $\mathrm{OF_2}$ as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
   - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$\begin{aligned} & \mathrm{SiH_4} \\ \mathrm{Si:}\ 4\ \text{valence electrons/atom} \times\ & 1\ \text{atom} = 4 \\ + \quad \mathrm{H}:\ 1\ \text{valence electron/atom} \times\ & 4\ \text{atoms} = 4 \\ & \text{total valence electrons} = 8 \end{aligned}$$

- For a *negative ion*, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{aligned} & CHO_2^- \\ \text{C: 4 valence electrons/atom} \times & \ 1 \text{ atom} &= 4 \\ \text{H: 1 valence electron/atom} \times & \ 1 \text{ atoms} &= 1 \\ \text{O: 6 valence electron/atom} \times & \ 2 \text{ atoms} &= 12 \\ + & \ 1 \text{ electron} &= 1 \\ & \text{total valence electrons} &= 18 \end{aligned}$$

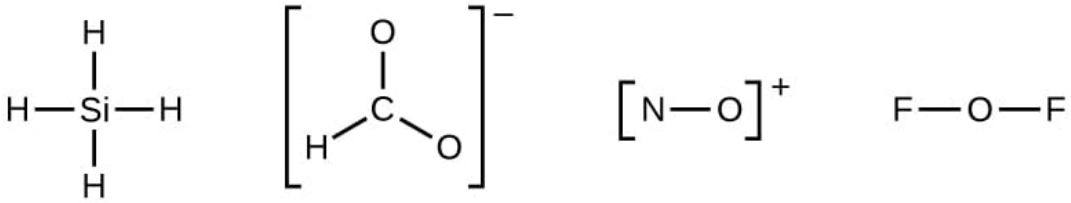
- For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{aligned} & NO^+ \\ \text{N: 5 valence electrons/atom} \times & \ 1 \text{ atom} &= 5 \\ \text{O: 6 valence electron/atom} \times & \ 1 \text{ atoms} &= 6 \\ + \quad \text{e: -1 electron (positive charge)} \times & \ 1 \text{ electron} &= -1 \\ & \text{total valence electrons} &= 10 \end{aligned}$$

- Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

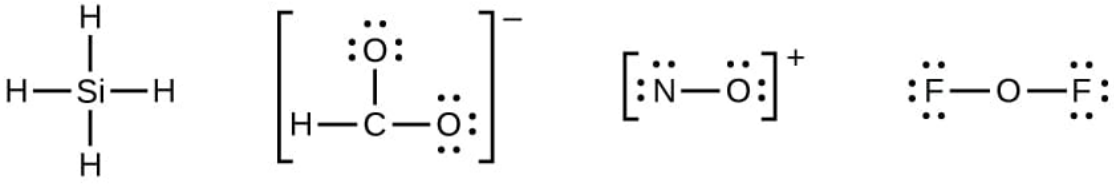
$$\begin{aligned} & OF_2 \\ \text{O: 6 valence electrons/atom} \times & \ 1 \text{ atom} &= 6 \\ + \quad \text{F: 7 valence electron/atom} \times & \ 2 \text{ atoms} &= 14 \\ & \text{total valence electrons} &= 20 \end{aligned}$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



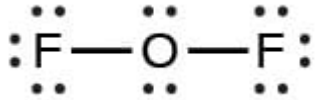
When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
   - There are no remaining electrons on SiH_4, so it is unchanged:

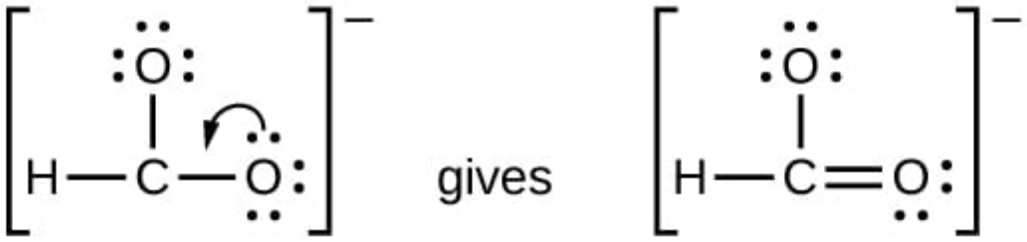


4. Place all remaining electrons on the central atom.

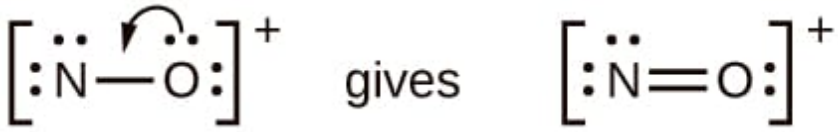
- For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
- For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



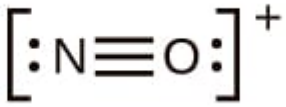
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - SiH_4: Si already has an octet, so nothing needs to be done.
   - $CHO\ 2^-$: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



   - NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



   This still does not produce an octet, so we must move another pair, forming a triple bond:



   - In OF_2, each atom has an octet as drawn, so nothing changes.

Example 5.5.1: Writing Lewis Structures

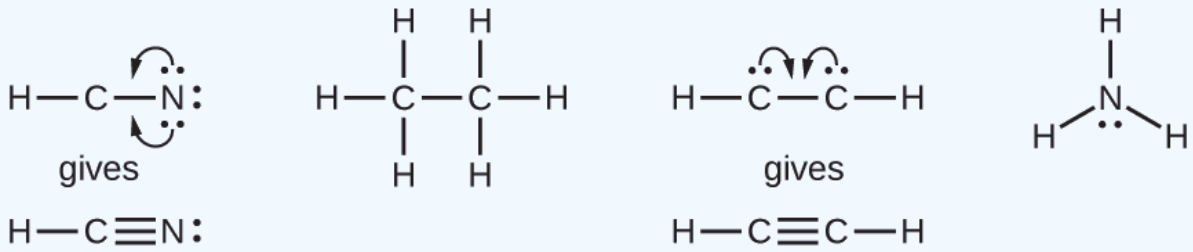
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

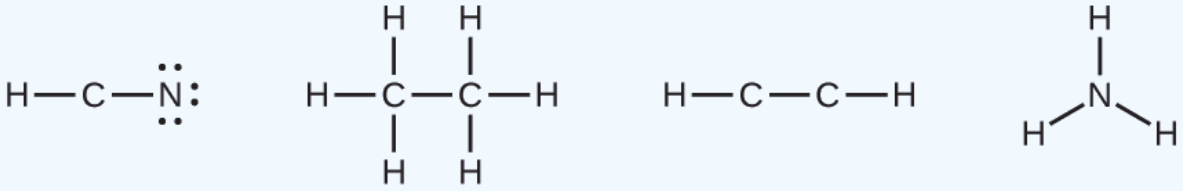
Step 1. *Calculate the number of valence electrons.*

HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
NH_3: (5 × 1) + (3 × 1) = 8

Step 2 *Draw a skeleton and connect the atoms with single bonds*. Remember that H is never a central atom:

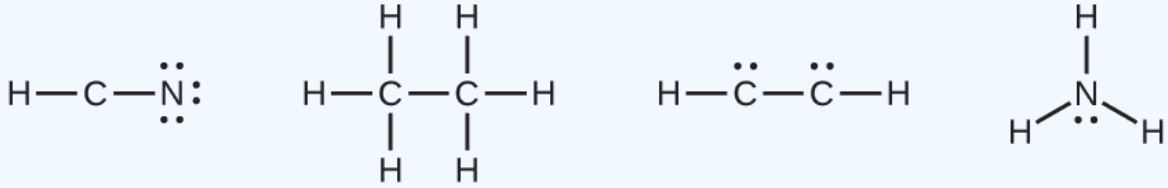


Step 3. *Where needed, distribute electrons to the terminal atoms:*



HCN: six electrons placed on N
H_3CCH_3: no electrons remain
HCCH: no terminal atoms capable of accepting electrons
NH_3: no terminal atoms capable of accepting electrons

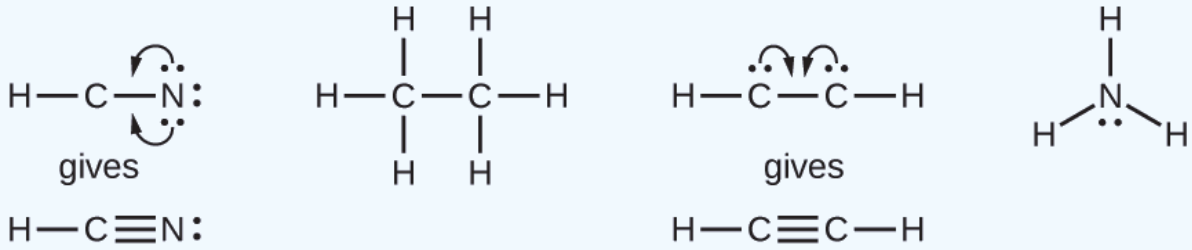
Step 4. *Where needed, place remaining electrons on the central atom:*



HCN: no electrons remain
H_3CCH_3: no electrons remain
HCCH: four electrons placed on carbon
NH_3: two electrons placed on nitrogen

Step 5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:*

HCN: form two more C–N bonds
H_3CCH_3: all atoms have the correct number of electrons
HCCH: form a triple bond between the two carbon atoms
NH_3: all atoms have the correct number of electrons



Exercise 5.5.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer available at the end of this section.

How Sciences Interconnect: Fullerene Chemistry

Carbon, in various forms and compounds, has been known since prehistoric times, . Soot has been used as a pigment (often called carbon black) for thousands of years. Charcoal, high in carbon content, has likewise been critical to human development. Carbon is the key additive to iron in the steelmaking process, and diamonds have a unique place in both culture and industry. With all this usage came significant study, particularly with the emergence of organic chemistry. And even with all the known forms and functions of the element, scientists began to uncover the potential for even more varied and extensive carbon structures.

As early as the 1960s, chemists began to observe complex carbon structures, but they had little evidence to support their concepts, or their work did not make it into the mainstream. Eiji Osawa predicted a spherical form based on observations of a similar structure, but his work was not widely known outside Japan. In a similar manner, the most comprehensive advance was likely computational chemist Elena Galpern's, who in 1973 predicted a highly stable, 60-carbon molecule; her work was also isolated to her native Russia. Still later, Harold Kroto, working with Canadian radio astronomers, sought to uncover the nature of long carbon chains that had been discovered in interstellar space.

Kroto sought to use a machine developed by Richard Smalley's team at Rice University to learn more about these structures. Together with Robert Curl, who had introduced them, and three graduate students—James Heath, Sean O'Brien, and Yuan Liu—they performed an intensive series of experiments that led to a major discovery.

In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley (Figure 5.5.3), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

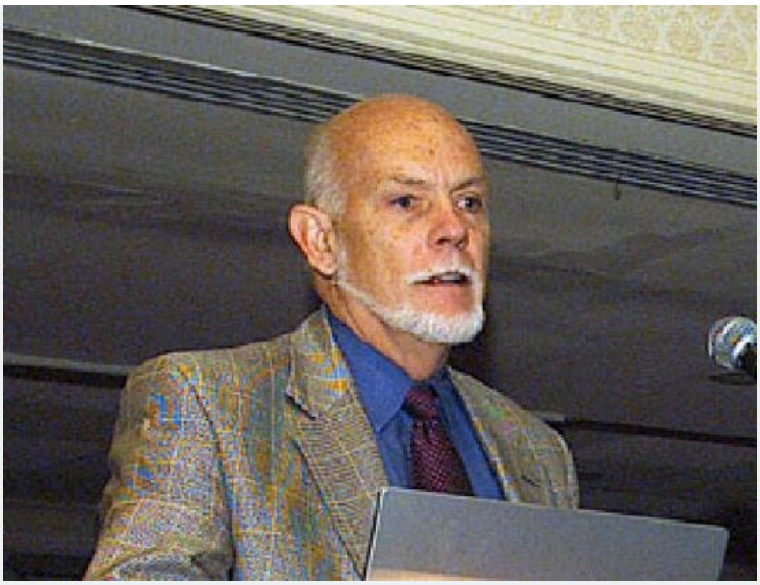


Figure 5.5.3: Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the “Father of Nanotechnology.” (credit: United States Department of Energy)

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

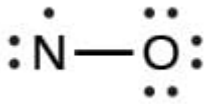
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

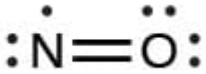
To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond:
   N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:



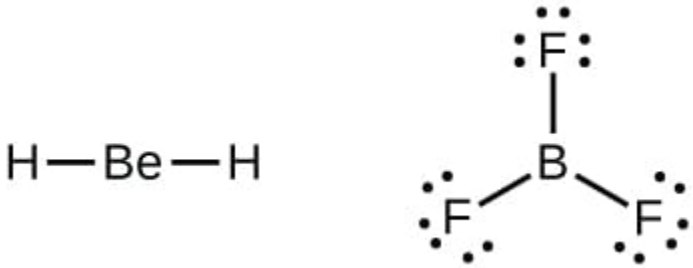
4. *Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible*. We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as

possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

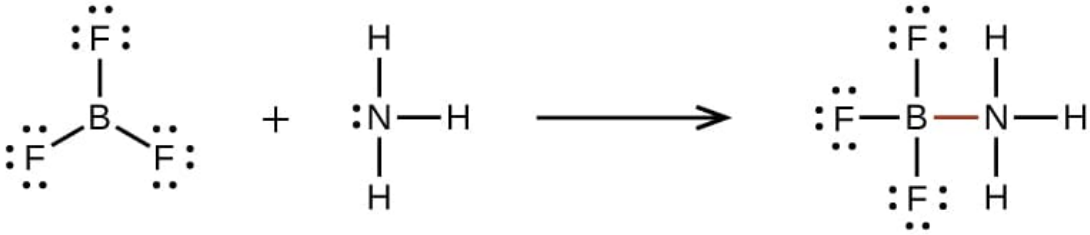


Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules. Figure 5.5.4: shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

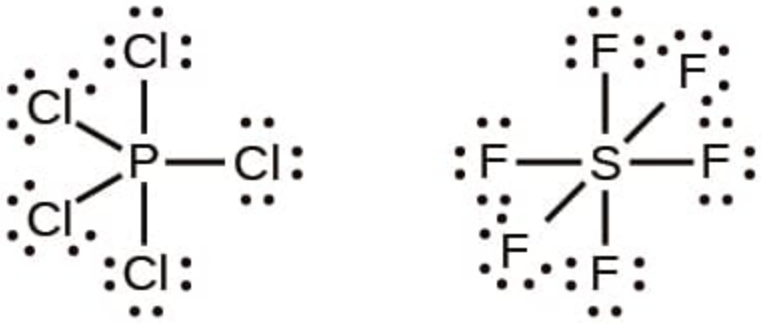
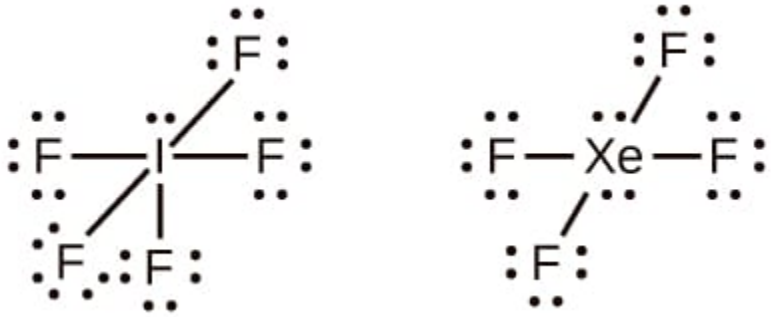


Figure 5.5.4: In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example 5.5.2: Writing Lewis Structures - Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

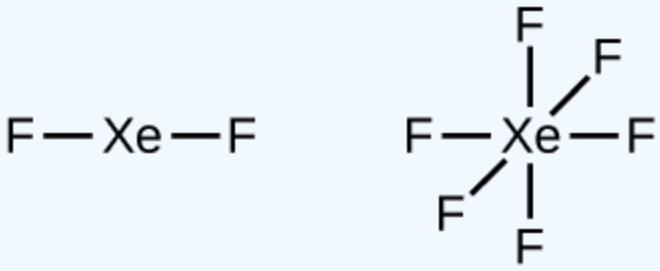
Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1. Calculate the number of valence electrons:

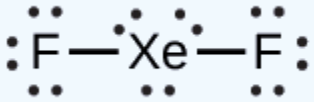
XeF_2: 8 + (2 × 7) = 22
XeF_6: 8 + (6 × 7) = 50

Step 2. Draw a skeleton joining the atoms by single bonds. Xenon will be the central atom because fluorine cannot be a central atom:

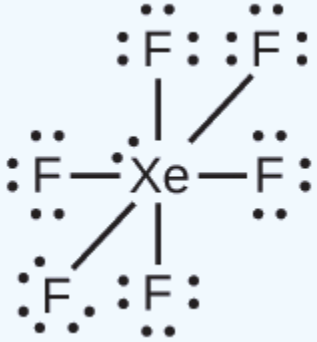


Step 3. Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:



XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



Exercise 5.5.2: Interhalogens

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

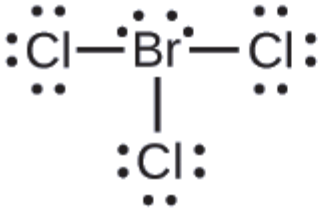
Answer available at the end of this section.

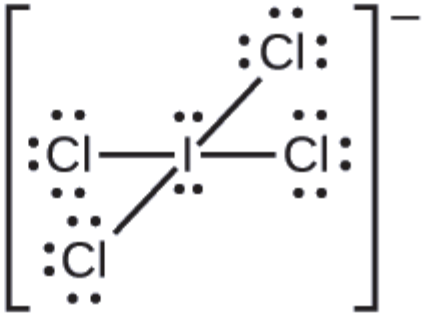
Answers

Exercise 5.5.1



Exercise 5.5.2**: Interhalogens**





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5.6: Strengths of Ionic and Covalent Bonds

Learning Objectives

By the end of this section, you will be able to:

- Order covalent bonds by **length, strength, energy,** and polarity.

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds, and then compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy. The stronger a bond, the greater the energy required to break it.

The energy required to break a specific covalent bond in one mole of gaseous molecules is called the **bond energy** or the **bond dissociation energy**. The bond energy for a diatomic molecule, $\mathrm{D_{X-Y}}$, is defined as the **standard enthalpy change** for the endothermic reaction:

$$\mathrm{XY\,(g)} \longrightarrow \mathrm{X\,(g) + Y\,(g)} \qquad \blacksquare = \Delta H^\circ$$

For example, the bond energy of the pure covalent $\mathrm{H{-}H}$ bond, $\mathrm{D_{H-H}}$, is 436 kJ per mole of $\mathrm{H{-}H}$ bonds broken:

$$\mathrm{H_2\,(g)} \longrightarrow \mathrm{2\,H\,(g)} \qquad D_{\mathrm{H-H}} = \Delta H^\circ = 436\,\mathrm{kJ}$$

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table 5.6.1, and a comparison of bond lengths and bond strengths for some common bonds appears in Table 5.6.2. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, $\mathrm{C{-}F}$ is 439 kJ/mol, $\mathrm{C{-}Cl}$ is 330 kJ/mol, and $\mathrm{C{-}Br}$ is 275 kJ/mol.

Table 5.6.1: Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	$\mathrm{N{=}N}$	418	Si–Cl	359
H–P	320	$\mathrm{N{\equiv}N}$	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
C–C	345	N–Br	245	P–Br	270
C=C	611	O–O	140	P–I	215
C≡C	837	O=O	498	S–S	215
C–N	290	O–F	160	S–Cl	250
C=N	615	O–Si	370	S–Br	215
C≡N	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
C=O	741	O–I	200	Cl–I	210
C≡O	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Table 5.6.2: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C=C	1.34	611
C≡C	1.20	837
C–N	1.43	290
C=N	1.38	615
C≡N	1.16	891
C–O	1.43	350
C=O	1.23	741
C≡O	1.13	1080

Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The **lattice energy** ($\Delta H_{lattice}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$MX(s) \longrightarrow M^{n+}(g) + X^{n-}(g) \quad \Delta H_{\text{lattice}}$$

Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be *endothermic* (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta H_{\text{lattice}}$ = 769 kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy $\Delta H_{\text{lattice}}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{\text{lattice}} = \frac{C\,(Z^+)\,(Z^-)}{R_0}$$

in which C is a constant that depends on the type of crystal structure; Z^+ and Z^- are the charges on the ions; and R_o is the interionic distance (the sum of the radii of the positive and negative ions). Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and Z^- = 1) is 1023 kJ/mol, whereas that of MgO (Z^+ and Z^- = 2) is 3900 kJ/mol (R_o is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

Example 5.6.2: Lattice Energy Comparisons

The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Cr^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will depend upon R_o. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

Exercise 5.6.1

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?

Answer available at the end of this section.

Answers

Exercise 5.6.1

ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

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5.7: VSEPR Theory Predicts Molecular Structure and Shape

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Compare and contrast major theories of chemical bonding (Lewis, **Valence-Shell-Electron-Pair Repulsion,** Valence Bond Theory, Molecular Orbital Theory)
- Draw Lewis structures, **predict molecular geometry,** and describe orbital hybridization according to accepted models of chemical bonding.

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 5.7.1). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

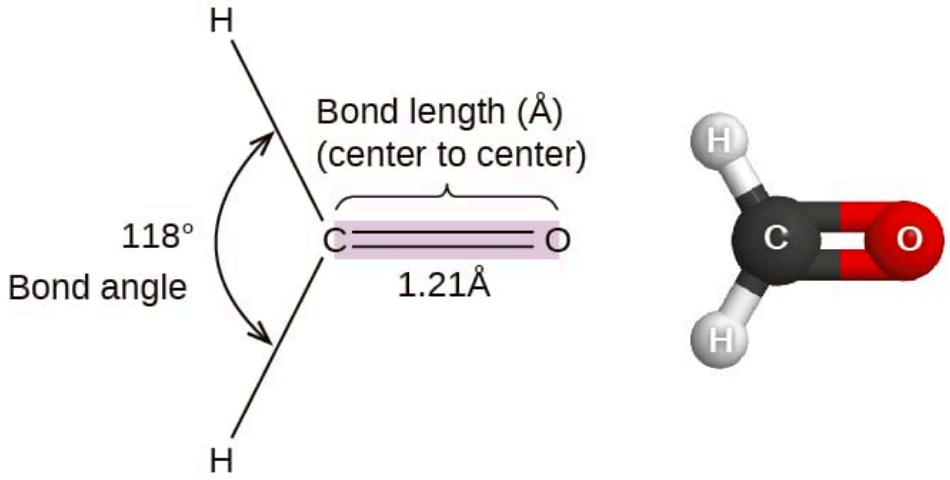


Figure 5.7.1: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 5.7.2) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron

density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 5.7.2).

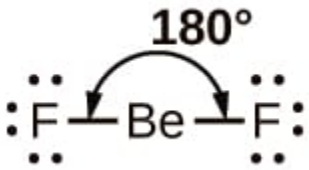


Figure 5.7.2: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 5.7.3 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

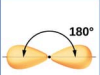
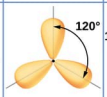
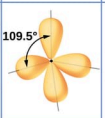
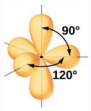
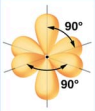
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron region geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 5.7.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 5.7.3 describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

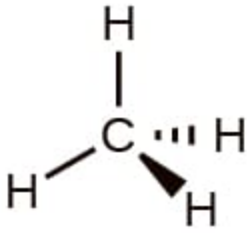


Figure 5.7.4: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 5.7.4). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 5.7.5).

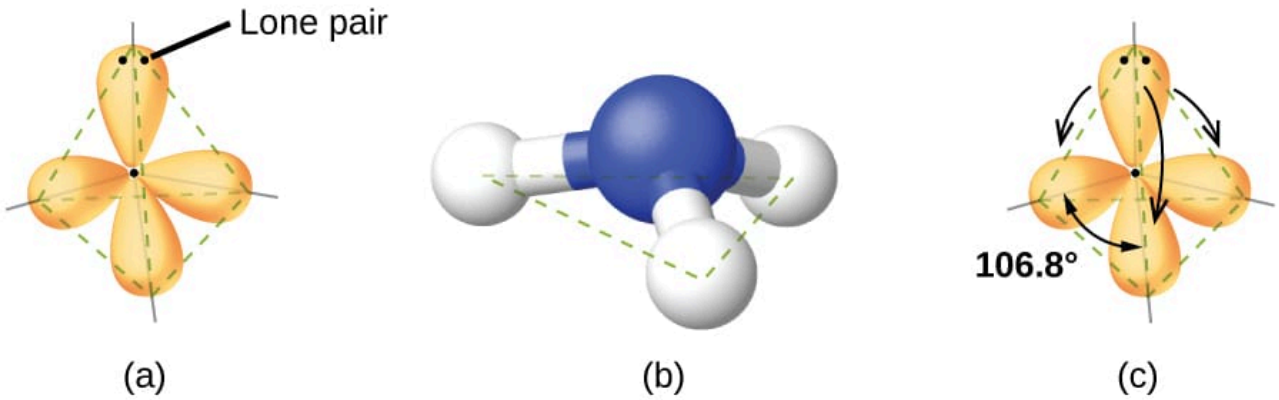


Figure 5.7.5: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

As seen in Figure 5.7.5, small distortions from the ideal angles in Figure 5.7.3 can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

$$\text{lone pair-lone pair} > \text{lone pair-bonding pair} > \text{bonding pair-bonding pair}$$

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

$$\text{lone pair} > \text{triple bond} > \text{double bond} > \text{single bond}$$

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens (Figure 5.7.1). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 5.7.5) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding

electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 5.7.3) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (Figure 5.7.5). Figure 5.7.6 illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

Number of electron regions	Electron region geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal planar	Bent or angular <120°			
4	109° Tetrahedral	Trigonal pyramid <109°	Bent or angular <<109°		
5	90°, 120° Trigonal bipyramid	Sawhorse or seesaw <90°, <120°	T-shape <90°	Linear 180°	
6	90° Octahedral	Square pyramid <90°	Square planar 90°	T-shape <90°	Linear 180°

Figure 5.7.6: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in Figure 5.7.6) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in Figure 5.7.7 an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). As shown in Figure 5.7.6, the axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure 5.7.7). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

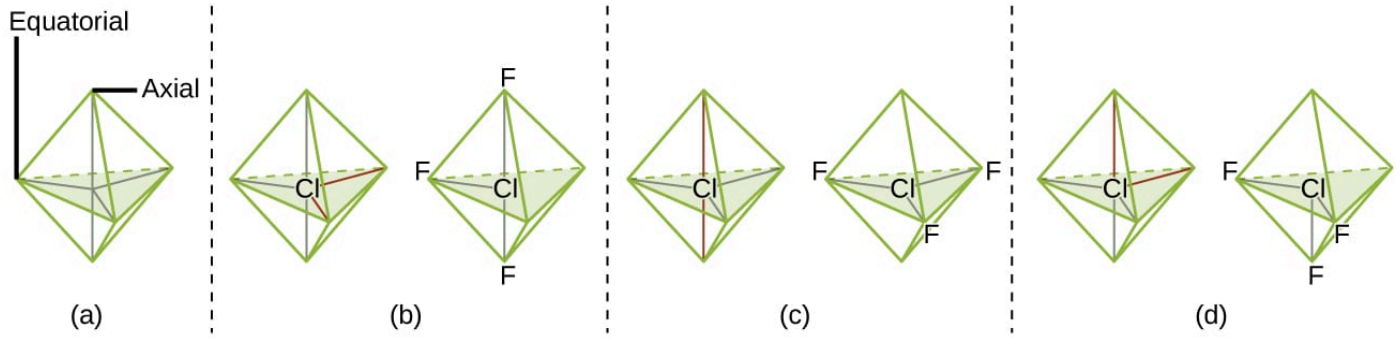


Figure 5.7.7: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The

two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (Figure 5.7.6).

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 5.7.6, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 5.7.6). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

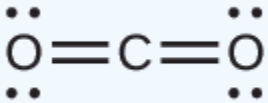
Example 5.7.1: Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

Predict the electron-pair geometry and molecular structure for each of the following:

a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
b. boron trichloride, BCl_3, an important industrial chemical

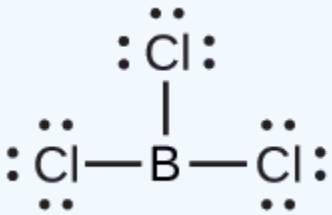
Solution

(a) We write the Lewis structure of CO_2 as:



This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure (Figure 5.7.8).

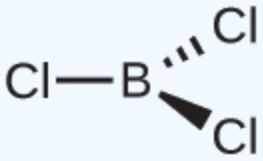


Figure 5.7.8:

The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Exercise 5.7.1

Carbonate, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

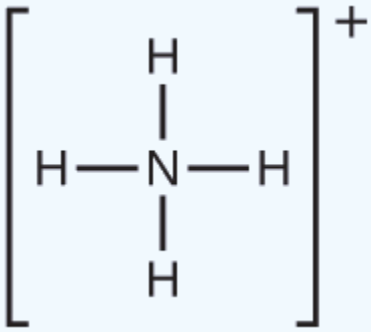
Answer available at the end of this section.

Example 5.7.2: Predicting Electron-pair Geometry and Molecular Structure: Ammonium

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the cation.

Solution

We write the Lewis structure of as:



We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (Figure 5.7.6). Therefore, the electron pair geometry of Figure 5.7.9.

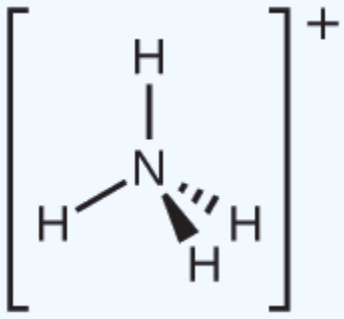


Figure 5.7.9: The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

Exercise 5.7.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer available at the end of this section.

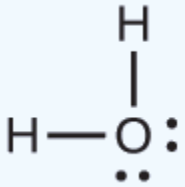
The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 5.7.3: Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion (Figure 5.7.10), as indicated in Figure 5.7.6. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

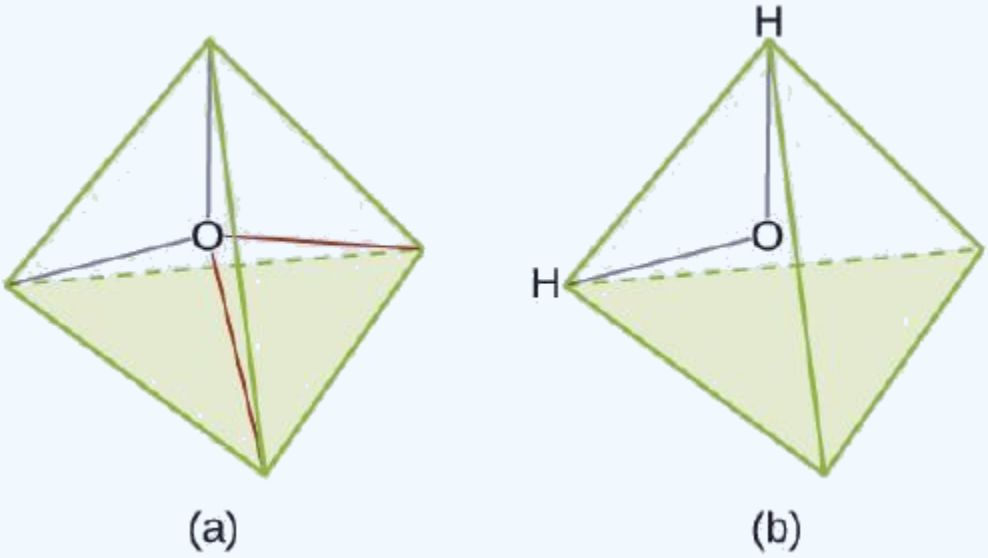


Figure 5.7.10: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Exercise 5.7.3

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

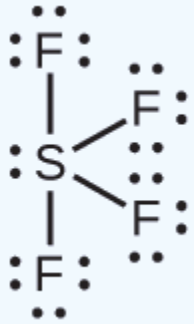
Answer available at the end of this section.

Example 5.7.4: Predicting Electron-pair Geometry and Molecular Structure: SF_4

Sulfur tetrafluoride, SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (Figure 5.7.11) is that of a seesaw (Figure 5.7.6).

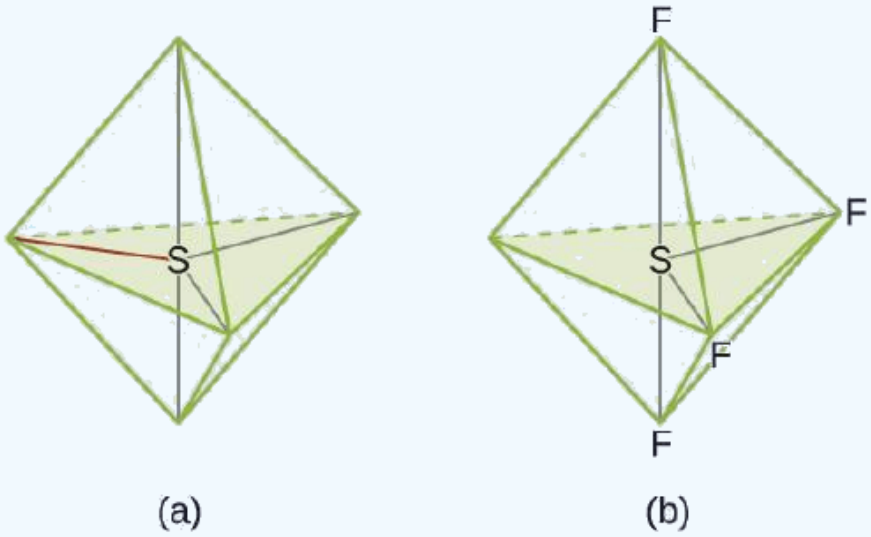


Figure 5.7.11: (a) SF4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Exercise 5.7.4

Predict the electron pair geometry and molecular structure for molecules of XeF_2.

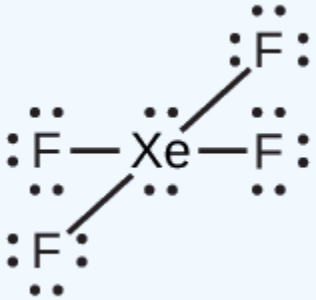
Answer available at the end of this section.

Example 5.7.5: Predicting Electron-pair Geometry and Molecular Structure: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement (Figure 5.7.6), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (Figure 5.7.12). The five atoms are all in the same plane and have a square planar molecular structure.

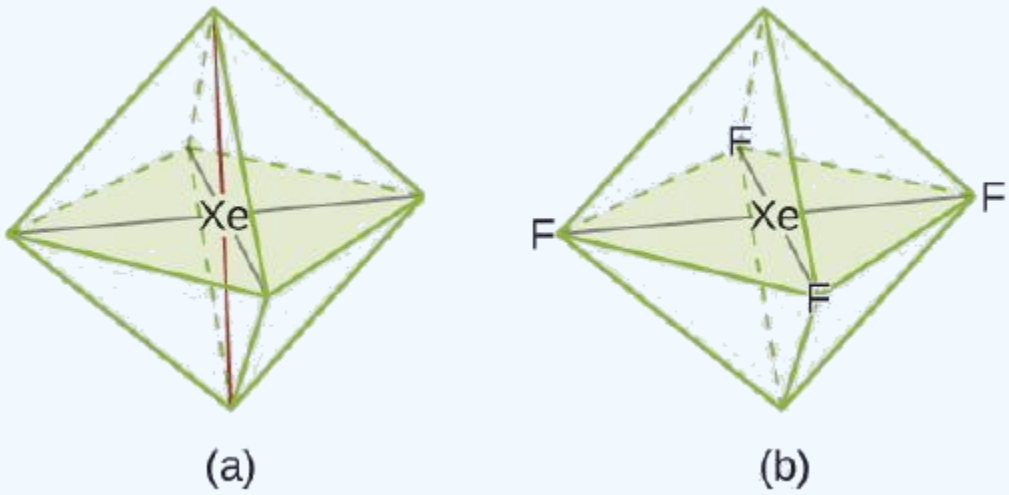


Figure 5.7.12: (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

Exercise 5.7.5

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

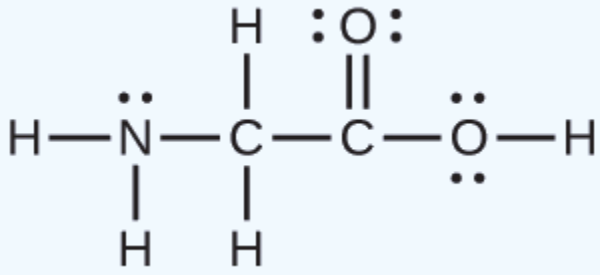
Answer available at the end of this section.

Molecular Structure for Multicenter Molecules

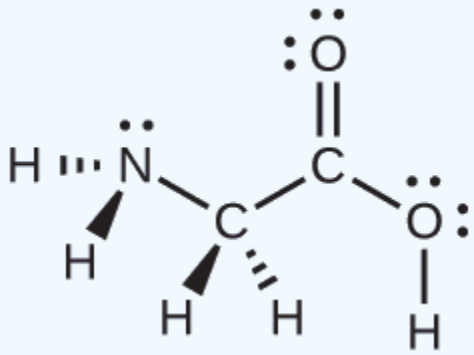
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

Example 5.7.6: Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

- nitrogen––four regions of electron density; tetrahedral
- carbon ($\underline{C}H_2$)––four regions of electron density; tetrahedral
- carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
- oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral

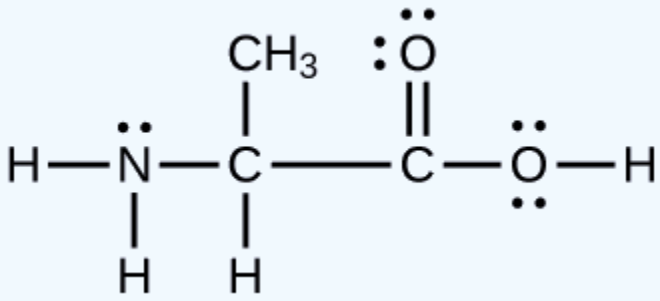
The local structures:

- nitrogen––three bonds, one lone pair; trigonal pyramidal

- carbon ($\underline{C}H_2$)—four bonds, no lone pairs; tetrahedral
- carbon ($\underline{C}O_2$)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ($\underline{O}H$)—two bonds, two lone pairs; bent (109°)

Exercise 5.7.6

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Answer available at the end of this section.

Link to Learning

The molecular shape simulator lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

Example 5.7.7: Molecular Simulation

Using molecular shape simulator allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under "Options" on the right. We can also use the "Name" checkboxes at bottom-left to display or hide the electron pair geometry (called "electron geometry" in the simulator) and/or molecular structure (called "molecular shape" in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

$$\mathrm{H{-}C{\equiv}N}$$

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

Exercise 5.7.7

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Answer available at the end of this section.

Answers

Exercise 5.7.1

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

Exercise 5.7.2

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.

Exercise 5.7.3

electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Exercise 5.7.4

The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

Exercise 5.7.5

electron pair geometry: trigonal bipyramidal; molecular structure: linear

Exercise 5.7.6

electron-pair geometries: nitrogen––tetrahedral; carbon (C<u>H</u>)—tetrahedral; carbon (C<u>H</u>$_3$)—tetrahedral; carbon (C<u>O</u>$_2$)—trigonal planar; oxygen (O<u>H</u>)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon (C<u>H</u>)—tetrahedral; carbon (C<u>H</u>$_3$)—tetrahedral; carbon (C<u>O</u>$_2$)—trigonal planar; oxygen (O<u>H</u>)—bent (109°)

Exercise 5.7.7

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. $XeOF_4$ is a molecule that adopts this structure.

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5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Order covalent bonds by length, strength, energy, and **polarity.**
- Predict whether a molecule/region of a molecule will be polar/nonpolar or hydrophobic/hydrophilic.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = Qr$$

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure 5.8.13). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

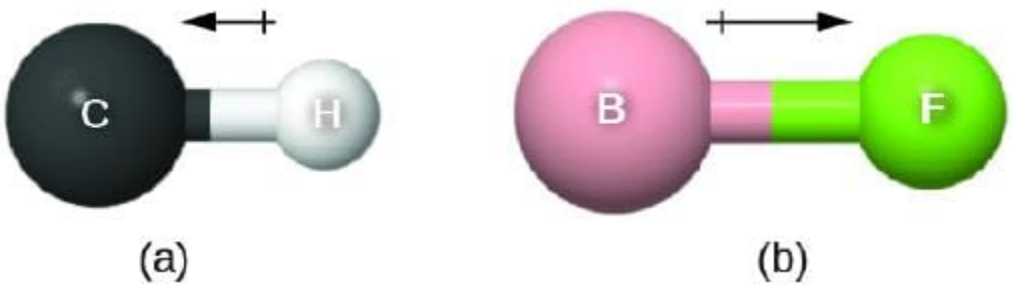


Figure 5.8.13: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegat difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule (or dipole); otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 5.8.14). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments

cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 5.8.14), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

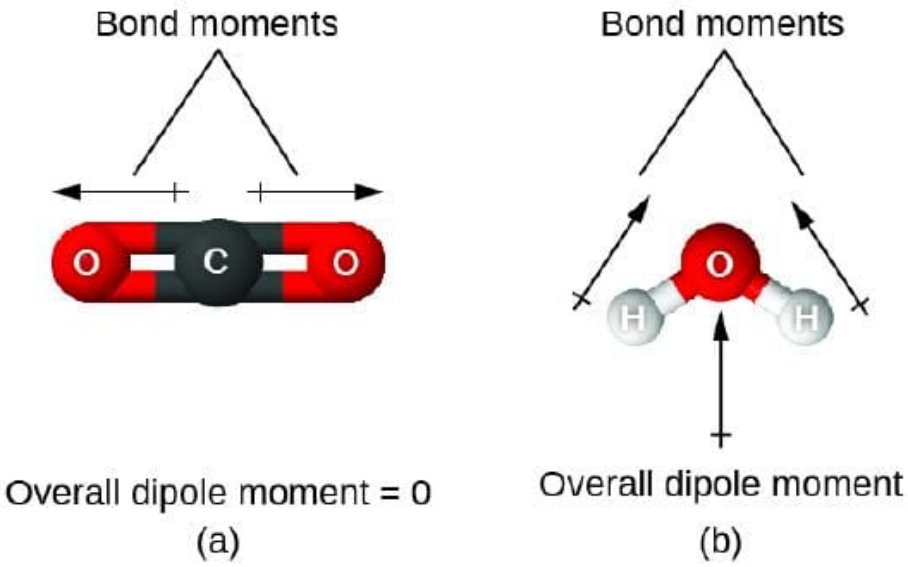
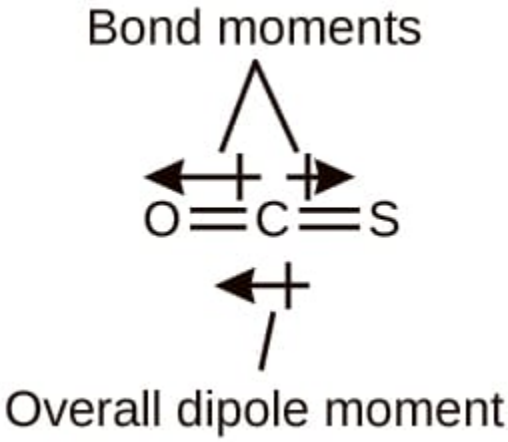


Figure 5.8.14: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

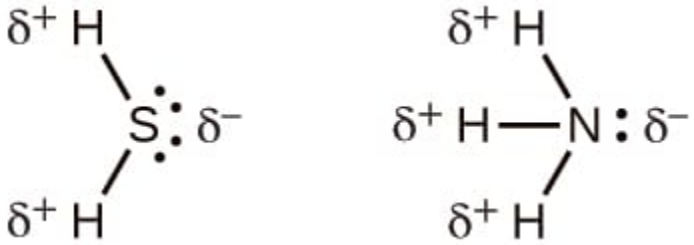


The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is a tetrahedral molecule with three slightly polar C-H bonds and a more polar C-Cl bond. The relative electronegativities of the bonded atoms is H < C < Cl, and so the bond moments all point toward the Cl end of the molecule and sum to yield a considerable dipole moment (the molecules are relatively polar).



For molecules of high symmetry such as BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), all the bonds are of identical polarity (same bond moment) and they are oriented in geometries that yield nonpolar molecules (dipole moment is zero). Molecules of less geometric symmetry, however, may be polar even when all bond moments are identical. For these molecules, the directions of the equal bond moments are such that they sum to give a nonzero dipole moment and a polar molecule. Examples of such molecules include hydrogen sulfide, H_2S (nonlinear), and ammonia, NH_3 (trigonal pyramidal).



To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 5.8.15). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

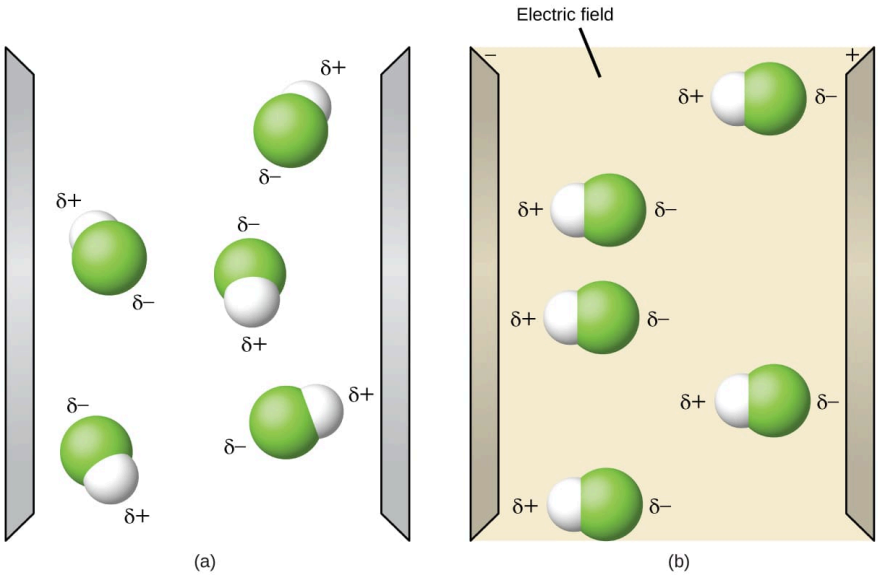


Figure 5.8.15: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Link to Learning

The molecule polarity simulation provides many ways to explore dipole moments of bonds and molecules.

Example 5.8.8: Polarity Simulations

Open the molecule polarity simulation and select the "Three Atoms" tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure 5.8.15.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution

a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

Exercise 5.8.8

Determine the partial charges that will give the largest possible bond dipoles.

Answer available at the end of this section.

Answers

Exercise 5.8.8

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

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5.9: Valence Bond Theory Describes Bonds as Overlapping Atomic Orbitals

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Compare and contrast major theories of chemical bonding (Lewis, Valence-Shell-Electron-Pair Repulsion, **Valence Bond Theory,** Molecular Orbital Theory)
- Draw Lewis structures, predict molecular geometry, and **describe orbital hybridization** according to accepted models of chemical bonding.

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

One theory that does provide an explanation of bonding is Valence Bond theory, which describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met: (1) an orbital on one atom overlaps an orbital on a second atom and (2) the single electrons in each orbital combine to form an electron pair. The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The orientation of orbitals also affects their overlap (other than for two s orbitals, which are spherically symmetric). Greater overlap is possible when atomic orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure 5.9.2 illustrates this for two *p* orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.

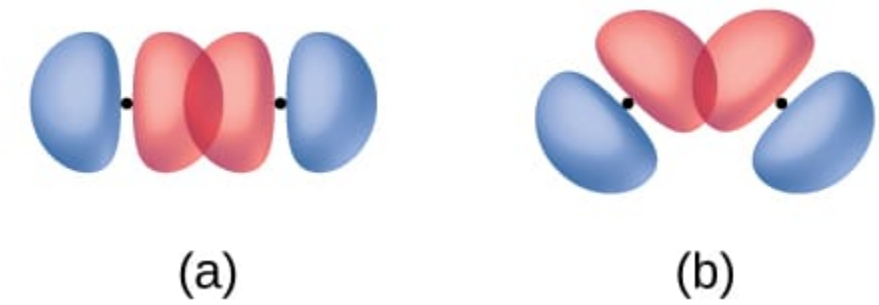


Figure 5.9.2: (a) The overlap of two *p* orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two s orbitals (as in H_2), the overlap of an *s* orbital and a *p* orbital (as in HCl), and the end-to-end overlap of two *p* orbitals (as in Cl_2) all produce sigma bonds (σ bonds), as illustrated in Figure 5.9.3. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

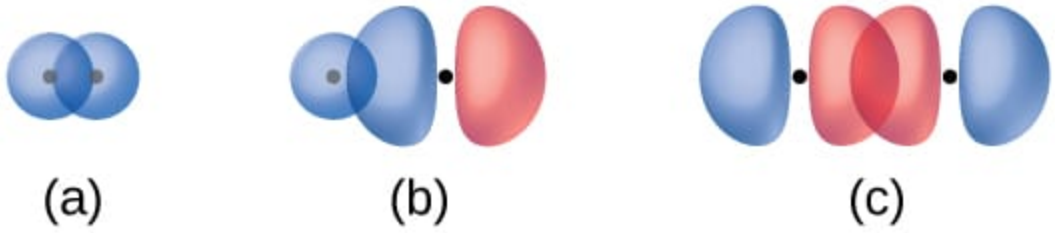


Figure 5.9.3: Sigma (σ) bonds form from the overlap of the following: (a) two *s* orbitals, (b) an *s* orbital and a *p* orbital, and (c) two *p* orbitals. The dots indicate the locations of the nuclei.

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in Figure 5.9.4. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.

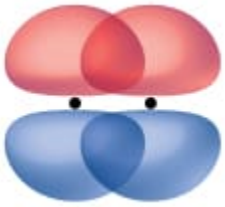
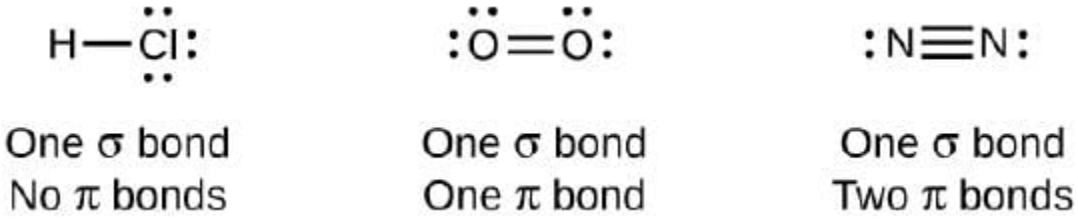


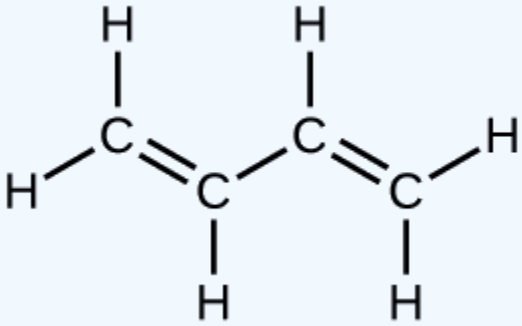
Figure 5.9.4: Pi (π) bonds form from the side-by-side overlap of two *p* orbitals. The dots indicate the location of the nuclei.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures below suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.



As seen in Figure 5.9.1, an average carbon-carbon single bond is 347 kJ/mol, while in a carbon-carbon double bond, the π bond increases the bond strength by 267 kJ/mol. Adding an additional π bond causes a further increase of 225 kJ/mol. We can see a similar pattern when we compare other σ and π bonds. Thus, each individual π bond is generally weaker than a corresponding σ bond between the same two atoms. In a σ bond, there is a greater degree of orbital overlap than in a π bond.

Example 5.9.1: Counting σ and π Bonds



Butadiene, C_4H_6, is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.

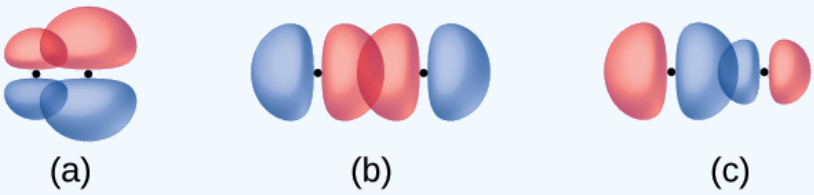
Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

Exercise 5.9.1

Identify each illustration as depicting a σ or π bond:

a. side-by-side overlap of a 4*p* and a 2*p* orbital
b. end-to-end overlap of a 4*p* and 4*p* orbital
c. end-to-end overlap of a 4*p* and a 2*p* orbital



Answer available at the end of this section.

Answers

Exercise 5.9.1

(a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

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5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Compare and contrast major theories of chemical bonding (Lewis, Valence-Shell-Electron-Pair Repulsion, **Valence Bond Theory,** Molecular Orbital Theory)
- Draw Lewis structures, predict molecular geometry, and **describe orbital hybridization** according to accepted models of chemical bonding.

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two 2*p* orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two 2*p* orbitals with the 1s orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90°, as shown in Figure 5.10.1, because *p* orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.

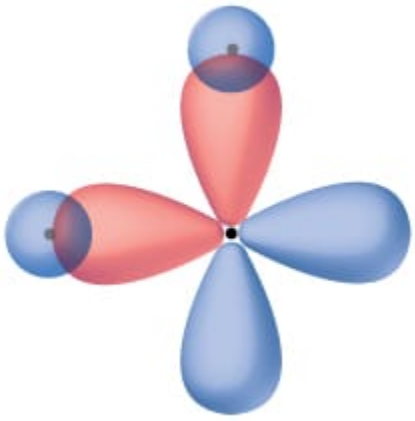


Figure 5.10.1: The hypothetical overlap of two of the 2*p* orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the 1s orbital of the hydrogen atoms with the 2*p* orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ, contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called **hybridization** and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later). The new orbitals that result are called **hybrid orbitals**. The valence orbitals in an *isolated* oxygen atom are a 2*s* orbital and three 2*p* orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure 5.10.2). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

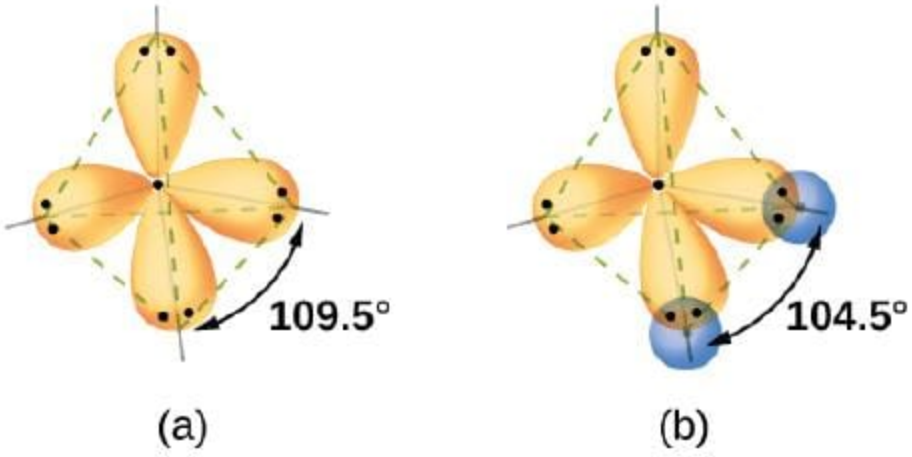


Figure 5.10.2: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence *s* orbital with one of the valence *p* orbitals to yield two equivalent ***sp* hybrid orbitals** that are oriented in a linear geometry (Figure 5.10.3). In this figure, the set of *sp* orbitals appears similar in shape to the original *p* orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The *p* orbital is one orbital that can hold up to two electrons. The *sp* set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the *s* orbital are now distributed to the two *sp* orbitals, which are half filled. In gaseous $BeCl_2$, these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.

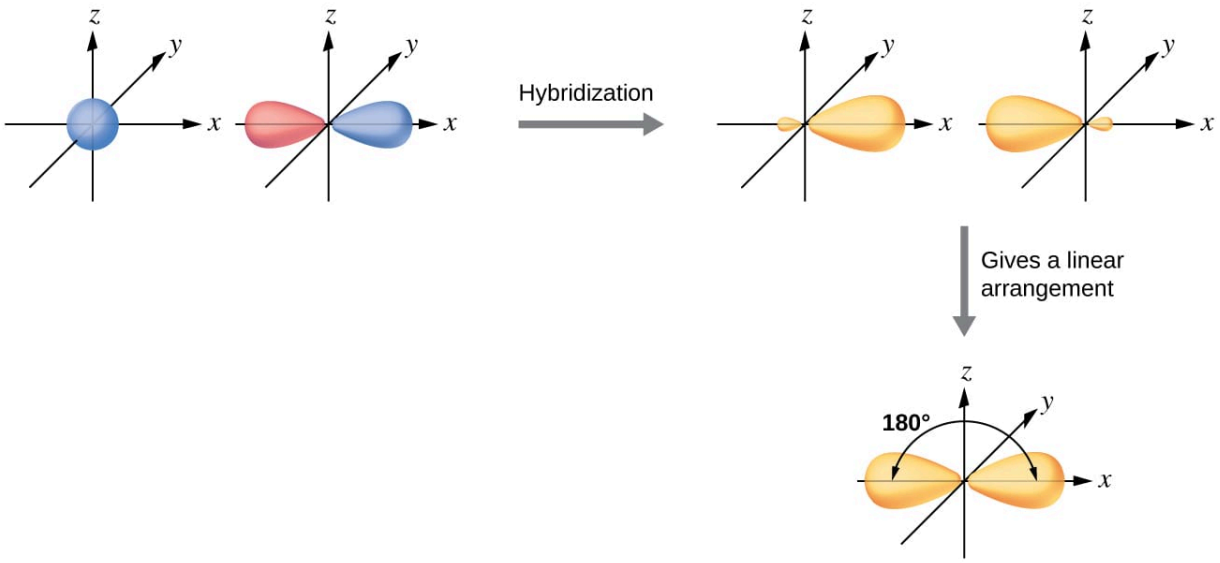


Figure 5.10.3: Hybridization of an *s* orbital (blue) and a *p* orbital (red) of the same atom produces two *sp* hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each *sp* orbital contains one lobe that is significantly larger than the other. The set of two *sp* orbitals are oriented at 180°, which is consistent with the geometry for two domains.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure 5.10.4. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.

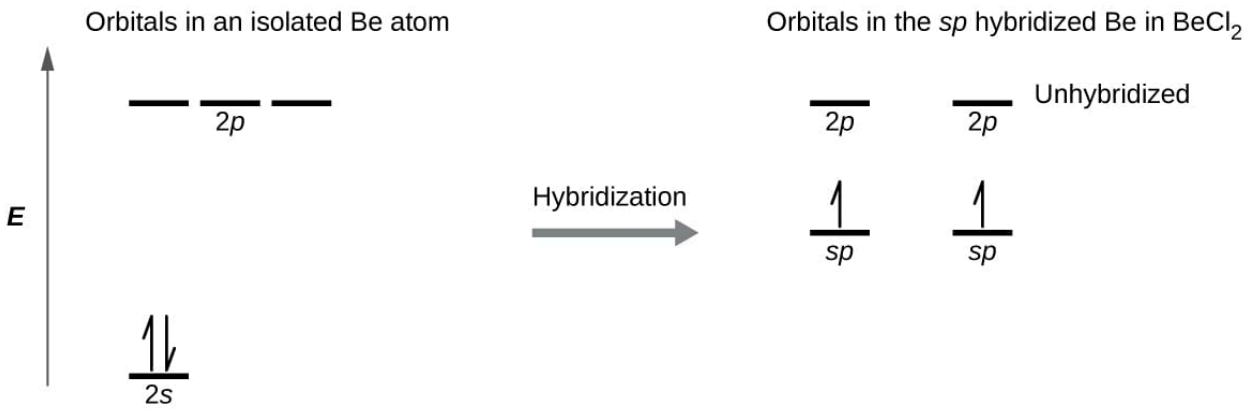


Figure 5.10.4: This orbital energy-level diagram shows the *sp* hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two *sp* hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3*p* orbital.

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds.

Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit *sp* hybridization. Other examples include the mercury atom in the linear $HgCl_2$ molecule, the zinc atom in $Zn(CH_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2.

Link to Learning

Check out the University of Wisconsin-Oshkosh website to learn about visualizing hybrid orbitals in three dimensions.

sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three **sp^2 hybrid orbitals** and one unhybridized *p* orbital. This arrangement results from sp^2 hybridization, the mixing of one s orbital and two *p* orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (Figure 5.10.5).

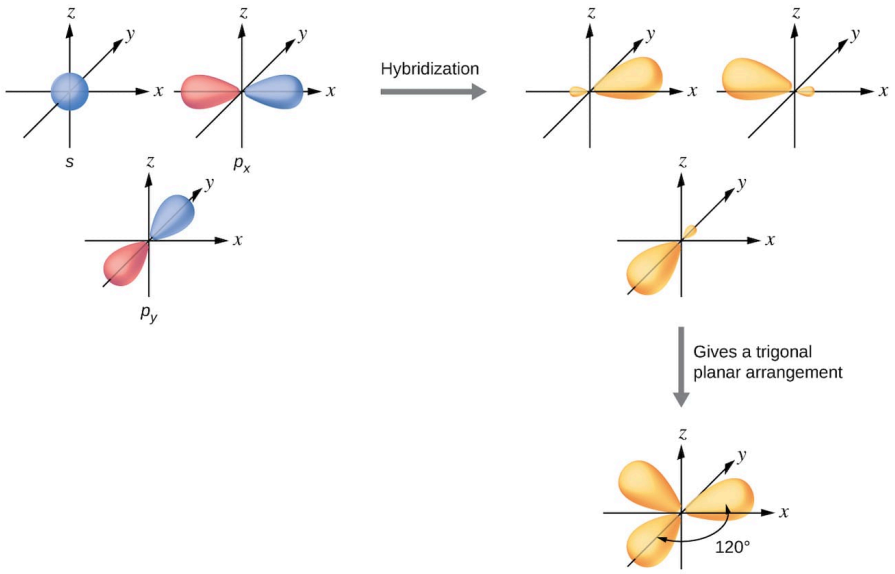


Figure 5.10.5: The hybridization of an s orbital (blue) and two *p* orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized *p* orbital is not shown here, but is located along the z axis.

Although quantum mechanics yields the "plump" orbital lobes as depicted in Figure 5.10.5, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure 5.10.6, to avoid obscuring other features of a given illustration. We will use these "thinner" representations whenever the true view is too crowded to easily visualize.

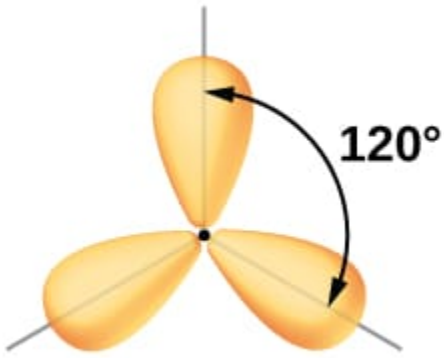


Figure 5.10.6: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

The observed structure of the borane molecule, BH_3, suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure 5.10.7). We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH_3 as shown in the orbital energy level diagram in Figure 5.10.8. We redistribute the three valence electrons of the boron atom in the three sp^2 hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.

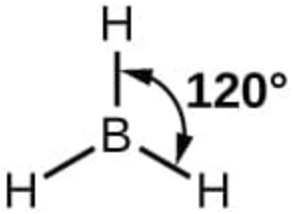


Figure 5.10.7: BH_3 is an electron-deficient molecule with a trigonal planar structure.

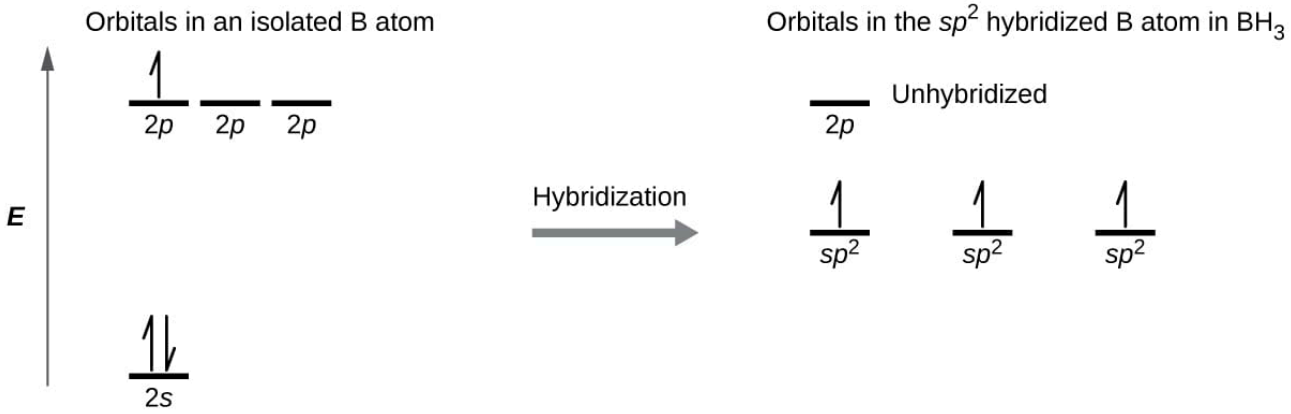


Figure 5.10.8: In an isolated B atom, there are one 2*s* and three 2*p* valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2*p* orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as ClNO (Figure 5.10.9), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O, and ethene, H_2CCH_2.

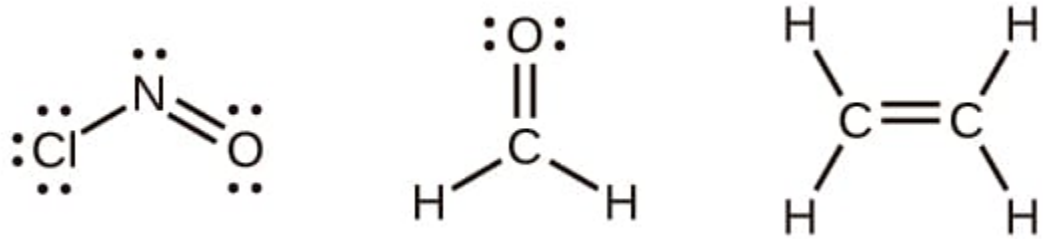


Figure 5.10.9: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four **sp^3 hybrid orbitals**. The hybrids result from the mixing of one *s* orbital and all three *p* orbitals that produces four identical sp^3 hybrid orbitals (Figure 5.10.10). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

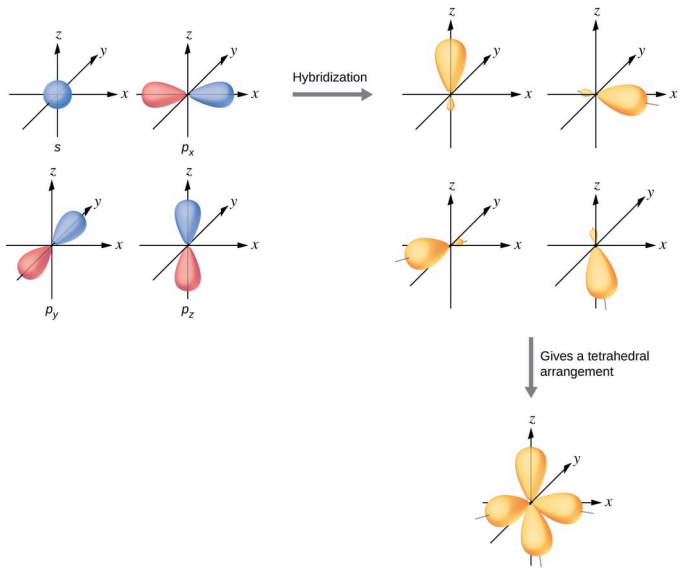


Figure 5.10.10: The hybridization of an *s* orbital (blue) and three *p* orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A molecule of methane, CH_4, consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in Figure 5.10.11. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.

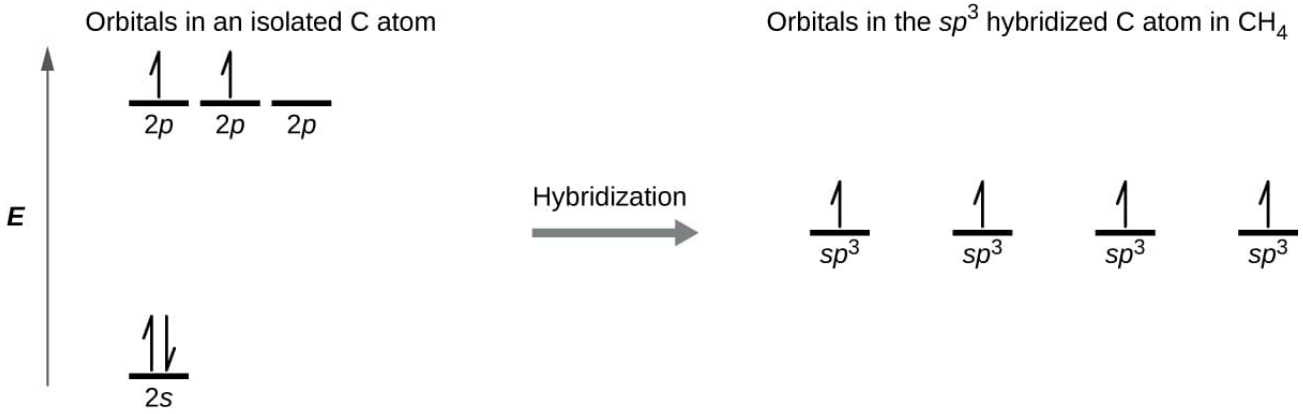


Figure 5.10.11: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

In a methane molecule, the 1s orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4.

The structure of ethane, C_2H_6, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure 5.10.12). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp^3 hybrid orbitals overlaps with an *s* orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure 5.10.12. The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

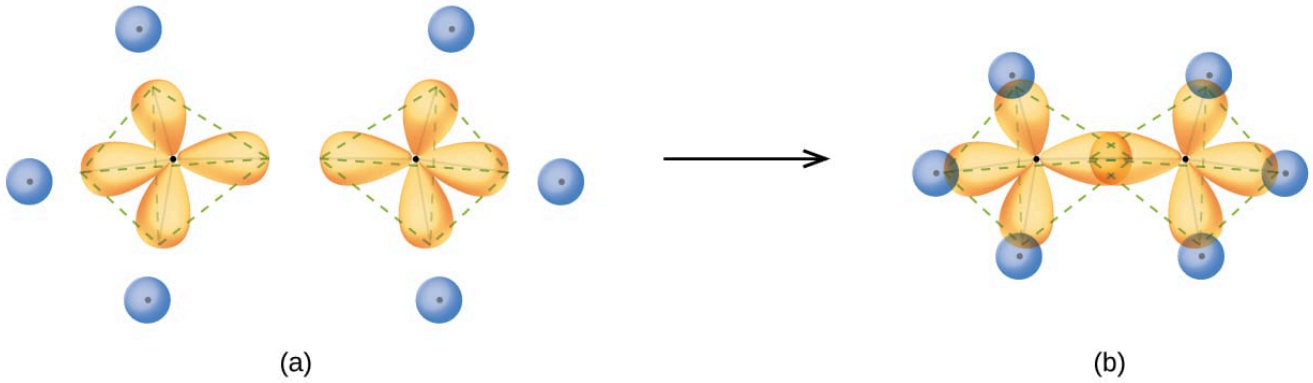


Figure 5.10.12: (a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl_4, PCl_3, and NCl_3.

sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the s orbital, the three *p* orbitals, and one of the *d* orbitals), which gives five **sp^3d hybrid orbitals**. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the s orbital, the three *p* orbitals, and two of the *d* orbitals in its valence shell), which gives six **sp^3d^2 hybrid orbitals**. These hybridizations are only possible for atoms that have *d* orbitals in their valence subshells (that is, not those in the first or second period).

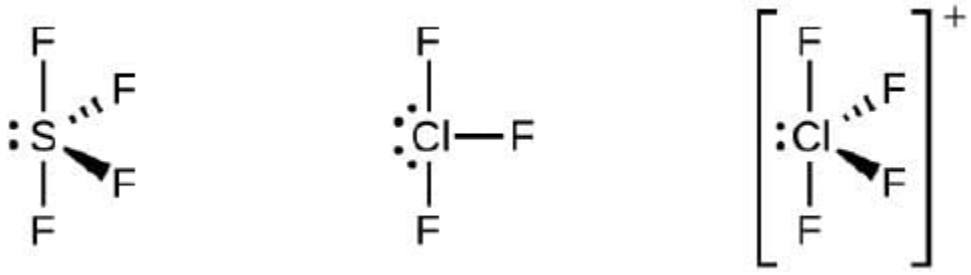


Figure 5.10.13: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and have one lone pair of electrons on the central atom, and ClF_3 has two lone pairs giving it the T-shape shown.

In a molecule of phosphorus pentachloride, PCl_5, there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the 3*s* orbital, the three 3*p* orbitals, and one of the 3*d* orbitals to form the set of five sp^3d hybrid orbitals (Figure 5.10.14) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in (The electrons on fluorine atoms are omitted for clarity.)

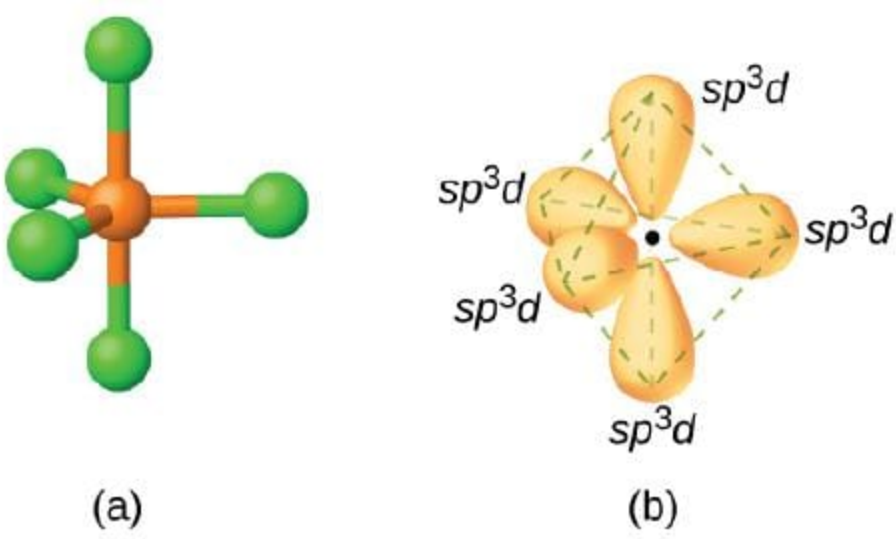


Figure 5.10.14: (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

The sulfur atom in sulfur hexafluoride, SF_6, exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the 3*s* orbital, the three 3*p* orbitals, and two of the 3*d* orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in the iodine atom in the interhalogens IF_5, and the xenon atom in XeF_4.

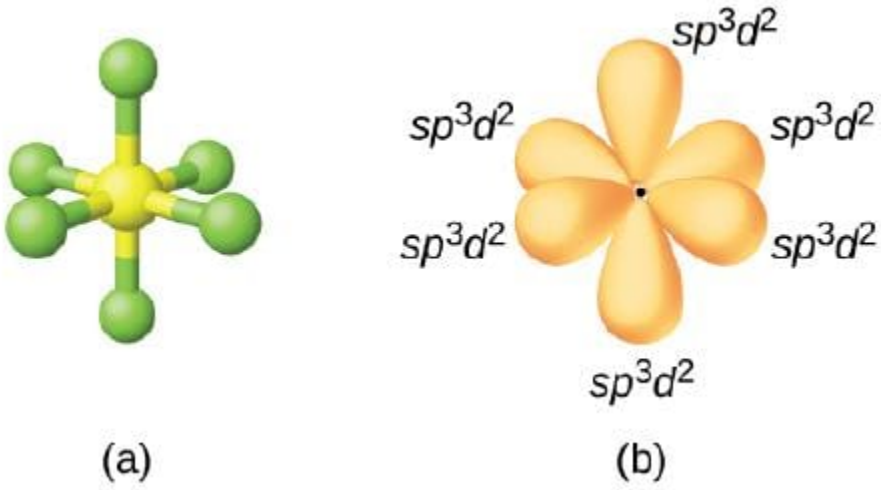


Figure 5.10.15: (a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

Summary - Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in Figure 5.10.16. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

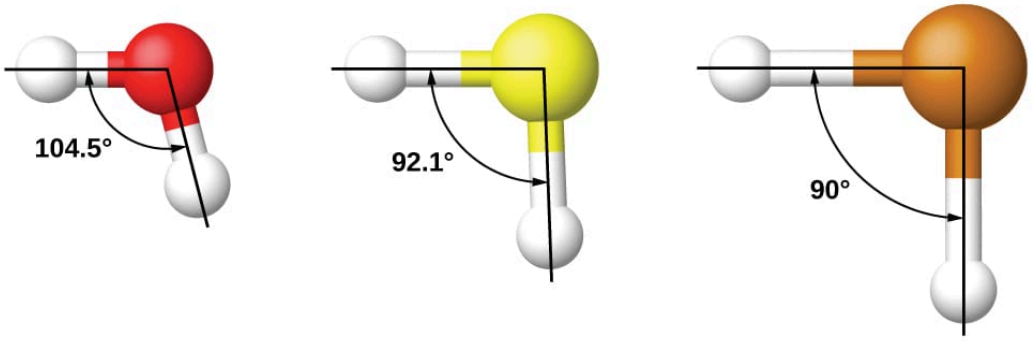
1. Determine the Lewis structure of the molecule.

2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure 5.10.16 that corresponds to this geometry.

Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	180°
3		trigonal planar	sp^2	120°
4		tetrahedral	sp^3	109.5°
5		trigonal bipyramidal	sp^3d	90°, 120°
6		octahedral	sp^3d^2	90°, 90°

Figure 5.10.16: The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion.

It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries. The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data. For example, we have discussed the H–O–H bond angle in H_2O, 104.5°, which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with 2*p* orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te, the observed bond angle (90°) is consistent with overlap of the 5*p* orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.

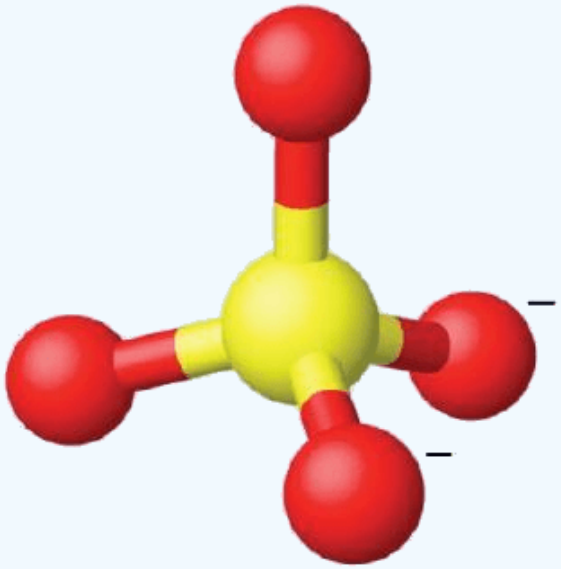


Example 5.10.1: Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion,

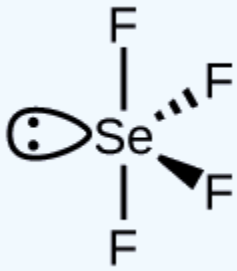
Solution

The Lewis structure of sulfate shows there are four regions of electron density. The hybridization is sp^3.



Exercise 5.10.1

What is the hybridization of the selenium atom in SeF_4?



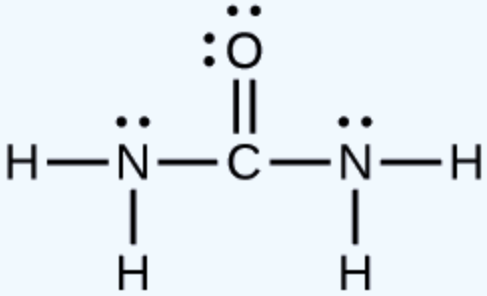
Answer available at the end of this section.

Example 5.10.2: Assigning Hybridization

Urea, $NH_2C(O)NH_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of the carbon atom in urea?

Solution

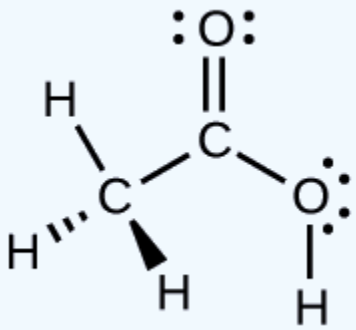
The Lewis structure of urea is



The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (Figure 5.10.16), which is the hybridization of the carbon atom in urea.

Exercise 5.10.1

Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?



Answer available at the end of this section.

Footnotes

- 1Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.

Answers

Exercise 5.10.1

The selenium atom is sp^3d hybridized.

Exercise 5.10.1

$H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

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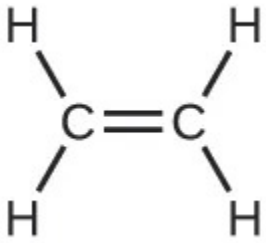
5.11: Valence Bond Treatment of Multiple Bonds

Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Compare and contrast major theories of chemical bonding (Lewis, Valence-Shell-Electron-Pair Repulsion, **Valence Bond Theory**, Molecular Orbital Theory)
- Draw Lewis structures, predict molecular geometry, and **describe orbital hybridization** according to accepted models of chemical bonding.

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4, shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.



The three bonding regions form a trigonal planar electron-pair geometry. Thus we expect the σ bonds from each carbon atom are formed using a set of sp^2 hybrid orbitals that result from hybridization of two of the 2*p* orbitals and the 2*s* orbital (Figure 5.11.1).

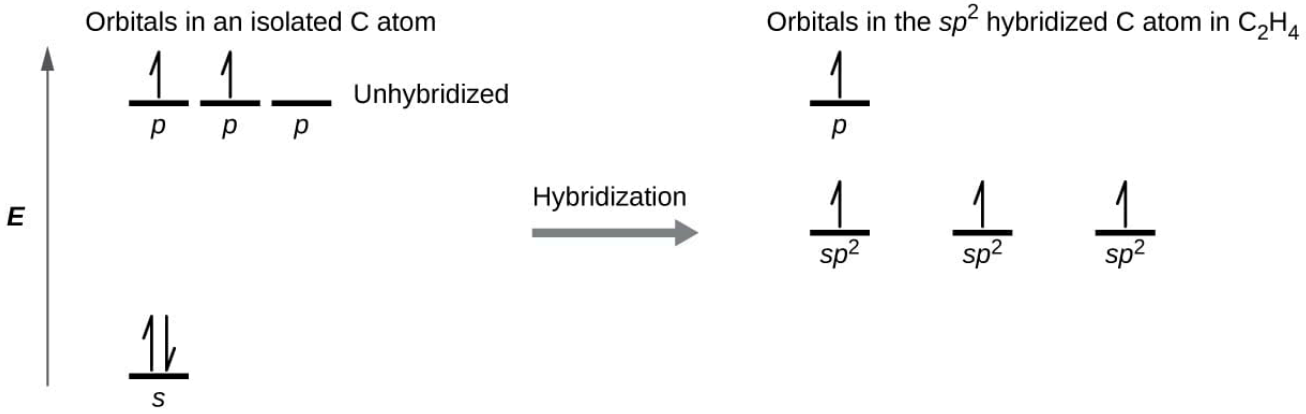


Figure 5.11.1: In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the *p* orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the *p* orbitals on each carbon atom overlap to form a π bond.

These orbitals form the C–H single bonds and the σ bond in the Figure 5.11.2. The π bond in the C=C double bond results from the overlap of the third (remaining) 2p orbital on each carbon atom that is not involved in hybridization. This unhybridized p orbital (lobes shown in red and blue in Figure 5.11.2) is perpendicular to the plane of the sp2 hybrid orbitals. Thus the unhybridized 2p orbitals overlap in a side-by-side fashion, above and below the internuclear axis (Figure 5.11.2) and form a π bond.

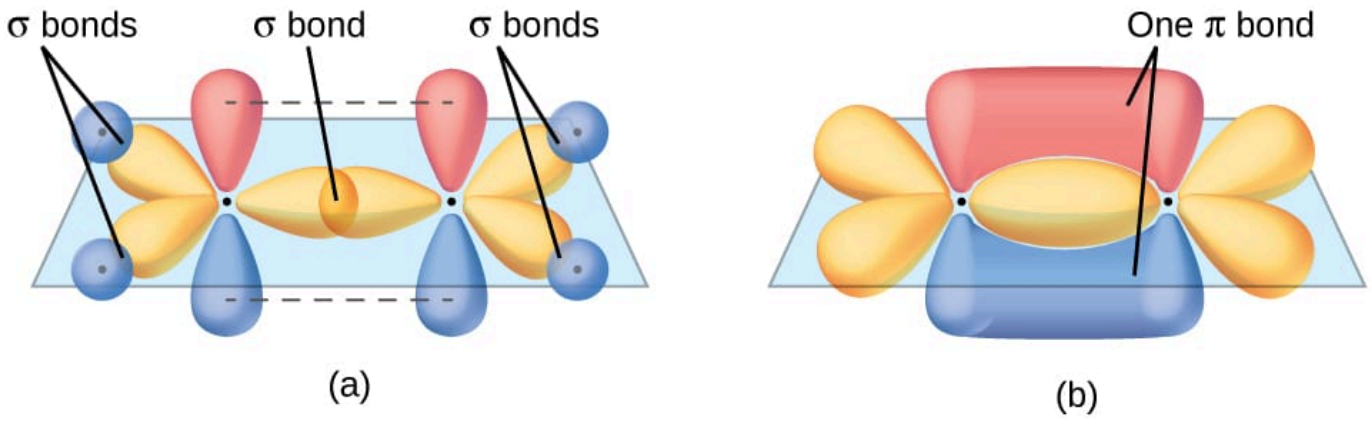


Figure 5.11.2: In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with s orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized *p* orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system.

In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the *p* orbitals would not be oriented to overlap efficiently to create the π bond. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.

In molecules with *sp* hybrid orbitals, two unhybridized *p* orbitals remain on the atom (Figure 5.11.3). We find this situation in acetylene, $\mathrm{H{-}C{\equiv}C{-}H}$ (Figure 5.11.4), The remaining sp orbitals form σ bonds with hydrogen atoms. The two unhybridized *p* orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

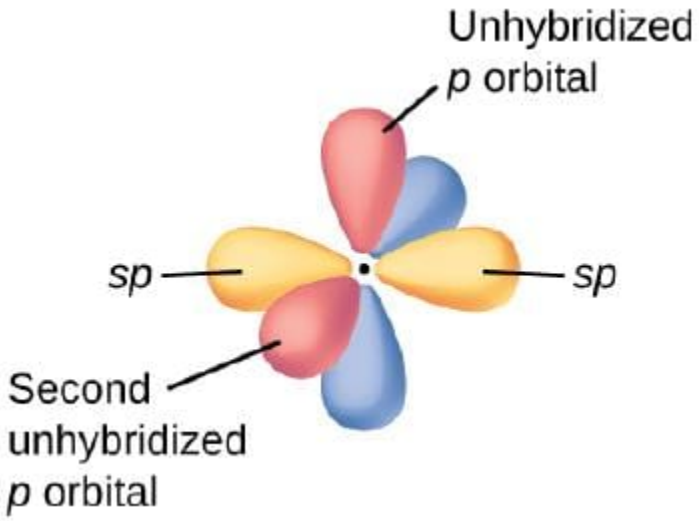


Figure 5.11.3: Diagram of the two linear *sp* hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized *p* orbitals at perpendicular angles.

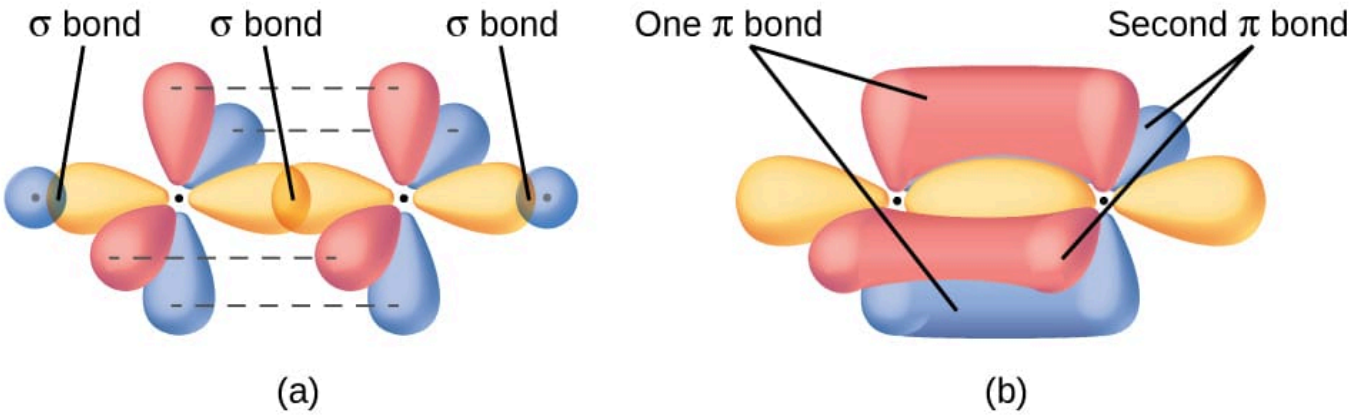


Figure 5.11.4: (a) In the acetylene molecule, C_2H_2, there are two C–H σ bonds and a triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized *p* orbitals. (b) This shows the overall outline of the bonds in C_2H_2. The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond.

Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms (Figure 5.11.5). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2. The electrons in the unhybridized *p* orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory. (See the next module.)

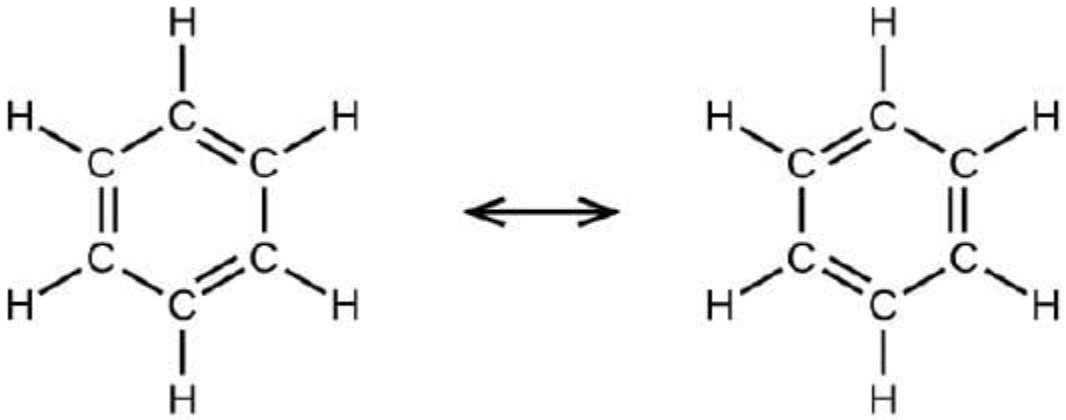


Figure 5.11.5: Each carbon atom in benzene, C_6H_6, is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of *p* orbitals or the other, but rather delocalized throughout the molecule.

Example 5.11.1: Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide, SO_2, is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the S atom in SO_2?

Solution

The resonance structures of SO_2 are



The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is sp^2.

Exercise 5.11.1

Another acid in acid rain is nitric acid, HNO_3, which is produced by the reaction of nitrogen dioxide, NO_2, with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

Answer available at the end of this section.

Answers

Exercise 5.11.1

sp^2

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5.12: Molecular Orbital Theory Resolves Issues in Other Bonding Theories

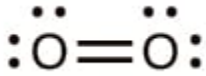
Learning Objectives

By the end of this section, you will have background information that will help you be able to:

- Compare and contrast major theories of chemical bonding (Lewis, Valence-Shell-Electron-Pair Repulsion, Valence Bond Theory, **Molecular Orbital Theory**)

Other Bonding Theories are Incomplete

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called **paramagnetism**, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure $5.12.1$), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

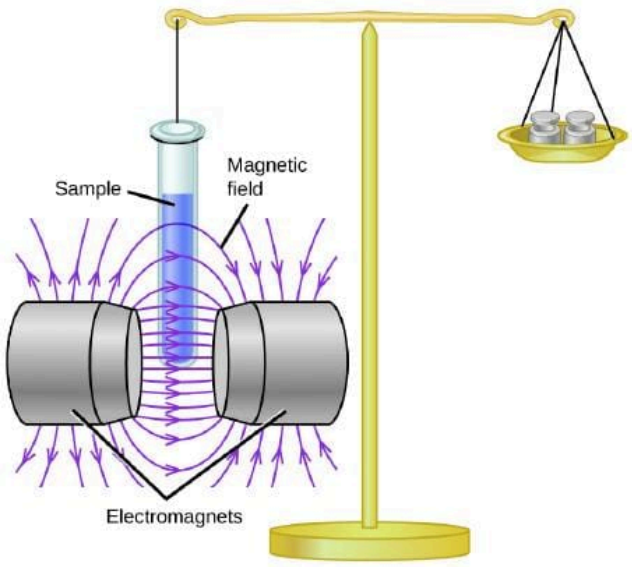


Figure 5.12.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.

Link to Learning

Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more.

What does Molecular Orbital Theory Do Differently?

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalized* over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table 5.12.1 summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Table 5.12.1: Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s, p, d*...) and hybrid orbitals (*sp, sp*^{2}, *sp*^{3}...)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)

Valence Bond Theory	Molecular Orbital Theory
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, Ψ, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a molecular orbital (Ψ^2). Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2, for example). Such molecules are called homonuclear diatomic molecules. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the **linear combination of atomic orbitals** (LCAO). The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (Figure 5.12.2). In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.

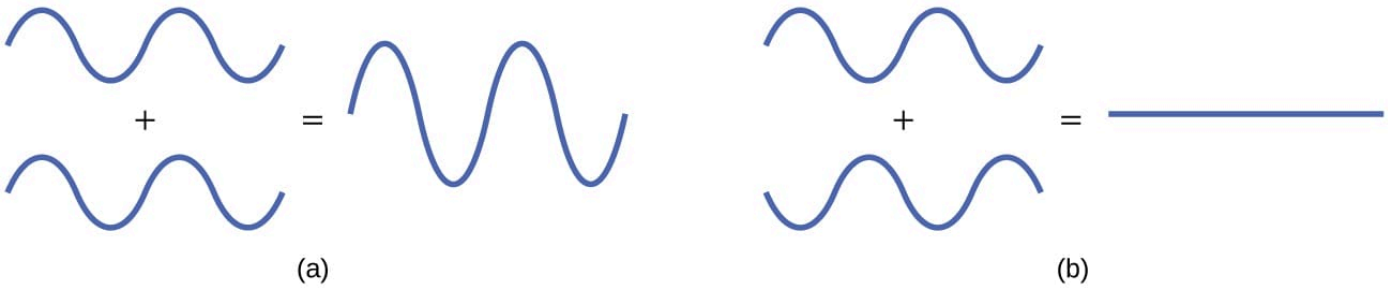


Figure 5.12.2: (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

There are two types of molecular orbitals that can form from the overlap of two atomic s orbitals on adjacent atoms. The two types are illustrated in Figure 5.12.3. The in-phase combination produces a lower energy σ_s molecular orbital (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy molecular orbital (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals bonding orbitals. Electrons in the orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

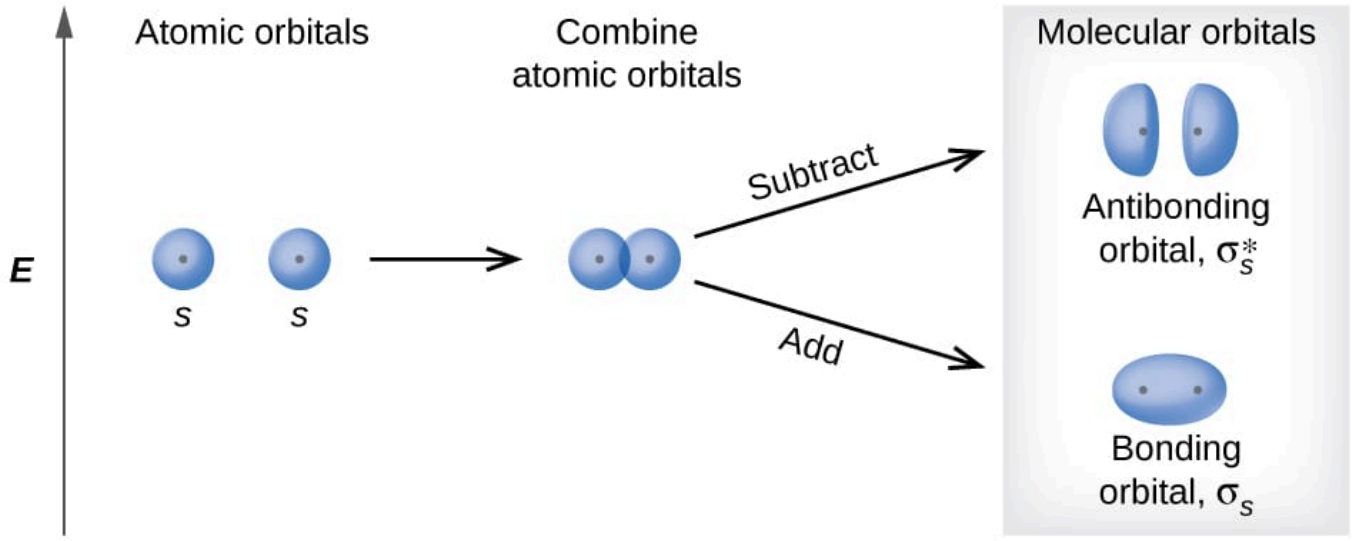


Figure 5.12.3: Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The dots (·) indicate the locations of nuclei.

Link to Learning

You can watch animations visualizing the calculated atomic orbitals combining to form various molecular orbitals at the Orbitron website.

In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When *p* orbitals overlap end to end, they create σ and σ* orbitals (Figure 5.12.4). If two atoms are located along the *x*-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with s-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.

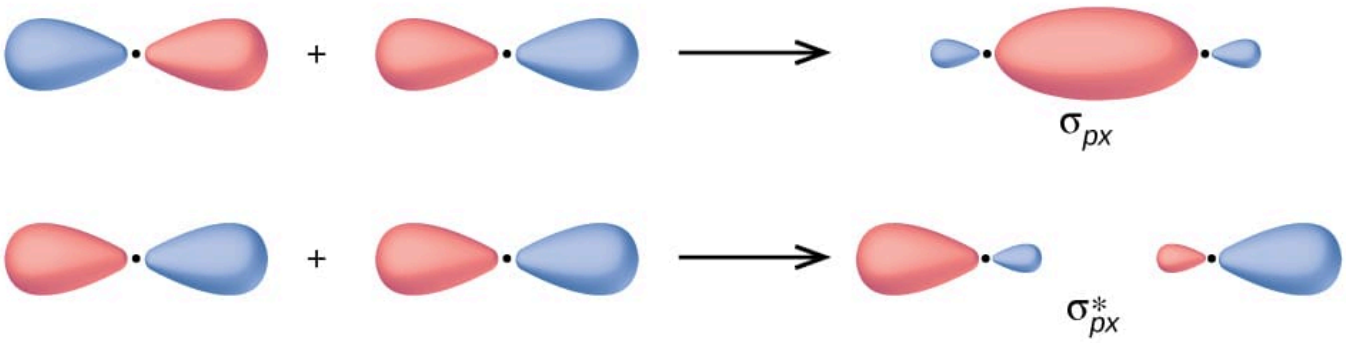


Figure 5.12.4: Combining wave functions of two *p* atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ_p^*.

The side-by-side overlap of two *p* orbitals gives rise to a **pi (π) bonding molecular orbital** and a **π* antibonding molecular orbital**, as shown in Figure 5.12.5. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.

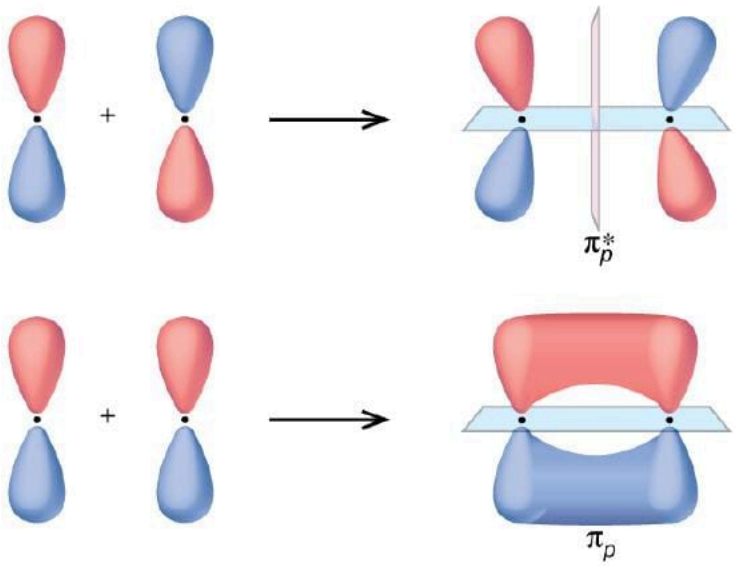
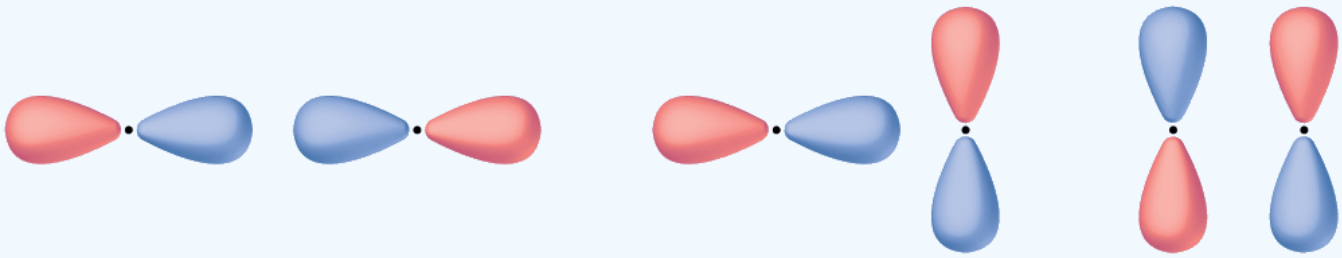


Figure 5.12.5: Side-by-side overlap of each two *p* orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) containing the internuclear axis with the two lobes of the orbital located above and below this node.

In the molecular orbitals of diatomic molecules, each atom also has two sets of *p* orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π* orbitals. The π_{py} and orbitals are oriented at right angles to the π_{pz} and π^*_{pz} orbitals. Except for their orientation, the \(π_{py}\) and \(π_{pz}\) orbitals are identical and have the same energy; they are **degenerate orbitals**. The π^*_{py} and π^*_{pz} antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic p orbitals in two atoms: σ_{px} and σ^*_{px}, π_{py} and π^*_{py}, π_{pz} and π^*_{pz}.

Example 5.12.1: Molecular Orbitals

Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.



Solution

a. is an in-phase combination, resulting in a π_{3p} orbital
b. will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.
c. is an out-of-phase combination, resulting in a π^*_{3p} orbital.

Exercise 5.12.1

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.



Answer available at the end of this section.

Portrait of a Chemist: Walter Kohn: Nobel Laureate

Walter Kohn (Figure 5.12.6) is a theoretical physicist who studies the electronic structure of solids. His work combines the principles of quantum mechanics with advanced mathematical techniques. This technique, called density functional theory, makes it possible to compute properties of molecular orbitals, including their shape and energies. Kohn and mathematician John Pople were awarded the Nobel Prize in Chemistry in 1998 for their contributions to our understanding of electronic structure. Kohn also made significant contributions to the physics of semiconductors.

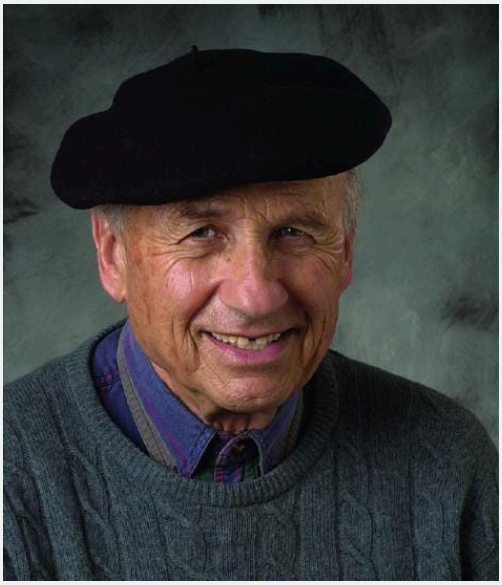


Figure 5.12.6: Walter Kohn developed methods to describe molecular orbitals. (credit: image courtesy of Walter Kohn)

Kohn's biography has been remarkable outside the realm of physical chemistry as well. He was born in Austria, and during World War II he was part of the Kindertransport program that rescued 10,000 children from the Nazi regime. His summer jobs included discovering gold deposits in Canada and helping Polaroid explain how its instant film worked. Dr. Kohn passed away in 2016 at the age of 93.

How Sciences Interconnect: Computational Chemistry in Drug Design

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (see Figure 5.12.7). Thousands of potential candidates can be narrowed down to a few of the most promising

candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.

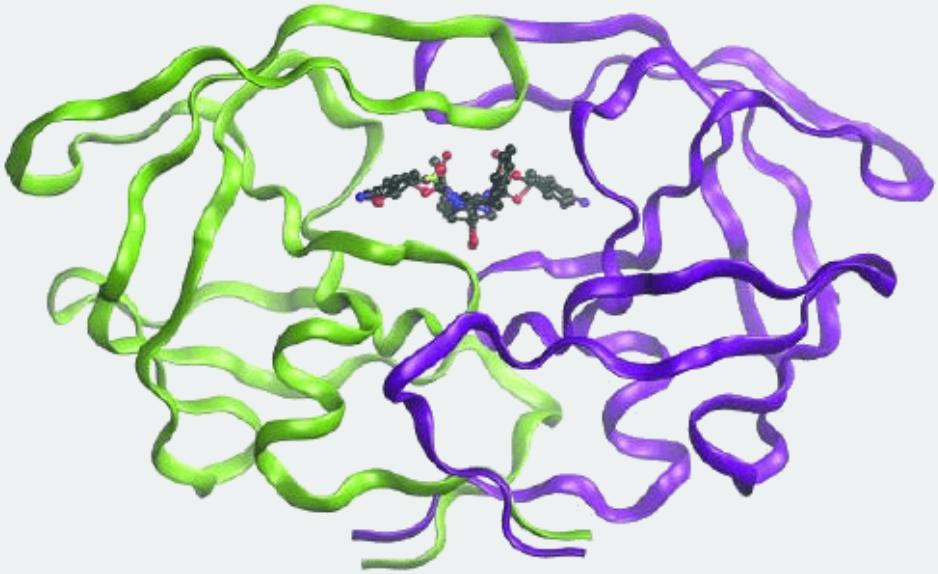


Figure 5.12.7: The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure 5.12.8). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2*p* atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (Figure 5.12.8). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as $\mathrm{Be_2}^+$) would have the molecular electron configuration $(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^1$. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

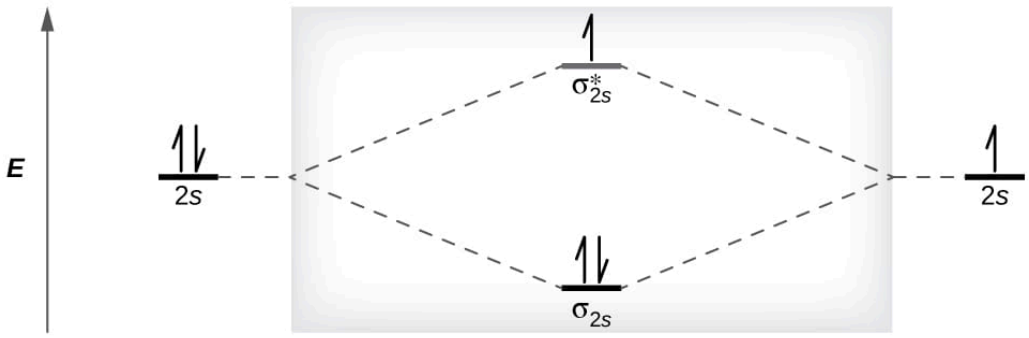


Figure 5.12.8: This is the molecular orbital diagram for the homonuclear diatomic showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the **bond order** that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\text{bond order } = \frac{(\text{number of bonding electrons }) - (\text{ number of antibonding electrons })}{2}$$

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases (Table 8.1). If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

Bonding in Diatomic Molecules

A dihydrogen molecule (H_2) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital. A dihydrogen molecule, H_2, readily forms because the energy of a H_2 molecule is lower than that of two H atoms. The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1s atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ1s bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (Figure 5.12.9) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

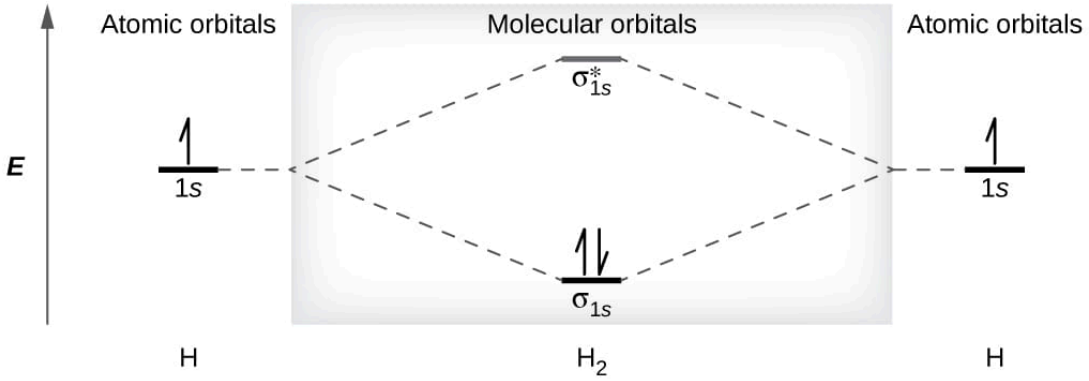


Figure 5.12.9: The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in } H_2 = \frac{(2-0)}{2} = 1$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

A helium atom has two electrons, both of which are in its 1s orbital. Two helium atoms do not combine to form a dihelium molecule, He_2, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He_2 as

$$\text{bond order in } He_2 = \frac{(2-2)}{2} = 0$$

A bond order of zero indicates that no bond is formed between two atoms.

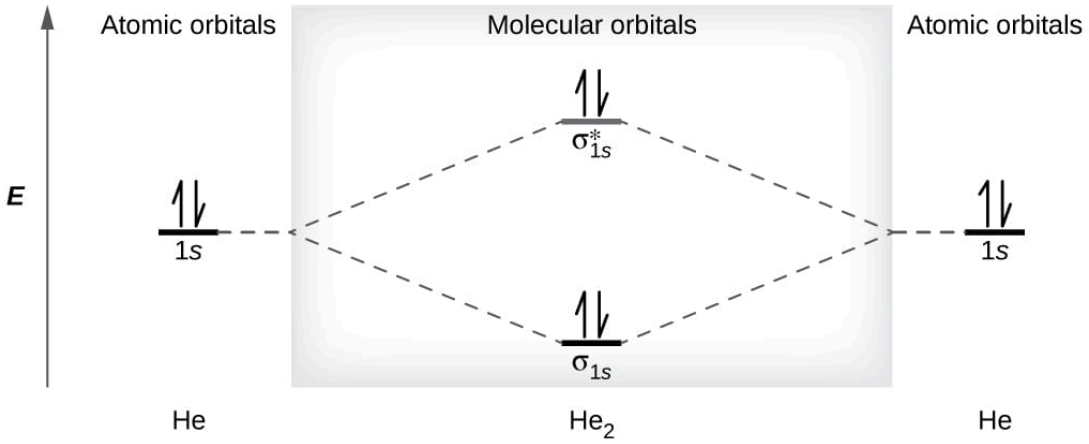


Figure 5.12.10: The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

Example 5.12.2: Molecular Orbital Diagrams, Bond Order, and Number of Unpaired Electrons

Draw the molecular orbital diagram for the oxygen molecule, O_2. From this diagram, calculate the bond order for O_2. How does this diagram account for the paramagnetism of O_2?

Solution

We draw a molecular orbital energy diagram similar to that shown in Figure 5.12.11. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 5.12.14.

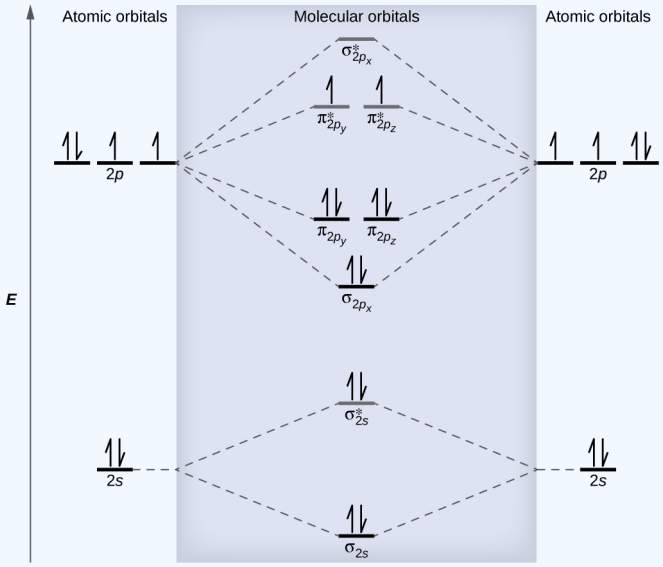


Figure 5.12.14: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

We calculate the bond order as

$$O_2 = \frac{(8-4)}{2} = 2$$

Oxygen's paramagnetism is explained by the presence of two unpaired electrons in the (π_{2py}, π_{2pz})* molecular orbitals.

Answers

Exercise 5.12.1

The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.



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5.13: Coordinate Covalent Bonding is Different

Learning Objectives

By the end of this section, you will be able to:

- Predict the oxidation state, coordination number, spin state, magnetic properties, or color of a coordinate covalent complex.

The hemoglobin in your blood, the chlorophyll in green plants, vitamin B-12, and the catalyst used in the manufacture of polyethylene all contain coordination compounds. Ions of the metals, especially the transition metals, are likely to form complexes. Many of these compounds are highly colored (Figure 5.13.1). In the remainder of this chapter, we will consider the structure and bonding of these remarkable compounds.



Figure 5.13.1: Metal ions that contain partially filled *d* subshell usually form colored complex ions; ions with empty *d* subshell (d^0) or with filled *d* subshells (d^{10}) usually form colorless complexes. This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with *M* = $Sc^{3+}(d^0)$, $Cr^{3+}(d^3)$, $Co^{2+}(d^7)$, $Ni^{2+}(d^8)$, $Cu^{2+}(d^9)$, and $Zn^{2+}(d^{10})$. (credit: Sahar Atwa)

Remember that in most main group element compounds, the valence electrons of the isolated atoms combine to form chemical bonds that satisfy the octet rule. For instance, the four valence electrons of carbon overlap with electrons from four hydrogen atoms to form CH_4. The one valence electron leaves sodium and adds to the seven valence electrons of chlorine to form the ionic formula unit NaCl (Figure 5.13.2). Transition metals do not normally bond in this fashion. They primarily form coordinate covalent bonds, a form of the Lewis acid-base interaction in which both of the electrons in the bond are contributed by a donor (Lewis base) to an electron acceptor (Lewis acid). The Lewis acid in coordination complexes, often called a **central metal** ion (or atom), is often a transition metal or inner transition metal, although main group elements can also form **coordination compounds**. The Lewis base donors, called **ligands**, can be a wide variety of chemicals—atoms, molecules, or ions. The only requirement is that they have one or more electron pairs, which can be donated to the central metal. Most often, this involves a **donor atom** with a lone pair of electrons that can form a coordinate bond to the metal.

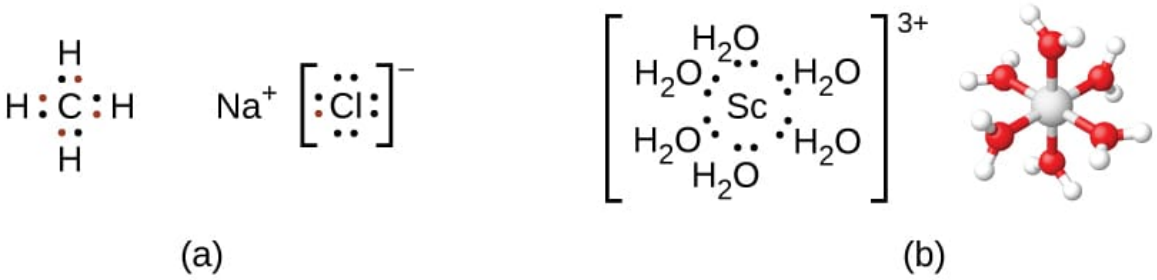


Figure 5.13.2: (a) Covalent bonds involve the sharing of electrons, and ionic bonds involve the transferring of electrons associated with each bonding atom, as indicated by the colored electrons. (b) However, coordinate covalent bonds involve electrons from a Lewis base being donated to a metal center. The lone pairs from six water molecules form bonds to the scandium ion to form an octahedral complex. (Only the donated pairs are shown.)

The coordination sphere consists of the central metal ion or atom plus its attached ligands. Brackets in a formula enclose the coordination sphere; species outside the brackets are not part of the coordination sphere. The coordination number of the central metal ion or atom is the number of donor atoms bonded to it. The coordination number for the silver ion in $[Ag(NH_3)_2]^+$ is two (Figure 5.13.3). For the copper(II) ion in $[CuCl_4]^{2-}$, the coordination number is four, whereas for the cobalt(II) ion in $[Co(H_2O)_6]^{2+}$ the coordination number is six. Each of these ligands is monodentate, from the Greek for "one toothed," meaning that they connect with the central metal through only one atom. In this case, the number of ligands and the coordination number are equal.

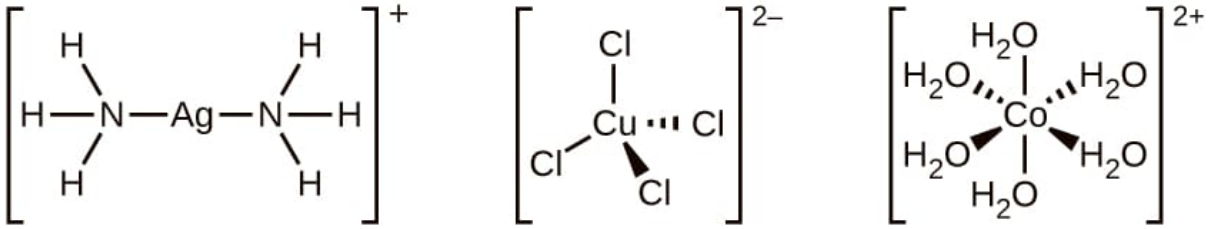


Figure 5.13.3: The complexes (a) $[Ag(NH_3)_2]^+$, (b) $[Cu(Cl)_4]^{2-}$, and (c) $[Co(H_2O)_6]^{2+}$ have coordination numbers of two, four, and six, respectively. The geometries of these complexes are the same as we have seen with VSEPR theory for main group elements: linear, tetrahedral, and octahedral.

Many other ligands coordinate to the metal in more complex fashions. **Bidentate ligands** are those in which two atoms coordinate to the metal center. For example, ethylenediamine (en, $H_2NCH_2CH_2NH_2$) contains two nitrogen atoms, each of which has a lone pair and can serve as a Lewis base (Figure 5.13.4). Both of the atoms can coordinate to a single metal center. In the complex $[Co(en)_3]^{3+}$, there are three bidentate en ligands, and the coordination number of the cobalt(III) ion is six. The most common coordination numbers are two, four, and six, but examples of all coordination numbers from 1 to 15 are known.

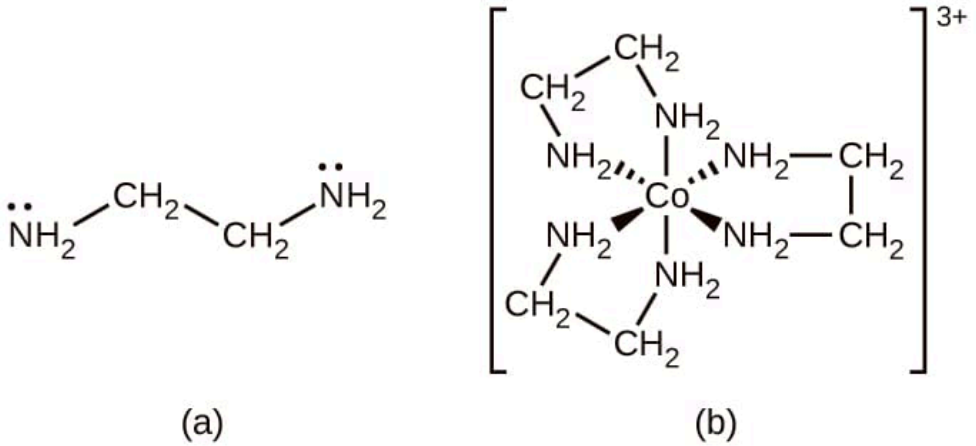


Figure 5.13.4: (a) The ethylenediamine (en) ligand contains two atoms with lone pairs that can coordinate to the metal center. (b) The cobalt(III) complex contains three of these ligands, each forming two bonds to the cobalt ion.

Any ligand that bonds to a central metal ion by more than one donor atom is a **polydentate ligand** (or "many teeth") because it can bite into the metal center with more than one bond. The term **chelate** (pronounced "KEY-late") from the Greek for "claw" is also used to describe this type of interaction. Many polydentate ligands are chelating ligands, and a complex consisting of one or more of these ligands and a central metal is a chelate. A **chelating ligand** is also known as a chelating agent. A chelating ligand holds the metal ion rather like a crab's claw would hold a marble. Figure 5.13.4: showed one example of a chelate. The heme complex in hemoglobin is another important example (Figure 5.13.5). It contains a polydentate ligand with four donor atoms that coordinate to iron.

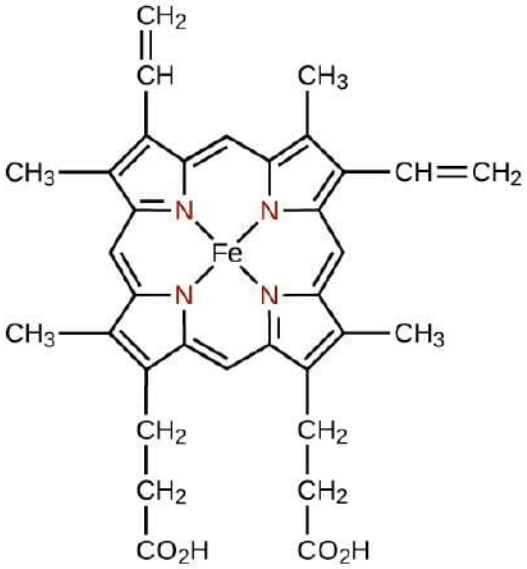


Figure 5.13.5: The single ligand heme contains four nitrogen atoms that coordinate to iron in hemoglobin to form a chelate.

Polydentate ligands are sometimes identified with prefixes that indicate the number of donor atoms in the ligand. As we have seen, ligands with one donor atom, such as NH_3, Cl^-, and H_2O, are monodentate ligands. Ligands with two donor groups are bidentate ligands. Ethylenediamine, $\cE H2NCH2CH2NH2$, and the anion of the acid glycine, $NH_2CH_2CO_2^-$ (Figure 5.13.6) are examples of bidentate ligands. Tridentate ligands, tetradentate ligands, pentadentate ligands, and hexadentate ligands contain three, four, five, and six donor atoms, respectively. The ligand in heme (Figure 5.13.5) is a tetradentate ligand.

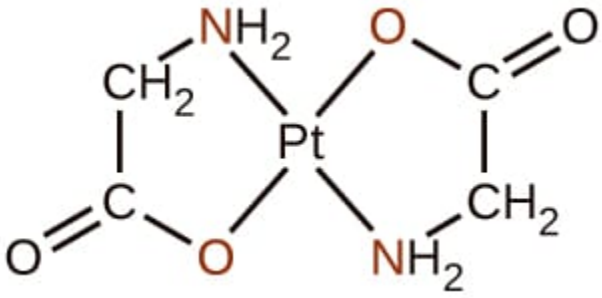


Figure 5.13.6: Each of the anionic ligands shown attaches in a bidentate fashion to platinum(II), with both a nitrogen and oxygen atom coordinating to the metal.

The Structures of Complexes

For transition metal complexes, the coordination number determines the geometry around the central metal ion. The most common structures of the complexes in coordination compounds are square planar, tetrahedral, and octahedral, corresponding to coordination numbers of four, four, and six, respectively. Coordination numbers greater than six are less common and yield a variety of structures (see Figure 5.13.7 and Table 5.13.5):

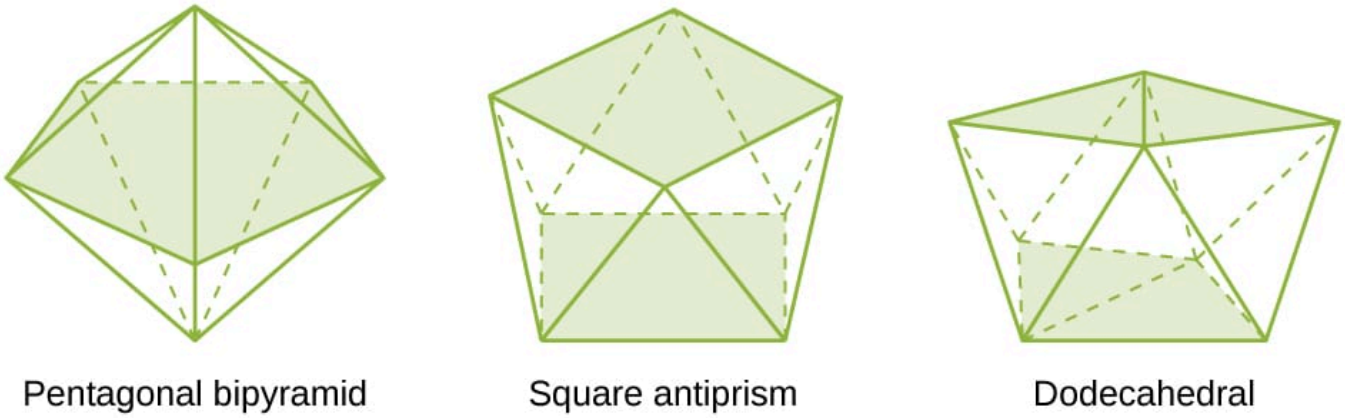


Figure 5.13.7: These are geometries of some complexes with coordination numbers of seven and eight.

Table 5.13.5: Coordination Numbers and Molecular Geometry

Coordination Number	Molecular Geometry	Example
2	linear	$[Ag(NH_3)_2]^+$
3	trigonal planar	$[Cu(CN)_3]^{2-}$
4	tetrahedral(d^0 or d^{10}), low oxidation states for M	$[Ni(CO)_4]$
4	square planar (d^8)	$[Ni(CN)_4]^{2-}$
5	trigonal bipyramidal	$[CoCl_5]^{2-}$
5	square pyramidal	$[VO(CN)_4]^{2-}$
6	octahedral	$[CoCl_6]^{3-}$
7	pentagonal bipyramid	$[ZrF_7]^{3-}$
8	square antiprism	$[ReF_8]^{2-}$
8	dodecahedron	$[Mo(CN)_8]^{4-}$
9 and above	more complicated structures	$[ReH_9]^{2-}$

Unlike main group atoms in which both the bonding and nonbonding electrons determine the molecular shape, the nonbonding *d*-electrons do not change the arrangement of the ligands. Octahedral complexes have a coordination number of six, and the six donor atoms are arranged at the corners of an octahedron around the central metal ion. Examples are shown in Figure 5.13.8. The chloride and nitrate anions in $[Co(H_2O)_6]Cl_2$ and $[Cr(en)_3](NO_3)_3$, and the potassium cations in $K_2[PtCl_6]$, are outside the brackets and are not bonded to the metal ion.

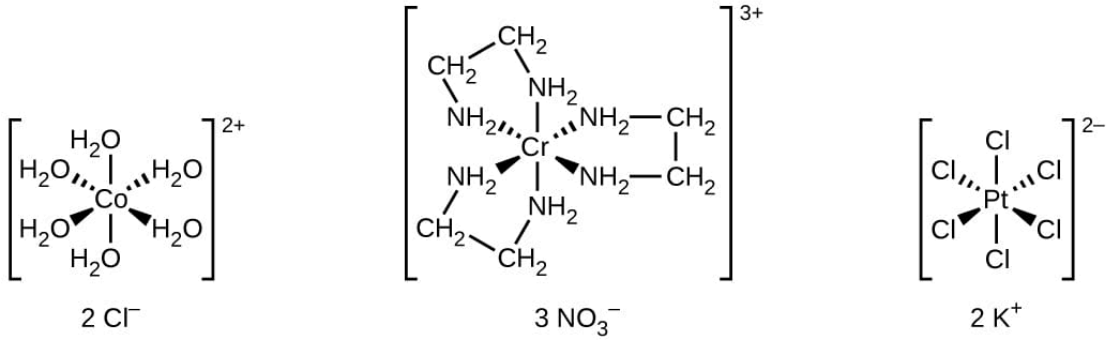


Figure 5.13.8: Many transition metal complexes adopt octahedral geometries, with six donor atoms forming bond angles of 90° about the central atom with adjacent ligands. Note that only ligands within the coordination sphere affect the geometry around the metal center.

For transition metals with a coordination number of four, two different geometries are possible: tetrahedral or square planar. Unlike main group elements, where these geometries can be predicted from VSEPR theory, a more detailed discussion of transition metal orbitals (discussed in the section on Crystal Field Theory) is required to predict which complexes will be tetrahedral and which will be square planar. In tetrahedral complexes such as $[Zn(CN)_4]^{2-}$ (Figure 5.13.9), each of the ligand pairs forms an angle of 109.5°. In square planar complexes, such as $[Pt(NH_3)_2Cl_2]$, each ligand has two other ligands at 90° angles (called the *cis* positions) and one additional ligand at an 180° angle, in the *trans* position.

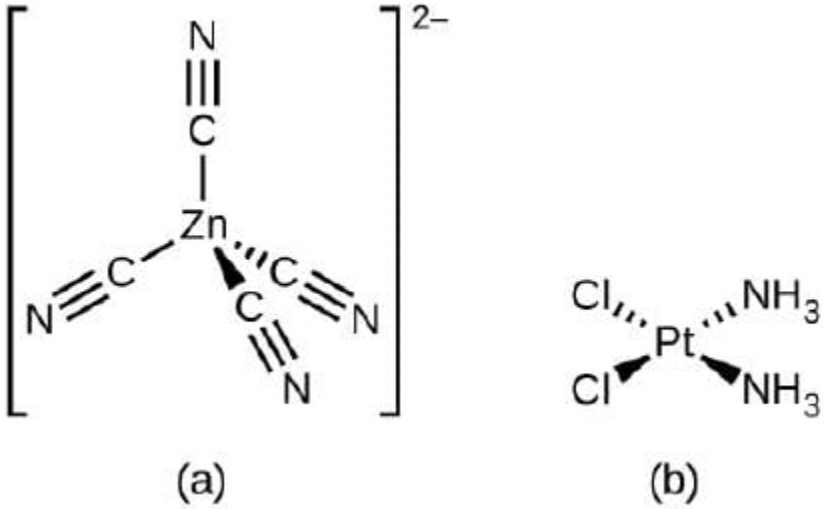


Figure 5.13.9: Transition metals with a coordination number of four can adopt a tetrahedral geometry (a) as in $K_2[Zn(CN)_4]$ or a square planar geometry (b) as shown in $[Pt(NH_3)_2Cl_2]$.

Coordination Complexes in Nature and Technology

Chlorophyll, the green pigment in plants, is a complex that contains magnesium (Figure 5.13.14). This is an example of a main group element in a coordination complex. Plants appear green because chlorophyll absorbs red and purple light; the reflected light consequently appears green. The energy resulting from the absorption of light is used in photosynthesis.

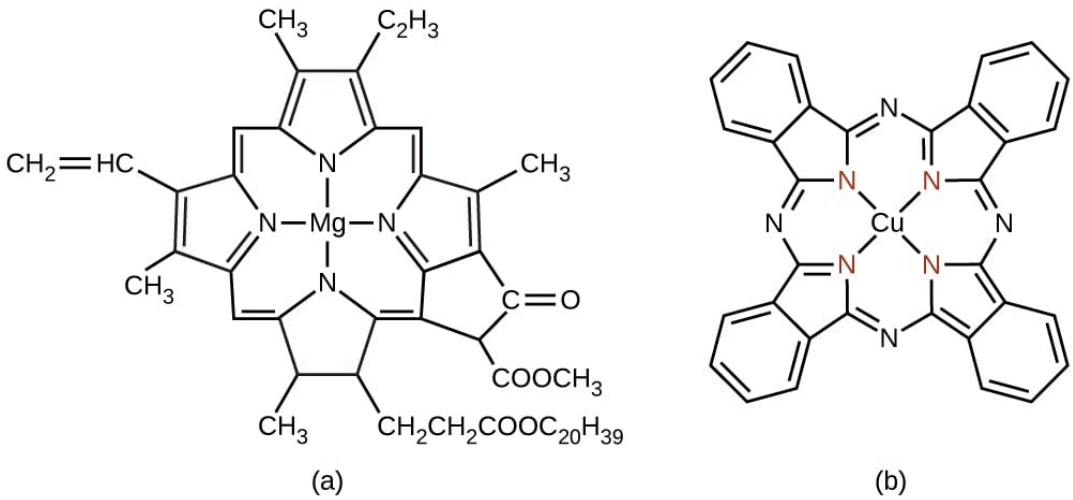


Figure 5.13.14: (a) Chlorophyll comes in several different forms, which all have the same basic structure around the magnesium center. (b) Copper phthalocyanine blue, a square planar copper complex, is present in some blue dyes.

Chemistry in Everyday Life: Transition Metal Catalysts

One of the most important applications of transition metals is as industrial catalysts. As you recall from the chapter on kinetics, a catalyst increases the rate of reaction by lowering the activation energy and is regenerated in the catalytic cycle. Over 90% of all manufactured products are made with the aid of one or more catalysts. The ability to bind ligands and change oxidation states makes transition metal catalysts well suited for catalytic applications. Vanadium oxide is used to produce 230,000,000 tons of sulfuric acid worldwide each year, which in turn is used to make everything from fertilizers to cans for food. Plastics are made with the aid of transition metal catalysts, along with detergents, fertilizers, paints, and more (see Figure 5.13.15). Very complicated pharmaceuticals are manufactured with catalysts that are selective, reacting with one specific bond out of a large number of possibilities. Catalysts allow processes to be more economical and more environmentally friendly. Developing new catalysts and better understanding of existing systems are important areas of current research.



Figure 5.13.15: (a) Detergents, (b) paints, and (c) fertilizers are all made using transition metal catalysts. (credit a: modification of work by "Mr. Brian"/Flickr; credit b: modification of work by Ewen Roberts; credit c: modification of work by "osseous"/Flickr)

Portrait of a Chemist: Deanna D'Alessandro

Dr. Deanna D'Alessandro develops new metal-containing materials that demonstrate unique electronic, optical, and magnetic properties. Her research combines the fields of fundamental inorganic and physical chemistry with materials engineering. She is working on many different projects that rely on transition metals. For example, one type of compound she is developing captures carbon dioxide waste from power plants and catalytically converts it into useful products (see Figure 5.13.16).

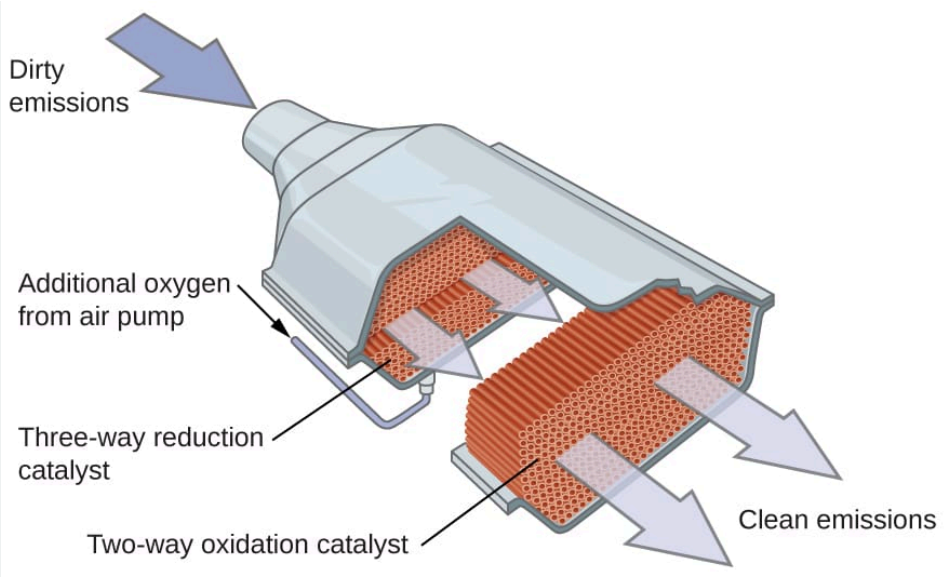


Figure 5.13.16: Catalytic converters change carbon dioxide emissions from power plants into useful products, and, like the one shown here, are also found in cars.

Another project involves the development of porous, sponge-like materials that are “photoactive.” The absorption of light causes the pores of the sponge to change size, allowing gas diffusion to be controlled. This has many potential useful applications, from powering cars with hydrogen fuel cells to making better electronics components. Although not a complex, self-darkening sunglasses are an example of a photoactive substance.

Watch this video to learn more about this research and listen to Dr. D’Alessandro (shown in Figure 5.13.17) describe what it is like being a research chemist.



Figure 5.13.17: Dr. Deanna D’Alessandro is a functional materials researcher. Her work combines the inorganic and physical chemistry fields with engineering, working with transition metals to create new systems to power cars and convert energy (credit: image courtesy of Deanna D'Alessandro).

Many other coordination complexes are also brightly colored. The square planar copper(II) complex phthalocyanine blue (from Figure 5.13.14) is one of many complexes used as pigments or dyes. This complex is used in blue ink, blue jeans, and certain blue paints.

The structure of heme (Figure 5.13.18), the iron-containing complex in hemoglobin, is very similar to that in chlorophyll. In hemoglobin, the red heme complex is bonded to a large protein molecule (globin) by the attachment of the protein to the heme

ligand. Oxygen molecules are transported by hemoglobin in the blood by being bound to the iron center. When the hemoglobin loses its oxygen, the color changes to a bluish red. Hemoglobin will only transport oxygen if the iron is Fe^{2+}; oxidation of the iron to Fe^{3+} prevents oxygen transport.

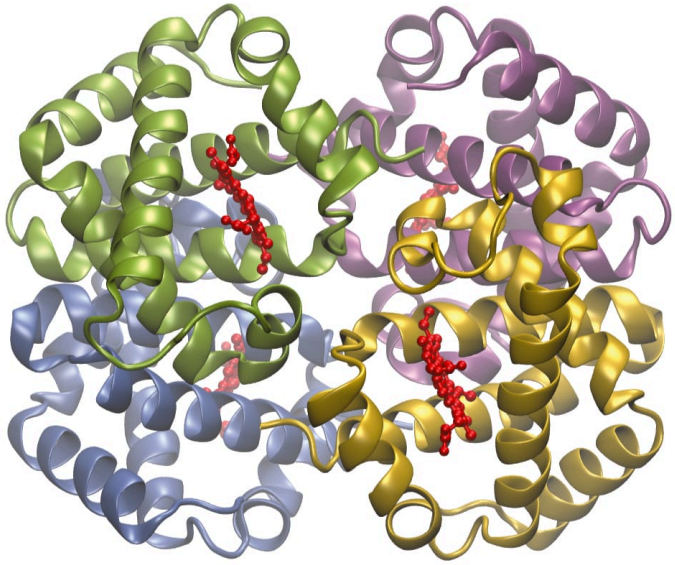


Figure 5.13.18: Hemoglobin contains four protein subunits, each of which has an iron center attached to a heme ligand (shown in red), which is coordinated to a globin protein. Each subunit is shown in a different color.

Complexing agents often are used for water softening because they tie up such ions as Ca^{2+}, Mg^{2+}, and Fe^{2+}, which make water hard. Many metal ions are also undesirable in food products because these ions can catalyze reactions that change the color of food. Coordination complexes are useful as preservatives. For example, the ligand EDTA, $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$, coordinates to metal ions through six donor atoms and prevents the metals from reacting (Figure 5.13.19). This ligand also is used to sequester metal ions in paper production, textiles, and detergents, and has pharmaceutical uses.

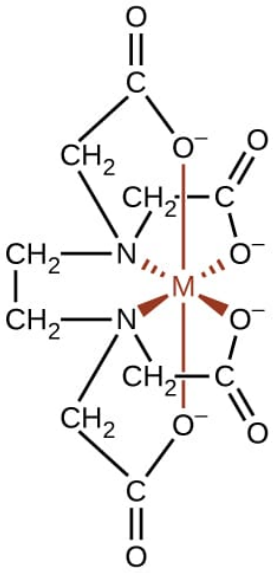


Figure 5.13.19: The ligand EDTA binds tightly to a variety of metal ions by forming hexadentate complexes.

Complexing agents that tie up metal ions are also used as drugs. British Anti-Lewisite (BAL), $HSCH_2CH(SH)CH_2OH$, is a drug developed during World War I as an antidote for the arsenic-based war gas Lewisite. BAL is now used to treat poisoning by heavy metals, such as arsenic, mercury, thallium, and chromium. The drug is a ligand and functions by making a water-soluble chelate of the metal; the kidneys eliminate this metal chelate (Figure 5.13.20). Another polydentate ligand, enterobactin, which is isolated from certain bacteria, is used to form complexes of iron and thereby to control the severe iron buildup found in patients suffering

from blood diseases such as Cooley's anemia, who require frequent transfusions. As the transfused blood breaks down, the usual metabolic processes that remove iron are overloaded, and excess iron can build up to fatal levels. Enterobactin forms a water-soluble complex with excess iron, and the body can safely eliminate this complex.

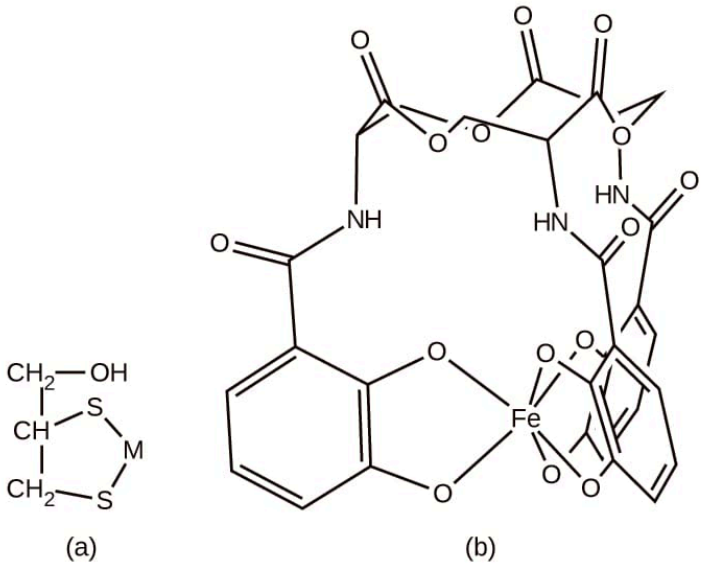


Figure 5.13.20: Coordination complexes are used as drugs. (a) British Anti-Lewisite is used to treat heavy metal poisoning by coordinating metals (M), and enterobactin (b) allows excess iron in the blood to be removed.

Ligands are also used in the electroplating industry. When metal ions are reduced to produce thin metal coatings, metals can clump together to form clusters and nanoparticles. When metal coordination complexes are used, the ligands keep the metal atoms isolated from each other. It has been found that many metals plate out as a smoother, more uniform, better-looking, and more adherent surface when plated from a bath containing the metal as a complex ion. Thus, complexes such as $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ are used extensively in the electroplating industry.

In 1965, scientists at Michigan State University discovered that there was a platinum complex that inhibited cell division in certain microorganisms. Later work showed that the complex was *cis*-diamminedichloroplatinum(II), $[Pt(NH_3)_2(Cl)_2]$, and that the *trans* isomer was not effective. The inhibition of cell division indicated that this square planar compound could be an anticancer agent. In 1978, the US Food and Drug Administration approved this compound, known as cisplatin, for use in the treatment of certain forms of cancer. Since that time, many similar platinum compounds have been developed for the treatment of cancer. In all cases, these are the *cis* isomers and never the *trans* isomers. The diammine $(NH_3)_2$ portion is retained with other groups, replacing the dichloro $[(Cl)_2]$ portion. The newer drugs include carboplatin, oxaliplatin, and satraplatin.

Footnotes

- 1National Council against Health Fraud, *NCAHF Policy Statement on Chelation Therapy*, (Peabody, MA, 2002).

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5.14: Spectroscopic and Magnetic Properties of Coordination Compounds

Learning Objectives

By the end of this section, you will be able to:

- Predict the oxidation state, coordination number, spin state, magnetic properties, or color of a coordinate covalent complex.

The behavior of coordination compounds cannot be adequately explained by the same theories used for main group element chemistry. The observed geometries of coordination complexes are not consistent with hybridized orbitals on the central metal overlapping with ligand orbitals, as would be predicted by valence bond theory. The observed colors indicate that the *d* orbitals often occur at different energy levels rather than all being degenerate, that is, of equal energy, as are the three *p* orbitals. To explain the stabilities, structures, colors, and magnetic properties of transition metal complexes, a different bonding model has been developed. Just as valence bond theory explains many aspects of bonding in main group chemistry, crystal field theory is useful in understanding and predicting the behavior of transition metal complexes.

Crystal Field Theory

To explain the observed behavior of transition metal complexes (such as how colors arise), a model involving electrostatic interactions between the electrons from the ligands and the electrons in the unhybridized *d* orbitals of the central metal atom has been developed. This electrostatic model is **crystal field theory** (CFT). It allows us to understand, interpret, and predict the colors, magnetic behavior, and some structures of coordination compounds of transition metals.

CFT focuses on the nonbonding electrons on the central metal ion in coordination complexes not on the metal-ligand bonds. Like valence bond theory, CFT tells only part of the story of the behavior of complexes. However, it tells the part that valence bond theory does not. In its pure form, CFT ignores any covalent bonding between ligands and metal ions. Both the ligand and the metal are treated as infinitesimally small point charges.

All electrons are negative, so the electrons donated from the ligands will repel the electrons of the central metal. Let us consider the behavior of the electrons in the unhybridized *d* orbitals in an octahedral complex. The five *d* orbitals consist of lobe-shaped regions and are arranged in space, as shown in Figure 5.14.1. In an octahedral complex, the six ligands coordinate along the axes.

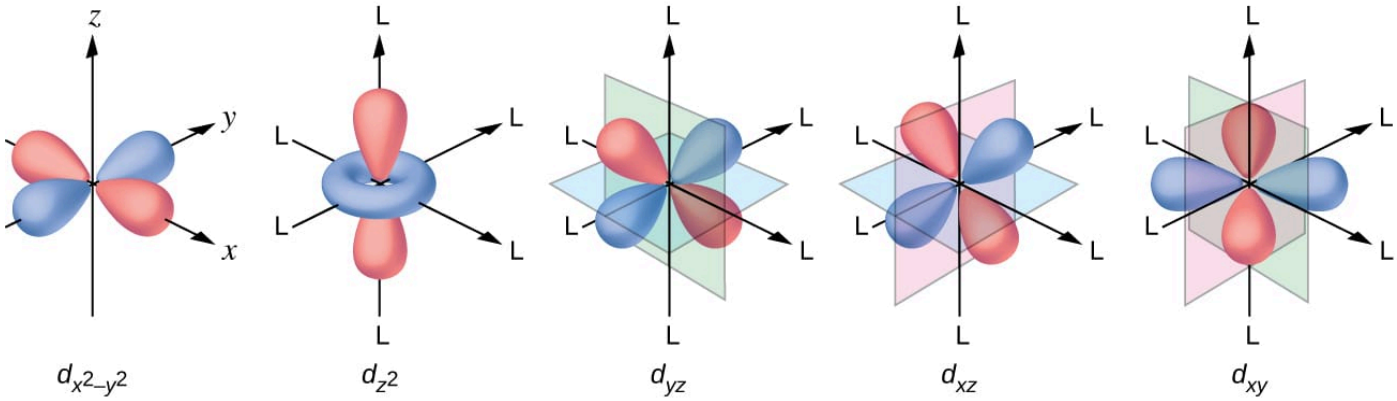


Figure 5.14.1: The directional characteristics of the five *d* orbitals are shown here. The shaded portions indicate the phase of the orbitals. The ligands (L) coordinate along the axes. For clarity, the ligands have been omitted from the orbital so that the axis labels could be shown.

In an uncomplexed metal ion in the gas phase, the electrons are distributed among the five *d* orbitals in accord with Hund's rule because the orbitals all have the same energy. However, when ligands coordinate to a metal ion, the energies of the *d* orbitals are no longer the same.

In octahedral complexes, the lobes in two of the five d orbitals, the d_{z^2} and $d_{x^2-y^2}$ orbitals, point toward the ligands (Figure 5.14.1). These two orbitals are called the e_g **orbitals** (the symbol actually refers to the symmetry of the orbitals, but we will use it as a convenient name for these two orbitals in an octahedral complex). The other three orbitals, the d_{xy}, d_{xz}, and d_{yz} orbitals, have lobes that point between the ligands and are called the t_{2g} **orbitals** (again, the symbol really refers to the symmetry of the orbitals). As six ligands approach the metal ion along the axes of the octahedron, their point charges repel the electrons in the *d* orbitals of the metal ion. However, the repulsions between the electrons in the e_g orbitals (the d_{z^2} and $d_{x^2-y^2}$ orbitals) and the ligands are greater than the repulsions between the electrons in the t_{2g} orbitals (the d_{zy}, d_{xz}, and d_{yz} orbitals) and the ligands. This is because the lobes of the eg orbitals point directly at the ligands, whereas the lobes of the t_{2g} orbitals point between them. Thus, electrons in the eg orbitals of the metal ion in an octahedral complex have higher potential energies than those of electrons in the t_{2g} orbitals. The difference in energy may be represented as shown in Figure 5.14.2.

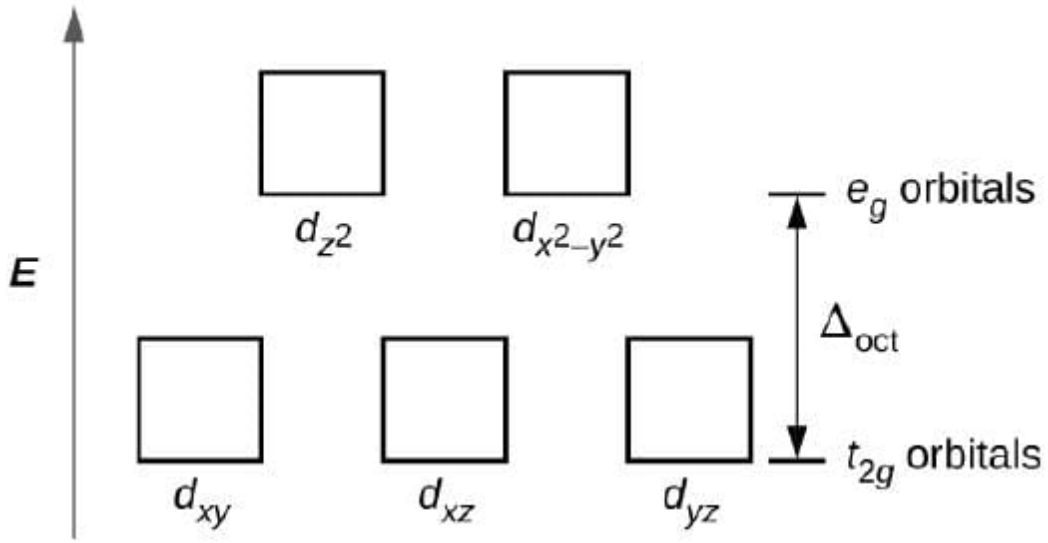


Figure 5.14.2: In octahedral complexes, the e_g orbitals are destabilized (higher in energy) compared to the t_{2g} orbitals because the ligands interact more strongly with the *d* orbitals at which they are pointed directly.

The difference in energy between the e_g and the t_{2g} orbitals is called the **crystal field splitting** and is symbolized by Δ_{oct}, where oct stands for octahedral.

The magnitude of Δ_{oct} depends on many factors, including the nature of the six ligands located around the central metal ion, the charge on the metal, and whether the metal is using 3*d*, 4*d*, or 5*d* orbitals. Different ligands produce different crystal field splittings. The increasing crystal field splitting produced by ligands is expressed in the **spectrochemical series**, a short version of which is given here:

$$\underset{\text{a few ligands of the spectrochemical series, in order of increasing field strength of the ligand}}{\xrightarrow{\quad I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^- \quad}}$$

In this series, ligands on the left cause small crystal field splittings and are **weak-field ligands**, whereas those on the right cause larger splittings and are **strong-field ligands**. Thus, the Δ_{oct} value for an octahedral complex with iodide ligands (I^-) is much smaller than the Δ_{oct} value for the same metal with cyanide ligands (CN^-).

Electrons in the *d* orbitals follow the *Aufbau* ("filling up") principle, which says that the orbitals will be filled to give the lowest total energy, just as in main group chemistry. When two electrons occupy the same orbital, the like charges repel each other. The energy needed to pair up two electrons in a single orbital is called the **pairing energy** (P). Electrons will always singly occupy each orbital in a degenerate set before pairing. P is similar in magnitude to Δ_{oct}. When electrons fill the *d* orbitals, the relative magnitudes of Δ_{oct} and P determine which orbitals will be occupied.

In $[Fe(CN)_6]^{4-}$, the strong field of six cyanide ligands produces a large Δ_{oct}. Under these conditions, the electrons require less energy to pair than they require to be excited to the e_g orbitals ($\Delta_{oct} > P$). The six 3*d* electrons of the Fe^{2+} ion pair in the three t_{2g} orbitals (Figure 5.14.3). Complexes in which the electrons are paired because of the large crystal field splitting are called **low-**

spin complexes because the number of unpaired electrons (spins) is minimized.

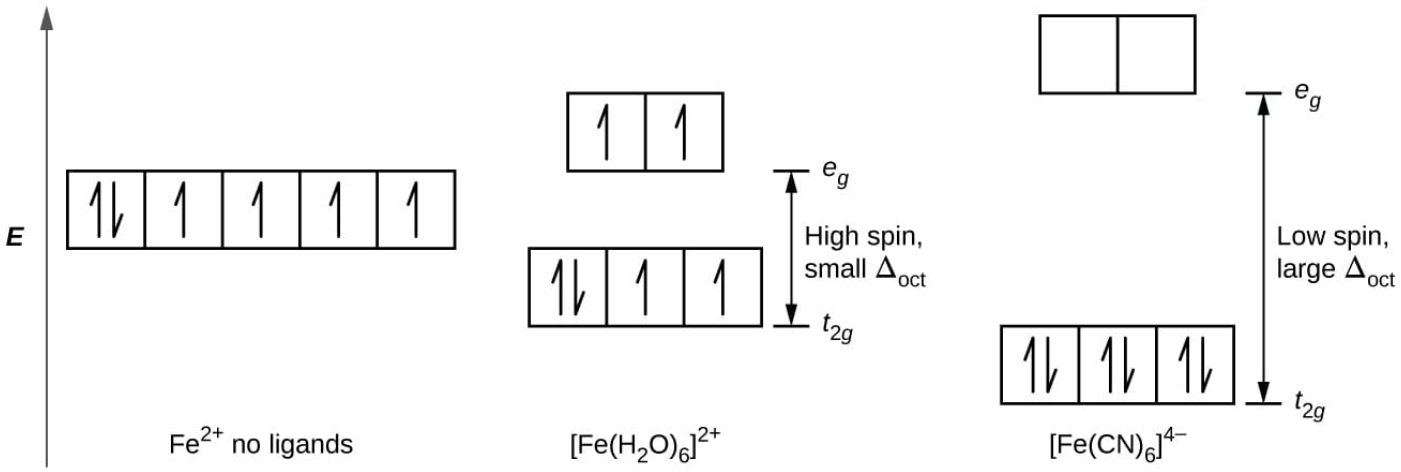


Figure 5.14.3: Iron(II) complexes have six electrons in the 5*d* orbitals. In the absence of a crystal field, the orbitals are degenerate. For coordination complexes with strong-field ligands such as $[Fe(CN)_6]^{4-}$, Δ_{oct} is greater than P, and the electrons pair in the lower energy t_{2g} orbitals before occupying the *eg* orbitals. With weak-field ligands such as H_2O, the ligand field splitting is less than the pairing energy, Δ_{oct} less than P, so the electrons occupy all *d* orbitals singly before any pairing occurs.

In $[Fe(H_2O)_6]^{2+}$, on the other hand, the weak field of the water molecules produces only a small crystal field splitting (Δ_{oct} < P). Because it requires less energy for the electrons to occupy the e_g orbitals than to pair together, there will be an electron in each of the five 3*d* orbitals before pairing occurs. For the six *d* electrons on the iron(II) center in $[Fe(H_2O)_6]^{2+}$, there will be one pair of electrons and four unpaired electrons (Figure 5.14.3). Complexes such as the $[Fe(H_2O)_6]^{2+}$ ion, in which the electrons are unpaired because the crystal field splitting is not large enough to cause them to pair, are called high-spin complexes because the number of unpaired electrons (spins) is maximized.

A similar line of reasoning shows why the $[Fe(CN)_6]^{3-}$ ion is a low-spin complex with only one unpaired electron, whereas both the $[Fe(H_2O)_6]^{3+}$ and $[FeF_6]^{3-}$ ions are high-spin complexes with five unpaired electrons.

Example 5.14.1: High- and Low-Spin Complexes

Predict the number of unpaired electrons.

a. $K_3[CrI_6]$
b. $[Cu(en)_2(H_2O)_2]Cl_2$
c. $Na_3[Co(NO_2)_6]$

Solution

The complexes are octahedral.

a. Cr^{3+} has a d^3 configuration. These electrons will all be unpaired.
b. Cu^{2+} is d^9, so there will be one unpaired electron.
c. Co^{3+} has d^6 valence electrons, so the crystal field splitting will determine how many are paired. Nitrite is a strong-field ligand, so the complex will be low spin. Six electrons will go in the t_{2g} orbitals, leaving 0 unpaired.

Exercise 5.14.1

The size of the crystal field splitting only influences the arrangement of electrons when there is a choice between pairing electrons and filling the higher-energy orbitals. For which *d*-electron configurations will there be a difference between high- and low-spin configurations in octahedral complexes?

Answer available at the end of this section.

Example 5.14.2: CFT for Other Geometries

CFT is applicable to molecules in geometries other than octahedral. In octahedral complexes, remember that the lobes of the e_g set point directly at the ligands. For tetrahedral complexes, the *d* orbitals remain in place, but now we have only four ligands located between the axes (Figure 5.14.4). None of the orbitals points directly at the tetrahedral ligands. However, the e_g set (along the Cartesian axes) overlaps with the ligands less than does the t_{2g} set. By analogy with the octahedral case, predict the energy diagram for the *d* orbitals in a tetrahedral crystal field. To avoid confusion, the octahedral e_g set becomes a tetrahedral *e* set, and the octahedral t_{2g} set becomes a t_2 set.

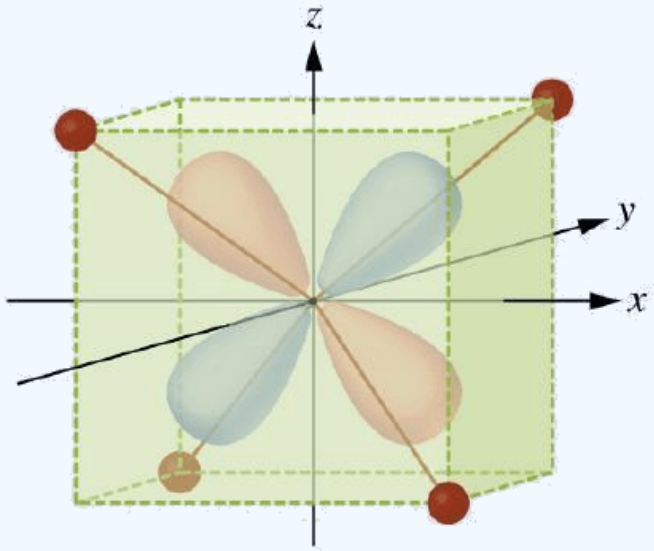
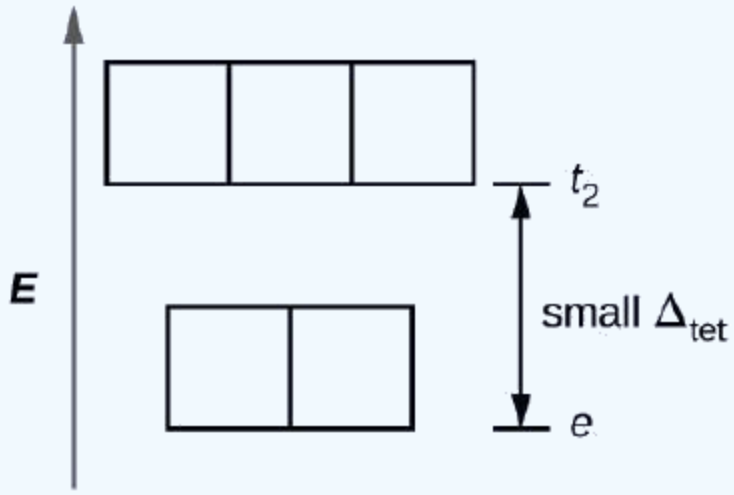


Figure 5.14.4: This diagram shows the orientation of the tetrahedral ligands with respect to the axis system for the orbitals.

Solution

Since CFT is based on electrostatic repulsion, the orbitals closer to the ligands will be destabilized and raised in energy relative to the other set of orbitals. The splitting is less than for octahedral complexes because the overlap is less, so Δ_{tet} is usually small $\left(\Delta_{\text{tet}} = \frac{4}{9}\Delta_{oct}\right)$

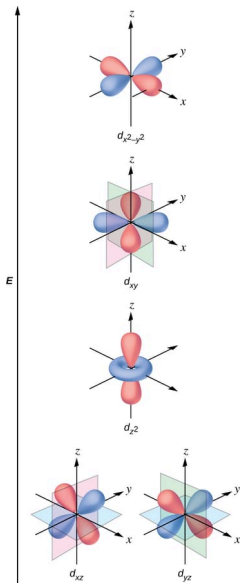


Exercise 5.14.2

Explain how many unpaired electrons a tetrahedral d^4 ion will have.

Answer available at the end of this section.

The other common geometry is square planar. It is possible to consider a square planar geometry as an octahedral structure with a pair of *trans* ligands removed. The removed ligands are assumed to be on the *z*-axis. This changes the distribution of the *d* orbitals, as orbitals on or near the *z*-axis become more stable, and those on or near the *x*- or *y*-axes become less stable. This results in the octahedral t_{2g} and the e_g sets splitting and gives a more complicated pattern, as depicted below:



Magnetic Moments of Molecules and Ions

Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as O_2 that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic. Molecules such as N_2 and ions

such as Na^+ and $[Fe(CN)_6]^{4-}$ that contain no unpaired electrons are diamagnetic. Diamagnetic substances have a slight tendency to be repelled by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion paramagnetic. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Therefore, the observed magnetic moment is used to determine the number of unpaired electrons present. The measured magnetic moment of low-spin d^6 $[Fe(CN)_6]^{4-}$ confirms that iron is diamagnetic, whereas high-spin d^6 $[Fe(H_2O)_6]^{2+}$ has four unpaired electrons with a magnetic moment that confirms this arrangement.

Colors of Transition Metal Complexes

When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the *d* orbitals often allows photons in the visible range to be absorbed.

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow. The blue color of the $[Cu(NH_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (Figure 5.14.5).

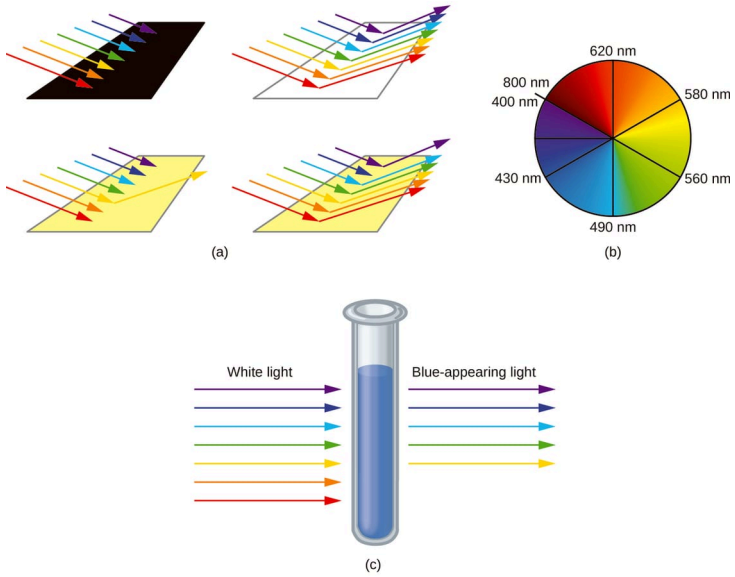


Figure 5.14.5: (a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (c) A solution of $[Cu(NH_3)_4]^{2+}$ ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue.

Example 5.14.3: Colors of Complexes

The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single *d* electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_{oct} and occurs at 499 nm. Calculate the value of Δ_{oct} in Joules and predict what color the solution will appear.

Solution

Using Planck's equation (refer to the section on electromagnetic energy), we calculate:

$$\nu = \frac{c}{\lambda} \text{ so } \frac{3.00 \times 10^8 m/s}{\frac{499nm \times 1m}{10^9 nm}} = 6.01 \times 10^{14} Hz$$

$$E = h\nu \text{ so } 6.63 \times 10^{-34} J \cdot s \times 6.01 \times 10^{14} Hz = 3.99 \times 10^{-19} \text{ Joules/ion}$$

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

Exercise 5.14.3

A complex that appears green, absorbs photons of what wavelengths?

Answer available at the end of this section.

Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in Figure 5.14.6, different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link below.



Figure 5.14.6: The partially filled *d* orbitals of the stable ions $Cr^{3+}(aq)$, $Fe^{3+}(aq)$, and $Co^{2+}(aq)$ (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)

The specific ligands coordinated to the metal center also influence the color of coordination complexes. For example, the iron(II) complex $[Fe(H_2O)_6]SO_4$ appears blue-green because the high-spin complex absorbs photons in the red wavelengths (Figure 5.14.7). In contrast, the low-spin iron(II) complex $K_4[Fe(CN)_6]$ appears pale yellow because it absorbs higher-energy violet photons.

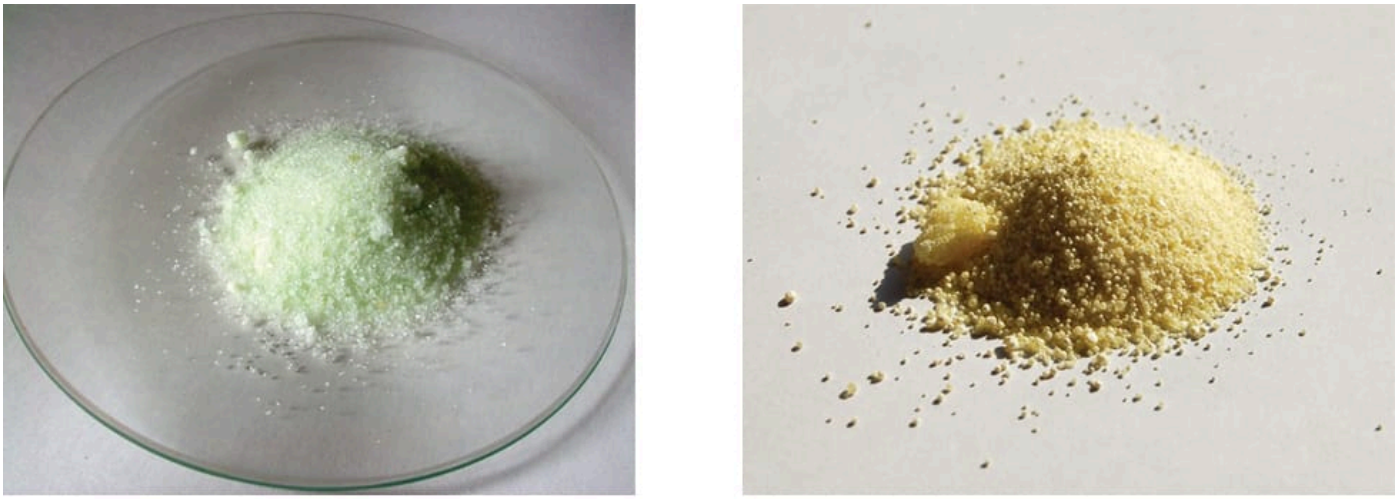


Figure 5.14.7: Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain d^6 iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum.

Link to Learning

Watch this video of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

In general, strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom (large Δ_{oct}). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

A coordination compound of the Cu^+ ion has a d^{10} configuration, and all the e_g orbitals are filled. To excite an electron to a higher level, such as the 4*p* orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing $[Cu(CN)_2]^-$, for example, is colorless. On the other hand, octahedral Cu^{2+} complexes have a vacancy in the e_g orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and Cu^{2+} complexes are almost always colored—blue, blue-green violet, or yellow (Figure 5.14.8). Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.

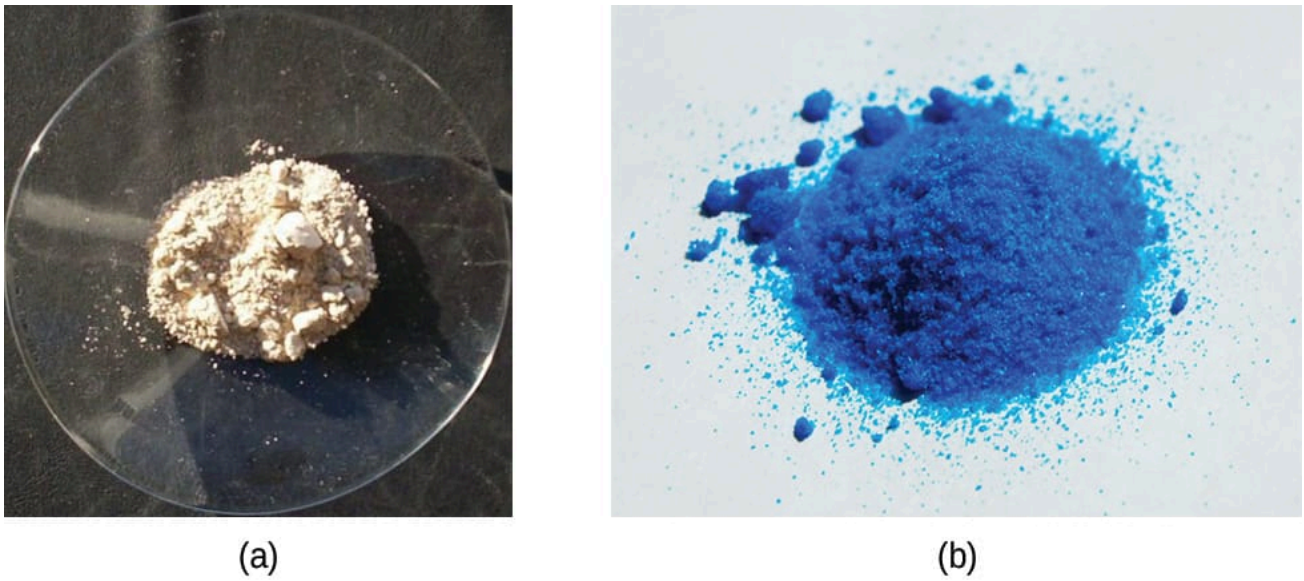


Figure 5.14.8: (a) Copper(I) complexes with d^{10} configurations such as CuI tend to be colorless, whereas (b) d^9 copper(II) complexes such as $Cu(NO_3)_2{\cdot}5H_2O$ are brightly colored.

Answers

Exercise 5.14.1

d^4, d^5, d^6, and d^7

Exercise 5.14.2

4; because Δ_{tet} is small, all tetrahedral complexes are high spin and the electrons go into the t_2 orbitals before pairing

Exercise 5.14.3

red, 620–800 nm

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6: INTERMOLECULAR INTERACTIONS DRIVE PHYSICAL PROPERTIES

6.1: Overview and Objectives

6.2: Skeletal Structures For Representing Organic Compounds

6.3: Intermolecular Forces

6.4: Phase Transitions

6.5: Phase Diagrams

6.6: The Dissolution Process

6.7: Dissolution of Electrolytes

6.8: Solubility

6.9: Colligative Properties

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6.1: Overview and Objectives

> "It has been recognized that hydrogen bonds restrain protein molecules to their native configurations, and I believe that as the methods of structural chemistry are further applied to physiological problems it will be found that the significance of the hydrogen bond for physiology is greater than that of any other single structural feature." (Linus Pauling)

Hydrogen bonding is only one of a broader class of interactions called *intermolecular forces*. These are of foremost importance in chemistry because we very rarely, if ever, work with single molecules. Instead, we work with *ensembles* - large groups - of neutral molecules and ions. In this chapter, we will take a look at intermolecular forces and how they dictate the properties of pure substances and mixtures, from phase (solid, liquid, or gas), to relative melting/boiling points, to whether certain mixtures even form in the first place.

Chapter Objectives

- Interpret skeletal structure representations of molecules by adding missing H atoms and lone pairs.
- Identify the dominant intermolecular force between molecules in a pure substance or in a mixture.
- Use the dominant intermolecular force to predict the relative boiling points and/or vapor pressures of pure substances. Describe the state of a pure substance at given temperature/pressure conditions.
- Predict the result of mixing two substances on the basis of intermolecular forces.
- Determine the freezing point or boiling point of a solution that contains a non-volatile solute.

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6.2: Skeletal Structures For Representing Organic Compounds

Learning Objectives

By the end of this section, you will have background information that helps you to be able to:

- Interpret skeletal structure representations of molecules by adding missing H atoms and lone pairs.

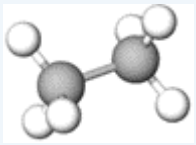
By now, we are used to using molecular formulas to tell us what elements are present in a chemical compound and in what proportion and Lewis structures to represent the arrangement of chemical bonds in those structures. However, many organic compounds - compounds that contain C, H, and other nonmetals like N, S, O, etc. - can get very large and difficult to represent using Lewis structures. Let's learn a shorthand way of representing chemical structures, called the **skeletal structure.**

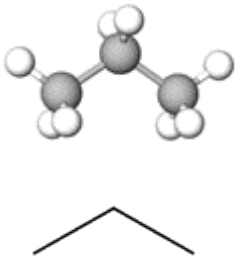
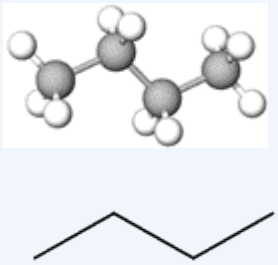
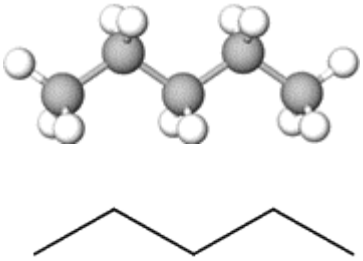
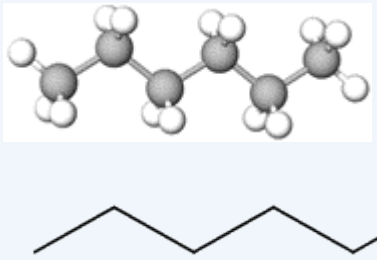
Skeletal Structures When Only C and H are Present

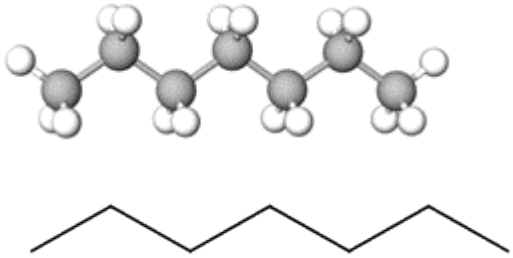
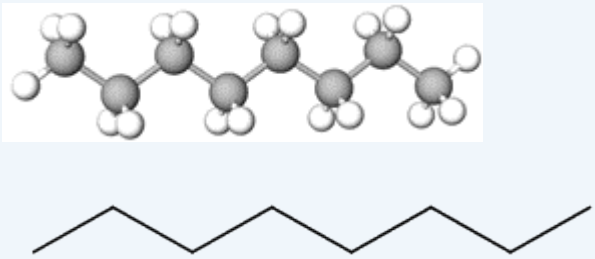
Skeletal formulas or line-angle formulas simplify the representation of organic compounds by omitting $\mathrm{C's}$ and $\mathrm{H's}$ in the formula and showing only the skeleton of the compound by C-to-C bonds as lines in a geometry that is closer to the actual geometry. Any heteroatom (non-C or non-H) and $\mathrm{H's}$ attached to the heteroatom are shown in the skeletal formula.

For example, see the skeletal structure of ethane in the table below. It consists of a line drawn to represent $\mathrm{C{-}C}$ bond. When three carbons are present (propane), the skeletal structure is an inverted V-shape, as shown in row three of Table 1. Additional lines represent additional carbons, as you see in further table rows.

Table 1: Names, molecular formulas, condensed formulas, models, and skeletal formulas of n-alkanes containing 2 to 12 $\mathrm{C's}$ in a chain. (Note: Methane has no structural formula as it has no $\mathrm{C{-}C}$ bond. The $\mathrm{C's}$ are black and $\mathrm{H's}$ are white color in the models))

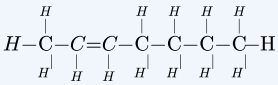
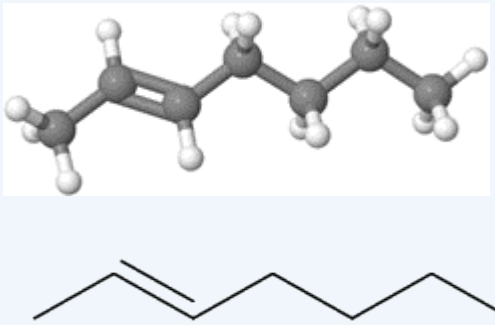
# of $\mathrm{C's}$	Name	Molecular formula	Model and Structural formula
2	Ethane	$\mathrm{C_2H_6}$	 

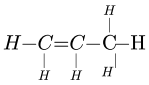
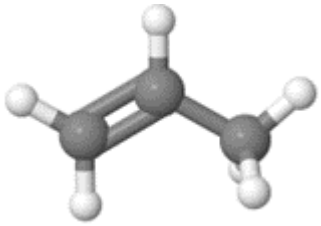
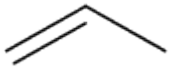
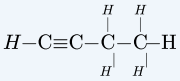
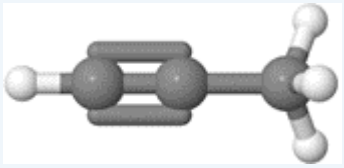
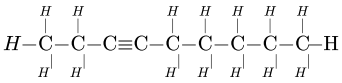
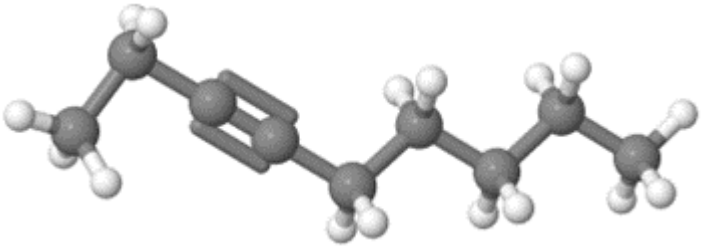
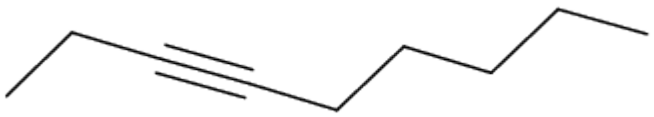
3	Propane	C_3H_8	
4	Butane	C_4H_{10}	
5	Pentane	C_5H_{12}	
6	Hexane	C_6H_{14}	

7	Heptane	C_7H_{16}	
8	Octane	C_8H_{18}	

When double or triple bonds are present, we simply add lines to the structure at the site(s) of those bond(s). See Table 2 below for a few examples. Note that for triple bonds, we draw the two involved C atoms in a straight line instead of a zig-zag. This reflects the true geometry of those carbons if you think back to the principles of VSEPR and Valence Bond theory in the last chapter.

Table 2: Names, Lewis structures, models, condensed formulas, and skeletal formulas of some alkene examples. (Note: $C's$ are black and $H's$ are white color in the models)

Name	Lewis structure	Model and Structural formula
Hept-2-ene		

Propene		 
Propyne		 
Non-3-yne		 

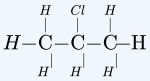
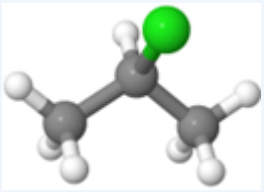
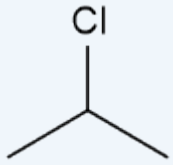
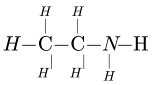
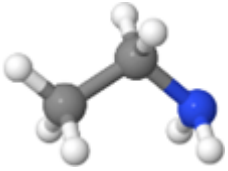
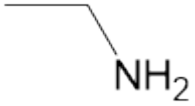
Skeletal Structures When Heteroatoms are Present

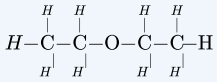
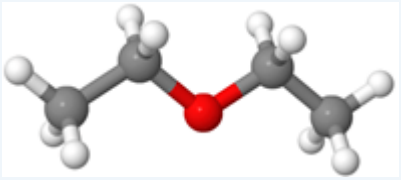
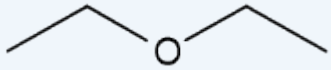
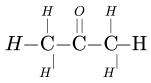
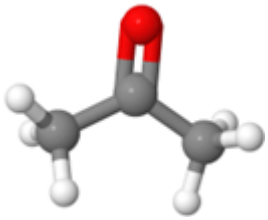
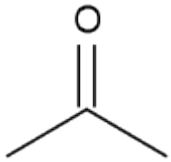
If any heteroatom, i.e., an atom other than C or H, is present in an organic compound:

- its symbol in the skeletal formula shows it and
- any H present on the heteroatom is also shown next to the heteroatom as in the condensed formulas.

The skeletal structure shows the rest of the structure as usual. Table 4 shows the names, Lewis structures, models, condensed formulas, and skeletal formulas of some example organic compounds containing heteroatoms. Their nomenclature will be explained later.

Table 4: Names, Lewis structures, models, condensed formulas, and skeletal formulas of some organic compounds containing heteroatoms. (Note: C′s are black, H′s are white, and heteroatom are in other colors in the models)

Name	Lewis structure	Model, Condensed formula, and Structural formula
2-Chloropropane		 $CH_3CHClCH_3$ 
Ethanamine		 $CH_3CH_2NH_2$ 

Diethyl ether		 $CH_3CH_2OCH_2CH_3$ 
Acetone		 CH_3COCH_3 or $CH3\overset{O}{\overset{\|\|}{C}}CH3$ 

In this class, you will not be asked to draw skeletal structures. But if you are given a skeletal structure, you will be expected to count the number of Cs and Hs in that structure.

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6.3: Intermolecular Forces

Learning Objectives

By the end of this section, you will have background information that helps you to be able to:

- Identify the dominant intermolecular force between molecules in a **pure substance** or in a mixture.
- Use the dominant intermolecular force to predict the relative boiling points and/or vapor pressures of pure substances.

Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 6.3.4: illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

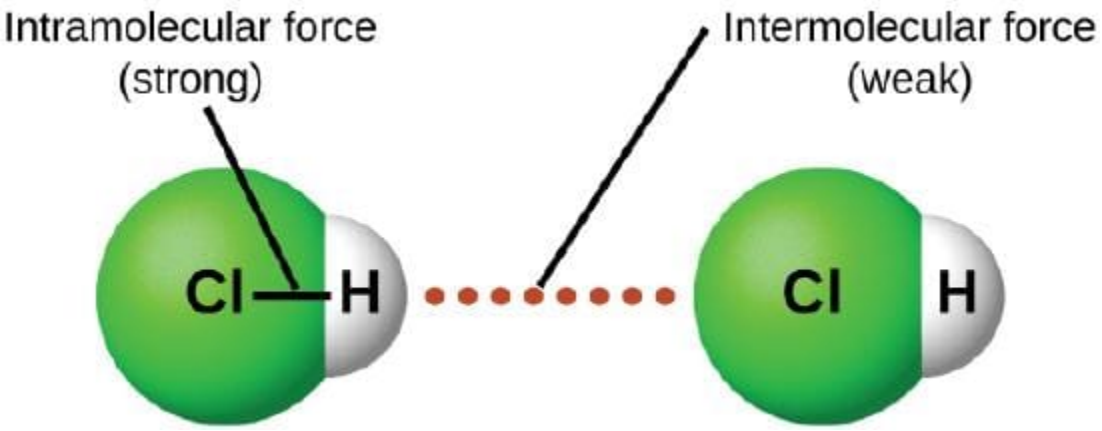


Figure 6.3.4: *Intra*molecular forces keep a molecule intact. *Inter*molecular forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as **van der Waals forces**, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 6.3.5.

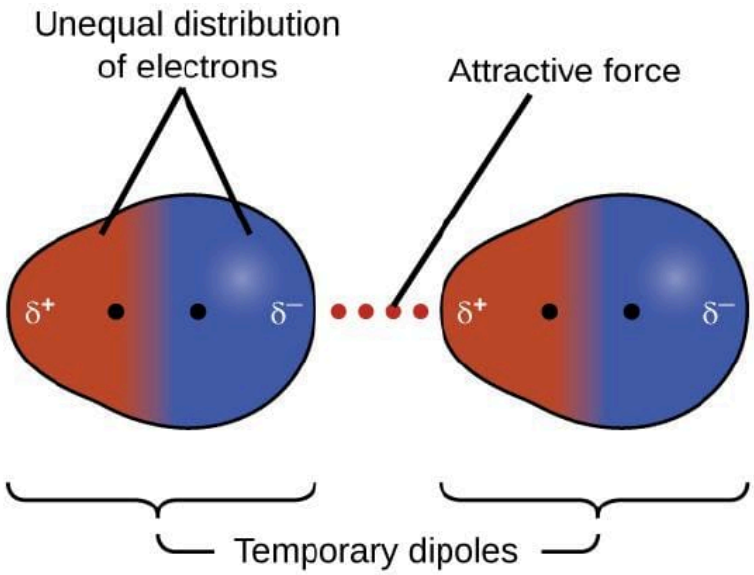


Figure 6.3.5: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed boiling points for the halogens clearly demonstrate this effect, as seen in Table 6.3.1.

Table 6.3.1: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Boiling Point
fluorine, F_2	38 g/mol	72 pm	85 K
chlorine, Cl_2	71 g/mol	99 pm	238 K
bromine, Br_2	160 g/mol	114 pm	332 K
iodine, I_2	254 g/mol	133 pm	457 K
astatine, At_2	420 g/mol	150 pm	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as polarizability. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 6.3.1: London Forces and Their Effects

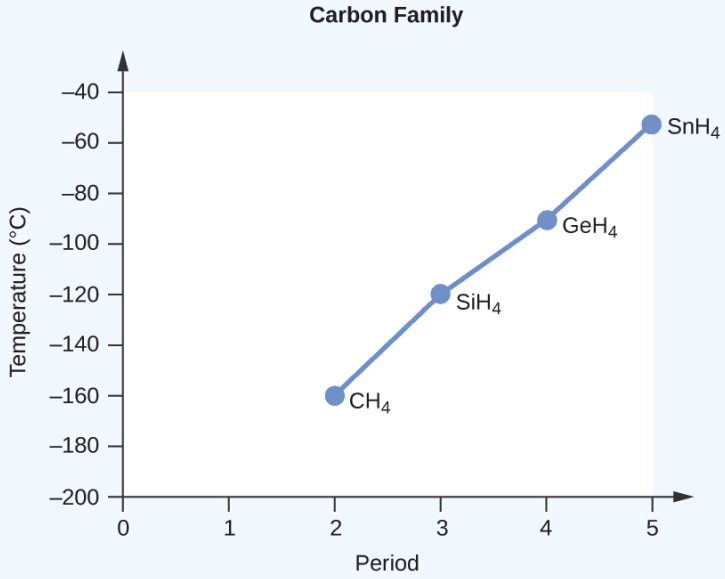
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4,

GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be $CH_4 < SiH_4 < GeH_4 < SnH_4$.

A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct:



Exercise 6.3.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer available at the end of this section.

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure 6.3.6) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

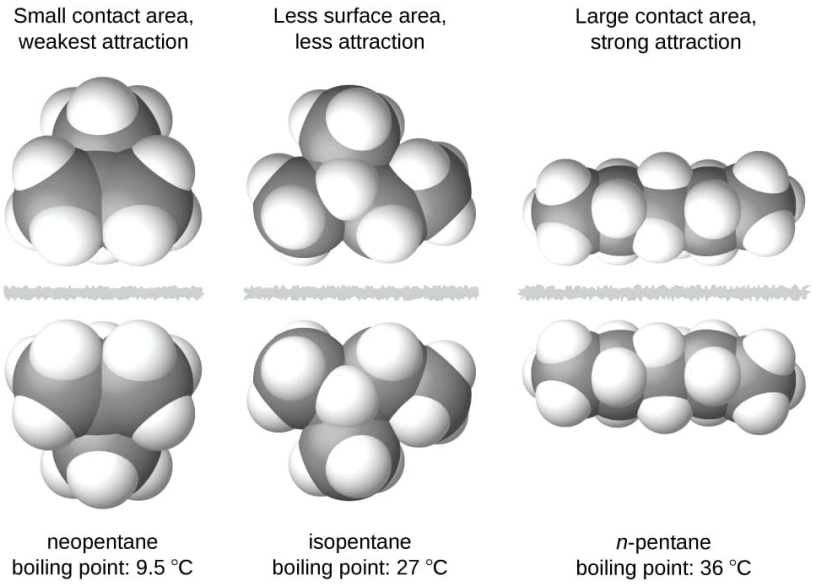


Figure 6.3.6: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

Chemistry in Everyday Life: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 6.3.7, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Later research led by Alyssa Stark at University of Akron showed that geckos can maintain their hold on hydrophobic surfaces (similar to the leaves in their habitats) equally well whether the surfaces were wet or dry. Stark's experiment used a ribbon to gently pull the geckos until they slipped, so that the researchers could determine the geckos' ability to hold various surfaces under wet and dry conditions. Further investigations may eventually lead to the development of better adhesives and other applications.

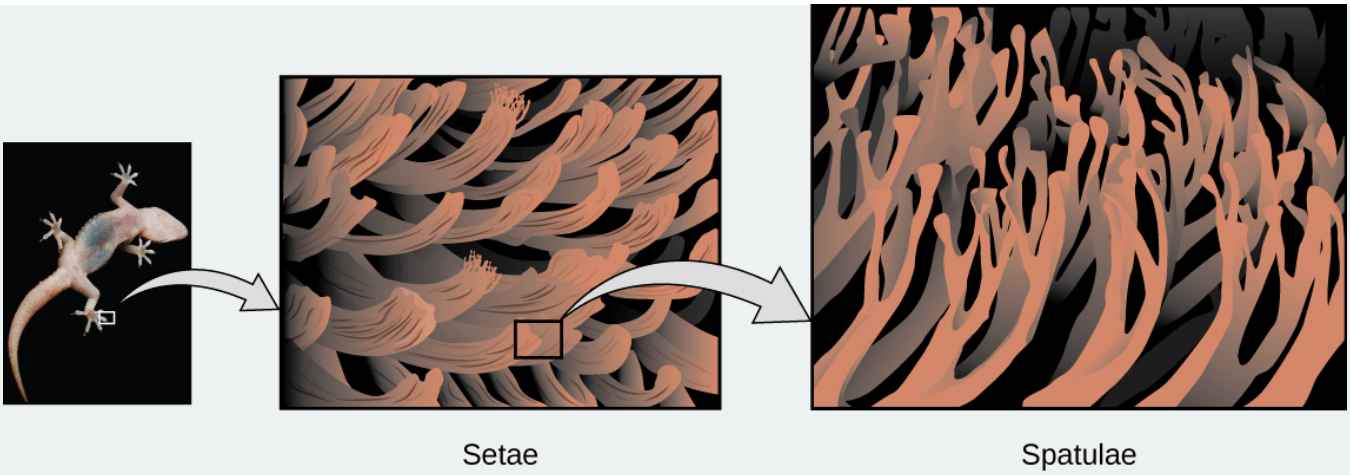


Figure 6.3.7: Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)

Link to Learning

Watch this video to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 6.3.8.

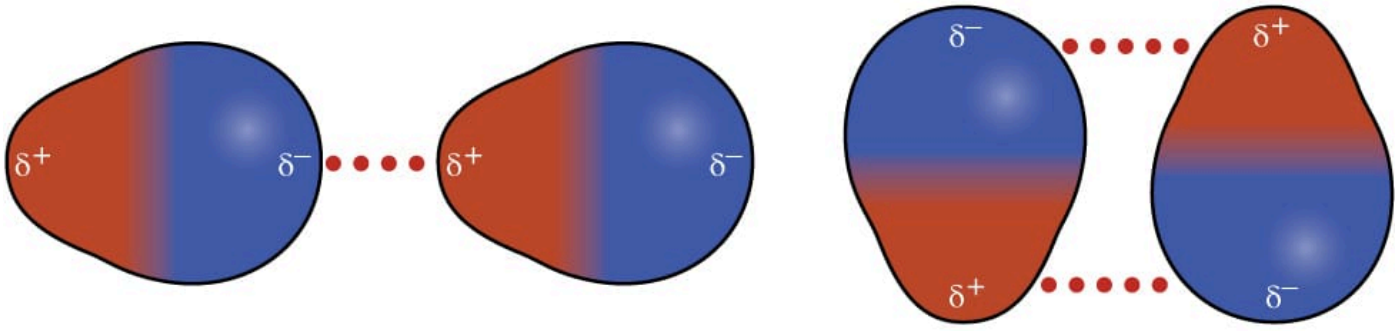


Figure 6.3.8: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to "stick together" to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of

vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

Example 6.3.2: Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

Exercise 6.3.2

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Answer available at the end of this section.

Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H_2O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called hydrogen bonding. Examples of hydrogen bonds include HF···HF, H_2O···HOH, and H_3N···HNH_2, in which the hydrogen bonds are denoted by dots. Figure 6.3.9 illustrates hydrogen bonding between water molecules.

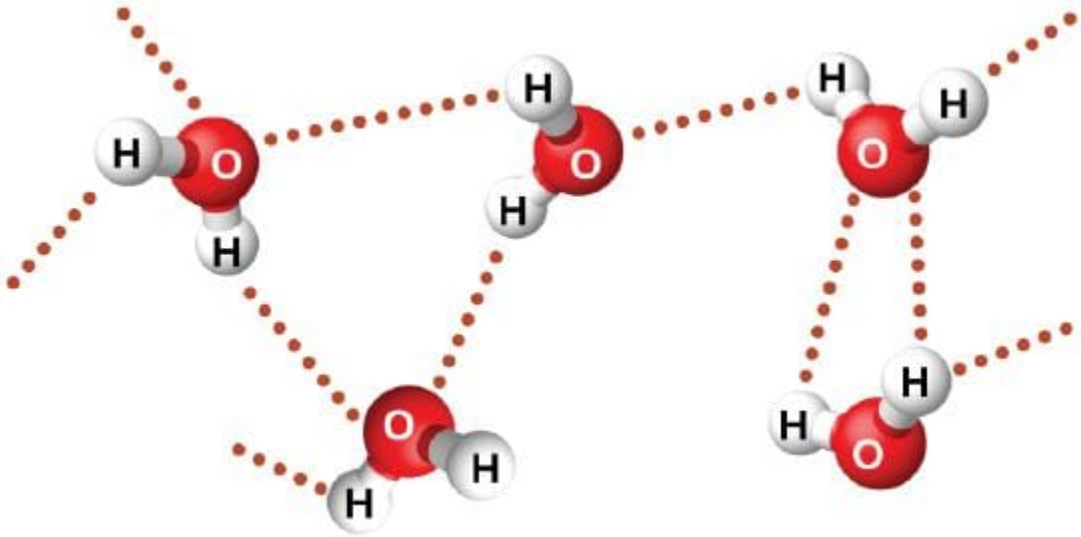


Figure 6.3.9: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3, PH_3, AsH_3, and SbH_3), group 16 hydrides (H_2O, H_2S, H_2Se, and H_2Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure 6.3.10. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.

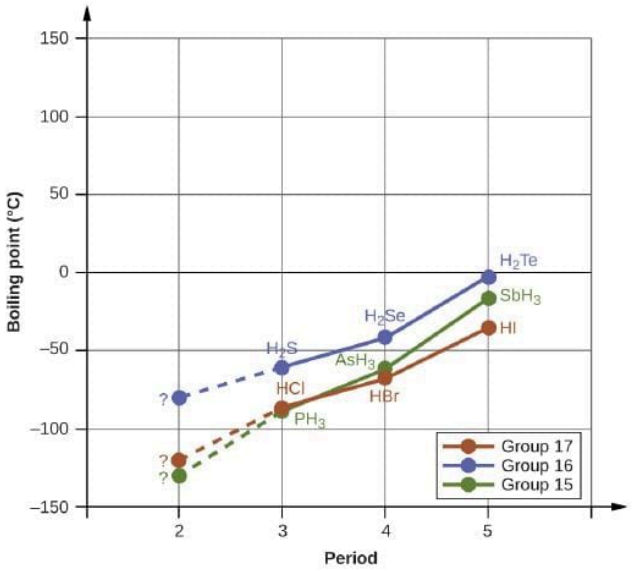


Figure 6.3.10: For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure 6.3.11. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

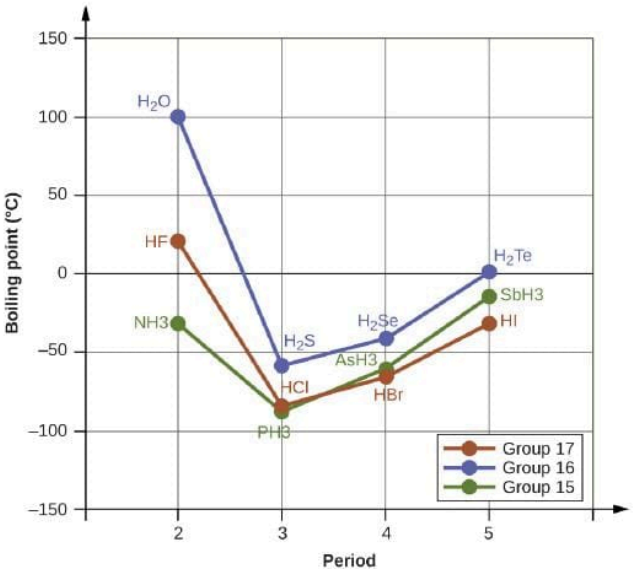


Figure 6.3.11: In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

Example 6.3.3: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are –42.1 °C, –24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an –OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is –42.1 °C, the boiling point of dimethylether is –24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 6.3.3

Ethane (CH_3CH_3) has a melting point of –183 °C and a boiling point of –89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer available at the end of this section.

How Sciences Interconnect: Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 6.3.12.

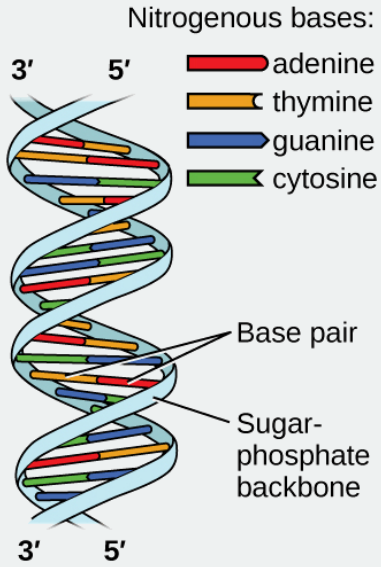


Figure 6.3.12: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs

consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 6.3.13.

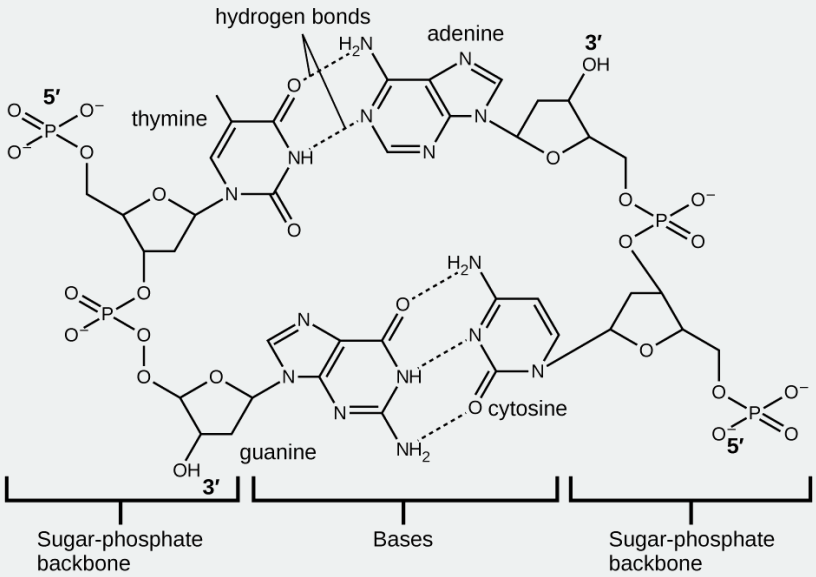


Figure 6.3.13: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Answers

Exercise 6.3.1

$C_2H_6 < C_3H_8 < C_4H_{10}$. All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore $C_2H_6 < C_3H_8 < C_4H_{10}$.

Exercise 6.3.2

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Exercise 6.3.3

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an –NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of –93 °C and a boiling point of –6 °C.

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6.4: Phase Transitions

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use the dominant intermolecular force to predict the relative boiling points and/or vapor pressures of pure substances.
- Describe the state of a pure substance at given temperature/pressure conditions.

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. The change from the gas phase to the liquid is called **condensation**. When the rate of condensation becomes equal to the rate of **vaporization**, neither the amount of the liquid nor the amount of the vapor in the container changes. The vapor in the container is then said to be *in equilibrium* with the liquid. Even though individual molecules are still transitioning back and forth between the two phases, the total amount of material in each phase remains constant. The pressure exerted by the vapor in equilibrium with a liquid in a closed container at a given temperature is called the liquid's **vapor pressure** (or equilibrium vapor pressure). The area of the surface of the liquid in contact with a vapor and the size of the vessel have no effect on the vapor pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapor pressure of a liquid by placing a sample in a closed container, like that illustrated in Figure 6.4.1, and using a manometer to measure the increase in pressure that is due to the vapor in equilibrium with the condensed phase.

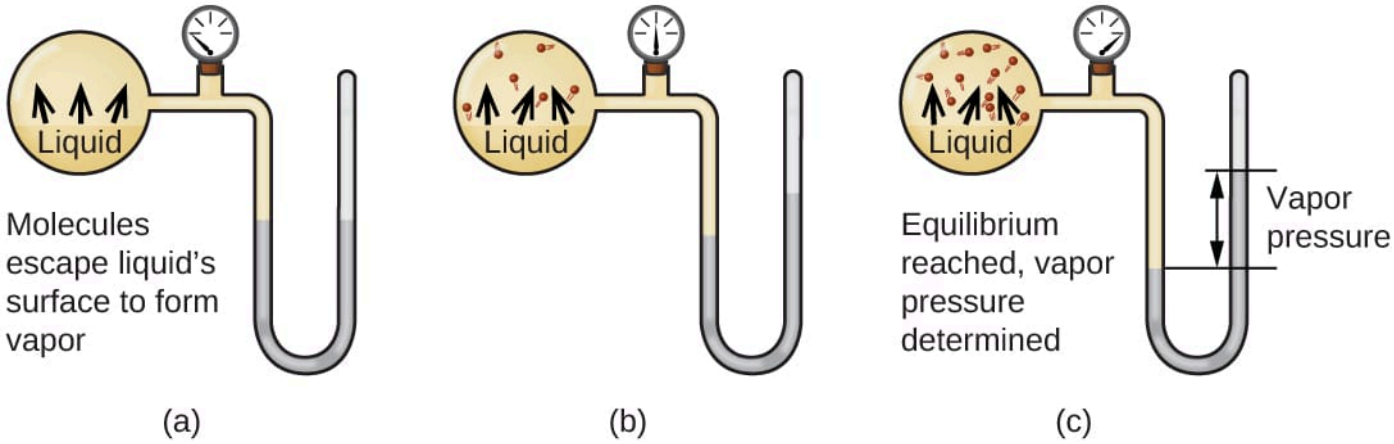
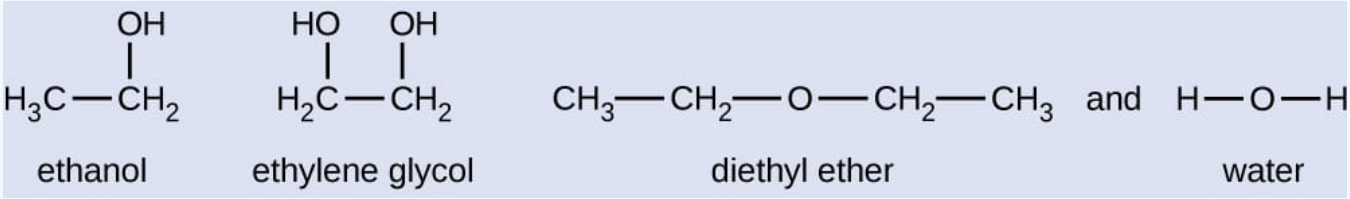


Figure 6.4.1: In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue.

The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapor pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization as well as favoring "recapture" of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapor pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapor pressures. The following example illustrates this dependence of vapor pressure on intermolecular attractive forces.

Example 6.4.1: Explaining Vapor Pressure in Terms of IMFs

Given the shown structural formulas for these four compounds, explain their relative vapor pressures in terms of types and extents of IMFs:



Solution

Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapor pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapor pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapor pressure than for either diethyl ether or ethanol. Ethylene glycol has two –OH groups, so, like water, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall IMFs are the largest of these four substances, which means its vaporization rate will be the slowest and, consequently, its vapor pressure the lowest.

Exercise 6.4.1

At 20 °C, the vapor pressures of several alcohols are given in this table. Explain these vapor pressures in terms of types and extents of IMFs for these alcohols:

Compound	methanol CH_3OH	ethanol C_2H_5OH	propanol C_3H_7OH	butanol C_4H_9OH
Vapor Pressure at 20 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

Answer available at the end of this section.

As temperature increases, the vapor pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in Figure 6.4.2. The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapor pressure.

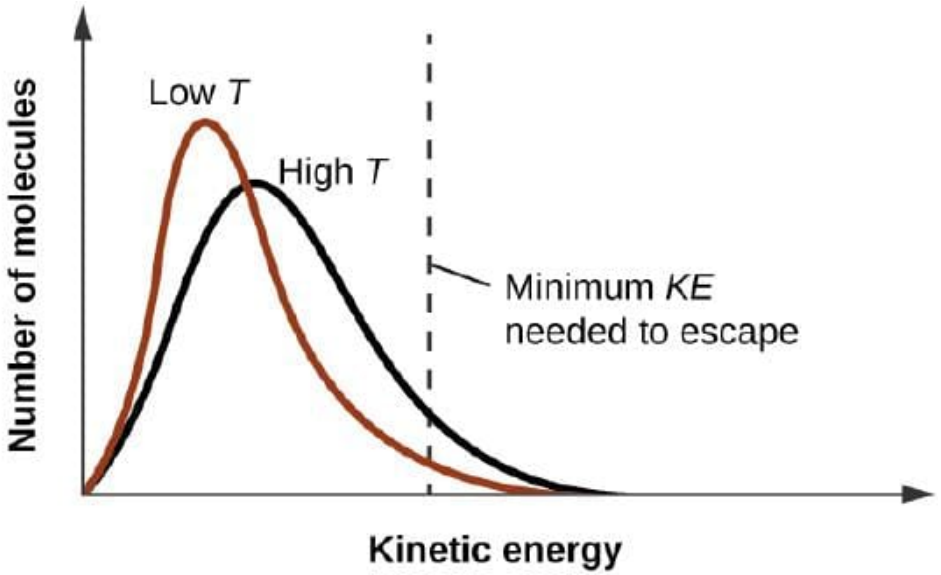


Figure 6.4.2: Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase.

Boiling Points

When the vapor pressure increases enough to equal the external atmospheric pressure, the liquid reaches its **boiling point**. The boiling point of a liquid is the temperature at which its equilibrium vapor pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers, this pressure is that due to the earth's atmosphere. The **normal boiling point** of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). Figure 6.4.3 shows the variation in vapor pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid's boiling point on surrounding pressure.

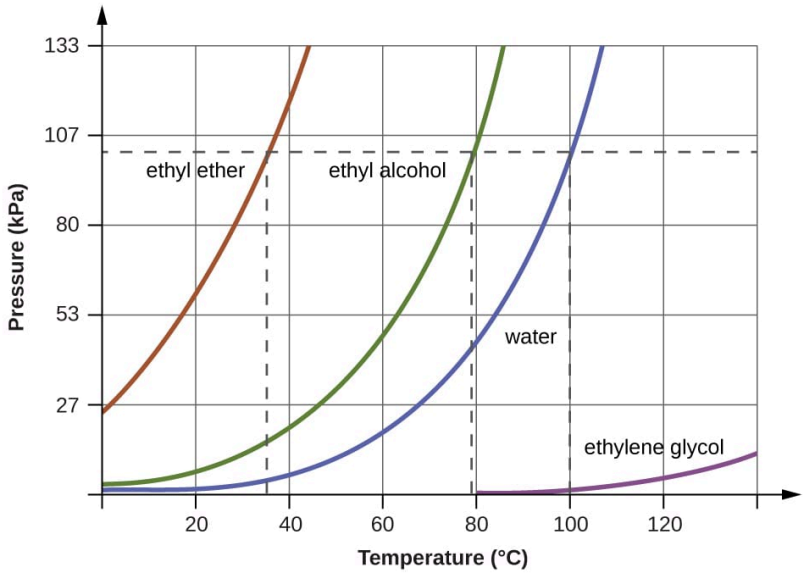


Figure 6.4.3: The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)

Melting and Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in

their fixed positions, and the solid begins the process of transitioning to the liquid state, or melting. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure 6.4.5).

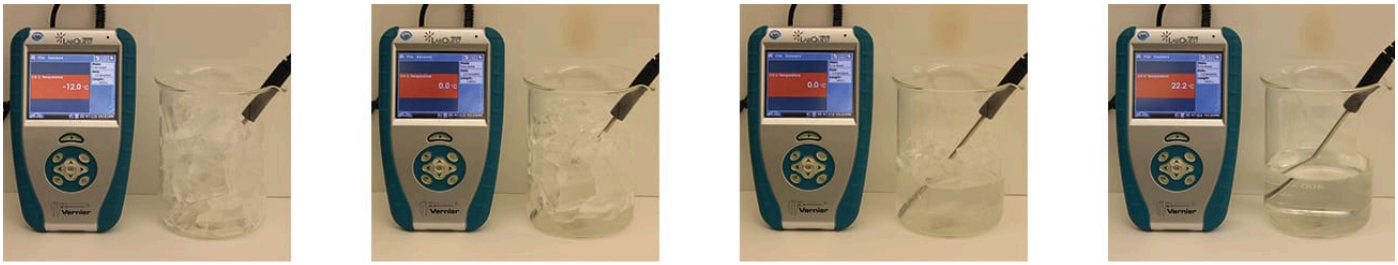


Figure 6.4.5: (a) This beaker of ice has a temperature of –12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott)

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal processes of melting and **freezing** occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the **melting point** of the solid or the freezing point of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as **sublimation**. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms (Figure 6.4.6). The reverse of sublimation is called **deposition**, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.



Figure 6.4.6: Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)

Heating and Cooling Curves

A substance that is being heated is always absorbing energy from the heat source. Sometimes, this results in an increase in the particles' kinetic energy and therefore the temperature of the substance. This is shown by the red, increasing lines in Figure 6.4.8. However, when a substance being heated or cooled reaches a temperature corresponding to one of its phase transitions, further gain or loss of heat results in diminishing or enhancing intermolecular attractions instead of increasing or decreasing molecular kinetic energies. This means that the substance's temperature remains constant, as in the blue, flat lines in Figure 6.4.8.

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behavior is observed for other phase transitions as well: For example, temperature remains constant while the change of state is in progress.

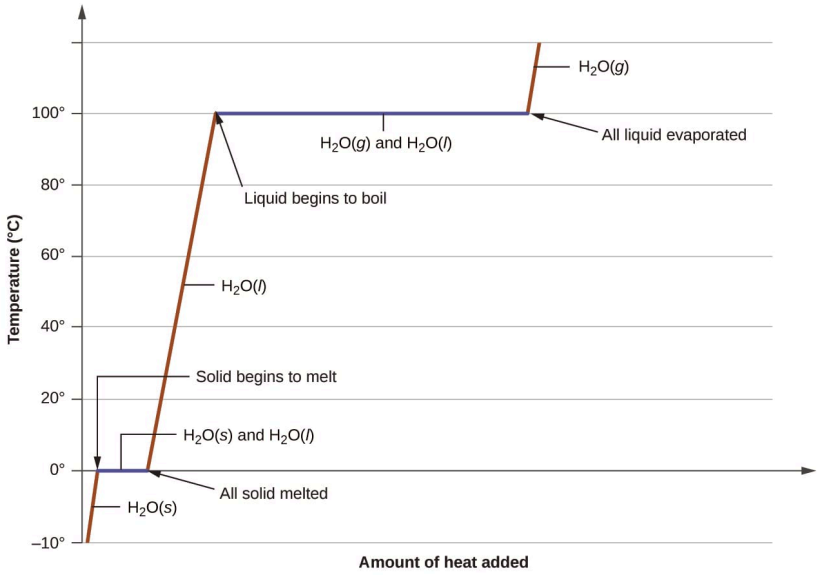


Figure 6.4.8: A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.

Answers

Exercise 6.4.1

All these compounds exhibit hydrogen bonding; these strong IMFs are difficult for the molecules to overcome, so the vapor pressures are relatively low. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapor pressures decrease as observed:

$$P_{methanol} > P_{ethanol} > P_{propanol} > P_{butanol}.$$

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6.5: Phase Diagrams

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Describe the state of a pure substance at given temperature/pressure conditions.

The variation of a liquid's equilibrium vapor pressure with temperature was described. Considering the definition of boiling point, plots of vapor pressure versus temperature represent how the boiling point of the liquid varies with pressure. Also described was the use of heating and cooling curves to determine a substance's melting (or freezing) point. Making such measurements over a wide range of pressures yields data that may be presented graphically as a phase diagram. A **phase diagram** combines plots of pressure versus temperature for the liquid-gas, solid-liquid, and solid-gas phase-transition equilibria of a substance. These diagrams indicate the physical states that exist under specific conditions of pressure and temperature, and also provide the pressure dependence of the phase-transition temperatures (melting points, sublimation points, boiling points). A typical phase diagram for a pure substance is shown in Figure 6.5.1.

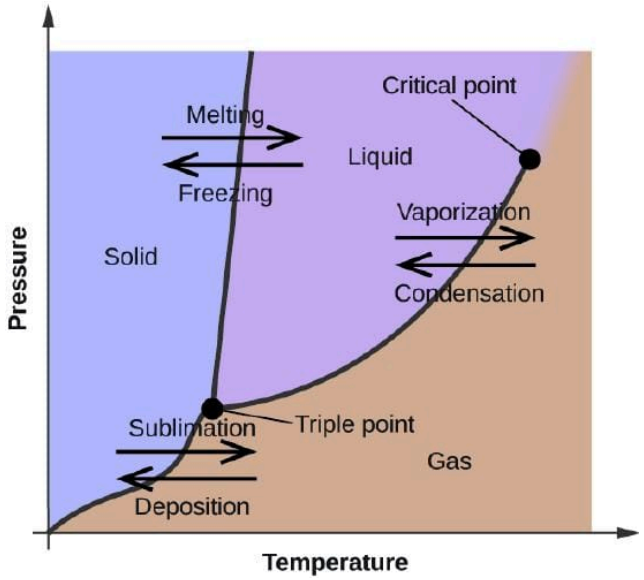


Figure 6.5.1: The physical state of a substance and its phase-transition temperatures are represented graphically in a phase diagram.

To illustrate the utility of these plots, consider the phase diagram for water shown in Figure 6.5.2.

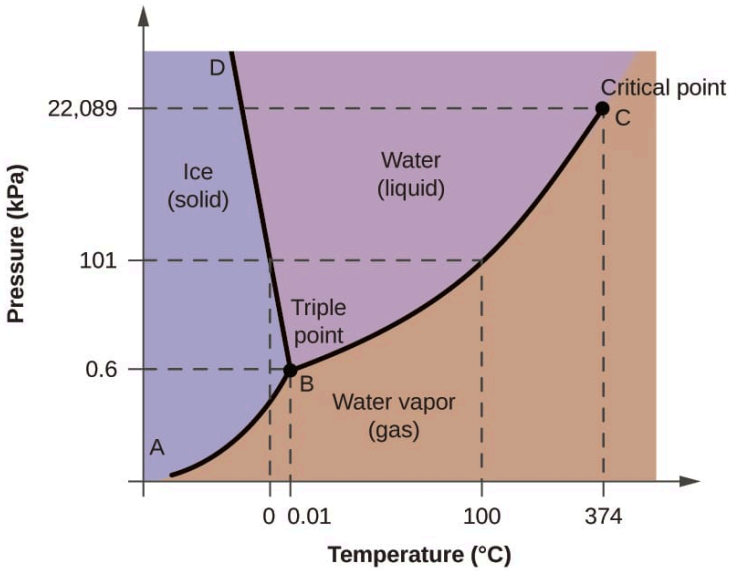


Figure 6.5.2: The pressure and temperature axes on this phase diagram of water are not drawn to constant scale in order to illustrate several important properties.

We can use the phase diagram to identify the physical state of a sample of water under specified conditions of pressure and temperature. For example, a pressure of 50 kPa and a temperature of –10 °C correspond to the region of the diagram labeled "ice." Under these conditions, water exists only as a solid (ice). A pressure of 50 kPa and a temperature of 50 °C correspond to the "water" region—here, water exists only as a liquid. At 25 kPa and 200 °C, water exists only in the gaseous state. Note that on the H_2O phase diagram, the pressure and temperature axes are not drawn to a constant scale in order to permit the illustration of several important features as described here.

The curve BC in Figure 6.5.2 is the plot of vapor pressure versus temperature as described in the previous module of this chapter. This "liquid-vapor" curve separates the liquid and gaseous regions of the phase diagram and provides the boiling point for water at any pressure. For example, at 1 atm, the boiling point is 100 °C. Notice that the liquid-vapor curve terminates at a temperature of 374 °C and a pressure of 218 atm, indicating that water cannot exist as a liquid above this temperature, regardless of the pressure. The physical properties of water under these conditions are intermediate between those of its liquid and gaseous phases. This unique state of matter is called a supercritical fluid, a topic that will be described in the next section of this module.

The solid-vapor curve, labeled AB in Figure 6.5.2, indicates the temperatures and pressures at which ice and water vapor are in equilibrium. These temperature-pressure data pairs correspond to the sublimation, or deposition, points for water. If we could zoom in on the solid-gas line in Figure 6.5.2, we would see that ice has a vapor pressure of about 0.20 kPa at –10 °C. Thus, if we place a frozen sample in a vacuum with a pressure less than 0.20 kPa, ice will sublime. This is the basis for the "freeze-drying" process often used to preserve foods, such as the ice cream shown in Figure 6.5.3.



Figure 6.5.3: Freeze-dried foods, like this ice cream, are dehydrated by sublimation at pressures below the triple point for water. (credit: "lwao"/ Flickr)

The solid-liquid curve labeled BD shows the temperatures and pressures at which ice and liquid water are in equilibrium, representing the melting/freezing points for water. Note that this curve exhibits a slight negative slope (greatly exaggerated for clarity), indicating that the melting point for water decreases slightly as pressure increases. Water is an unusual substance in this regard, as most substances exhibit an increase in melting point with increasing pressure. This behavior is partly responsible for the movement of glaciers, like the one shown in Figure 6.5.4. The bottom of a glacier experiences an immense pressure due to its weight that can melt some of the ice, forming a layer of liquid water on which the glacier may more easily slide.



Figure 6.5.4: The immense pressures beneath glaciers result in partial melting to produce a layer of water that provides lubrication to assist glacial movement. This satellite photograph shows the advancing edge of the Perito Moreno glacier in Argentina. (credit: NASA)

The point of intersection of all three curves is labeled B in Figure 6.5.2. At the pressure and temperature represented by this point, three phases of water coexist in equilibrium. This temperature-pressure data pair is called the triple point. At pressures lower than the triple point, water cannot exist as a liquid, regardless of the temperature.

Example 6.5.1: Determining the State of Water

Using the phase diagram for water given in Figure 6.5.2, determine the state of water at the following temperatures and pressures:

a. –10 °C and 50 kPa
b. 25 °C and 90 kPa
c. 50 °C and 40 kPa
d. 80 °C and 5 kPa
e. –10 °C and 0.3 kPa
f. 50 °C and 0.3 kPa

Solution

Using the phase diagram for water, we can determine that the state of water at each temperature and pressure given are as follows: (a) solid; (b) liquid; (c) liquid; (d) gas; (e) solid; (f) gas.

Exercise 6.5.1

What phase changes can water undergo as the temperature changes if the pressure is held at 0.3 kPa? If the pressure is held at 50 kPa?

Answer available at the end of this section.

Consider the phase diagram for carbon dioxide shown in Figure 6.5.5 as another example. The solid-liquid curve exhibits a positive slope, indicating that the melting point for CO_2 increases with pressure as it does for most substances (water being a notable exception as described previously). Notice that the triple point is well above 1 atm, indicating that carbon dioxide cannot exist as a liquid under ambient pressure conditions. Instead, cooling gaseous carbon dioxide at 1 atm results in its deposition into the solid state. Likewise, solid carbon dioxide does not melt at 1 atm pressure but instead sublimes to yield gaseous CO_2. Finally, notice that the critical point for carbon dioxide is observed at a relatively modest temperature and pressure in comparison to water.

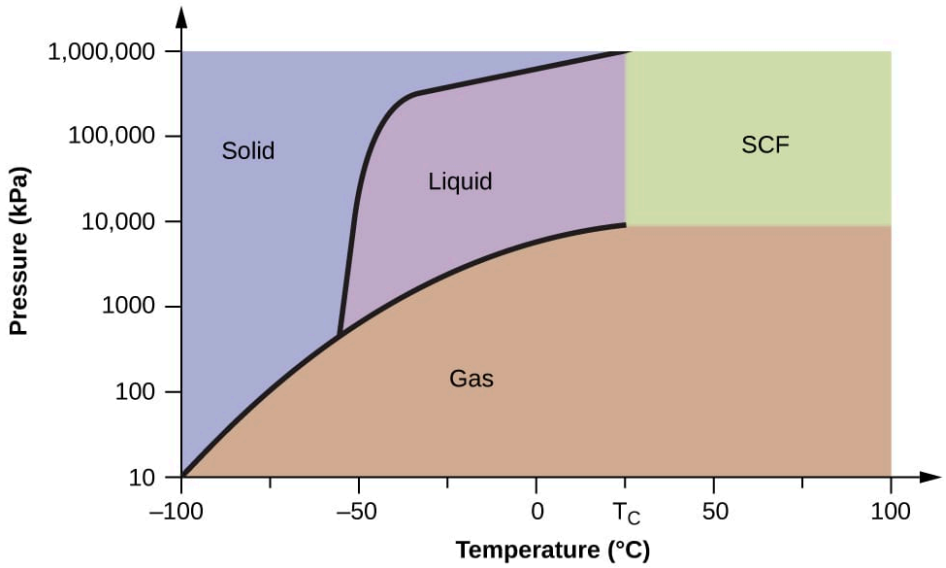


Figure 6.5.5: A phase diagram for carbon dioxide is shown. The pressure axis is plotted on a logarithmic scale to accommodate the large range of values.

Example 6.5.2: Determining the State of Carbon Dioxide

Using the phase diagram for carbon dioxide shown in Figure 6.5.5, determine the state of CO_2 at the following temperatures and pressures:

a. –30 °C and 2000 kPa
b. –90 °C and 1000 kPa
c. –60 °C and 100 kPa
d. –40 °C and 1500 kPa
e. 0 °C and 100 kPa
f. 20 °C and 100 kPa

Solution

Using the phase diagram for carbon dioxide provided, we can determine that the state of CO_2 at each temperature and pressure given are as follows: (a) liquid; (b) solid; (c) gas; (d) liquid; (e) gas; (f) gas.

Exercise 6.5.2

Identify the phase changes that carbon dioxide will undergo as its temperature is increased from –100 °C while holding its pressure constant at 1500 kPa. At 50 kPa. At what approximate temperatures do these phase changes occur?

Answer available at the end of this section.

Supercritical Fluids

If we place a sample of water in a sealed container at 25 °C, remove the air, and let the vaporization-condensation equilibrium establish itself, we are left with a mixture of liquid water and water vapor at a pressure of 0.03 atm. A distinct boundary between the more dense liquid and the less dense gas is clearly observed. As we increase the temperature, the pressure of the water vapor increases, as described by the liquid-gas curve in the phase diagram for water (Figure 6.5.2), and a two-phase equilibrium of liquid and gaseous phases remains. At a temperature of 374 °C, the vapor pressure has risen to 218 atm, and any further increase in temperature results in the disappearance of the boundary between liquid and vapor phases. All of the water in the container is now present in a single phase whose physical properties are intermediate between those of the gaseous and liquid states. This phase of matter is called a **supercritical fluid**, and the temperature and pressure above which this phase exists is the **critical point** (Figure 6.5.6). Above its critical temperature, a gas cannot be liquefied no matter how much pressure is applied. The pressure required to liquefy a gas at its critical temperature is called the critical pressure. The critical temperatures and critical pressures of some common substances are given in the following table.

Substance	Critical Temperature (°C)	Critical Pressure (kPa)
hydrogen	–240.0	1300
nitrogen	–147.2	3400
oxygen	–118.9	5000
carbon dioxide	31.1	7400
ammonia	132.4	11,300
sulfur dioxide	157.2	7800
water	374.0	22,000

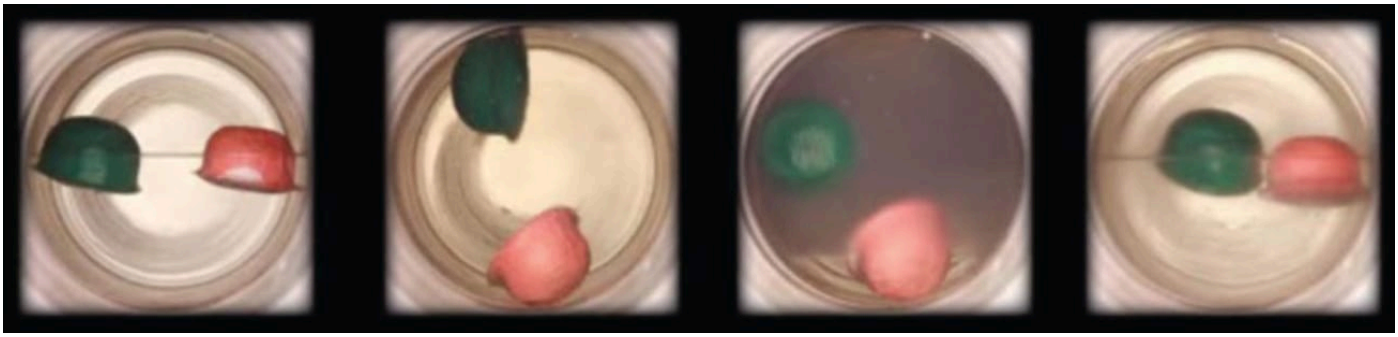


Figure 6.5.6: (a) A sealed container of liquid carbon dioxide slightly below its critical point is heated, resulting in (b) the formation of the supercritical fluid phase. Cooling the supercritical fluid lowers its temperature and pressure below the critical point, resulting in the reestablishment of separate liquid and gaseous phases (c and d). Colored floats illustrate differences in density between the liquid, gaseous, and supercritical fluid states. (credit: modification of work by "mrmrobin"/YouTube)

Link to Learning

Observe the liquid-to-supercritical fluid transition for carbon dioxide.

Like a gas, a supercritical fluid will expand and fill a container, but its density is much greater than typical gas densities, typically being close to those for liquids. Similar to liquids, these fluids are capable of dissolving nonvolatile solutes. They exhibit essentially no surface tension and very low viscosities, however, so they can more effectively penetrate very small openings in a solid mixture and remove soluble components. These properties make supercritical fluids extremely useful solvents for a wide range of applications. For example, supercritical carbon dioxide has become a very popular solvent in the food industry, being used to decaffeinate coffee, remove fats from potato chips, and extract flavor and fragrance compounds from citrus oils. It is nontoxic, relatively inexpensive, and not considered to be a pollutant. After use, the CO_2 can be easily recovered by reducing the pressure and collecting the resulting gas.

Chemistry in Everyday Life: Decaffeinating Coffee Using Supercritical CO_2

Coffee is the world's second most widely traded commodity, following only petroleum. Across the globe, people love coffee's aroma and taste. Many of us also depend on one component of coffee—caffeine—to help us get going in the morning or stay alert in the afternoon. But late in the day, coffee's stimulant effect can keep you from sleeping, so you may choose to drink decaffeinated coffee in the evening.

Since the early 1900s, many methods have been used to decaffeinate coffee. All have advantages and disadvantages, and all depend on the physical and chemical properties of caffeine. Because caffeine is a somewhat polar molecule, it dissolves well in water, a polar liquid. However, since many of the other 400-plus compounds that contribute to coffee's taste and aroma also dissolve in H_2O, hot water decaffeination processes can also remove some of these compounds, adversely affecting the smell and taste of the decaffeinated coffee. Dichloromethane (CH_2Cl_2) and ethyl acetate ($CH_3CO_2C_2H_5$) have similar polarity to caffeine, and are therefore very effective solvents for caffeine extraction, but both also remove some flavor and aroma components, and their use requires long extraction and cleanup times. Because both of these solvents are toxic, health concerns have been raised regarding the effect of residual solvent remaining in the decaffeinated coffee.

Supercritical fluid extraction using carbon dioxide is now being widely used as a more effective and environmentally friendly decaffeination method (Figure 6.5.7). At temperatures above 304.2 K and pressures above 7376 kPa, CO_2 is a supercritical fluid, with properties of both gas and liquid. Like a gas, it penetrates deep into the coffee beans; like a liquid, it effectively dissolves certain substances. Supercritical carbon dioxide extraction of steamed coffee beans removes 97–99% of the caffeine, leaving coffee's flavor and aroma compounds intact. Because CO_2 is a gas under standard conditions, its removal from the extracted coffee beans is easily accomplished, as is the recovery of the caffeine from the extract. The caffeine recovered from coffee beans via this process is a valuable product that can be used subsequently as an additive to other foods or drugs.

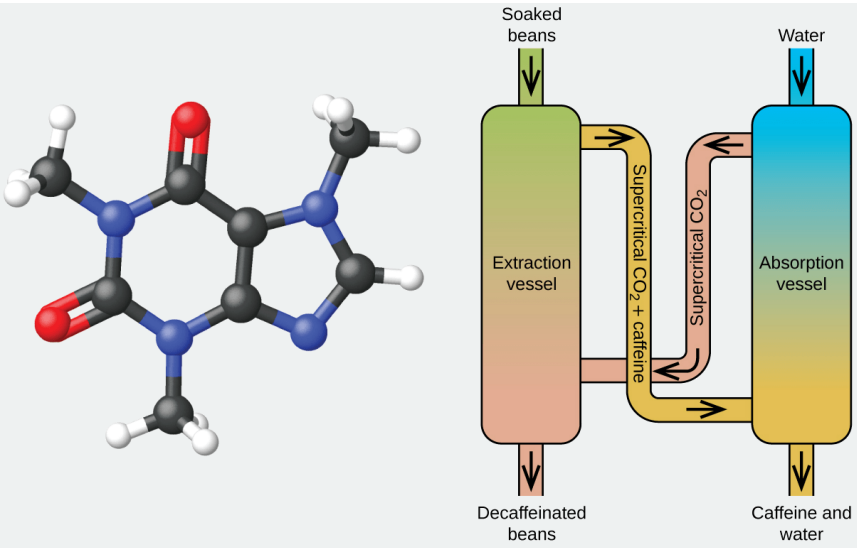


Figure 6.5.7: (a) Caffeine molecules have both polar and nonpolar regions, making it soluble in solvents of varying polarities. (b) The schematic shows a typical decaffeination process involving supercritical carbon dioxide.

Answers

Exercise 6.5.1

At 0.3 kPa: at −58 °C. At 50 kPa: at 0 °C, l ⇾ g at 78 °C

Exercise 6.5.2

at 1500 kPa: at −55 °C, at −10 °C;
at 50 kPa: at −60 °C

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6.6: The Dissolution Process

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Predict the result of mixing two substances on the basis of intermolecular forces.

An earlier chapter of this text introduced *solutions*, defined as homogeneous mixtures of two or more substances. Often, one component of a solution is present at a significantly greater concentration, in which case it is called the *solvent*. The other components of the solution present in relatively lesser concentrations are called *solutes*. Sugar is a covalent solid composed of sucrose molecules, $\mathrm{C_{12}H_{22}O_{11}}$. When this compound dissolves in water, its molecules become uniformly distributed among the molecules of water:

$$\mathrm{C_{12}H_{22}O_{11}\,(s)} \longrightarrow \mathrm{C_{12}H_{22}O_{11}\,(aq)}$$

The subscript "*aq*" in the equation signifies that the sucrose molecules are solutes and are therefore *individually dispersed* throughout the *aqueous solution* (water is the solvent). Although sucrose molecules are heavier than water molecules, they remain dispersed throughout the solution; gravity does not cause them to "settle out" over time.

Potassium dichromate, $\mathrm{K_2Cr_2O_7}$, is an ionic compound composed of colorless potassium ions, $\mathrm{K^+}$, and orange dichromate ions, $\mathrm{Cr_2O_7^{2-}}$. When a small amount of solid potassium dichromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture (Figure 6.6.1), as indicated in this equation:

$$\mathrm{K_2Cr_2O_7\,(s)} \longrightarrow \mathrm{2\,K^+\,(aq) + Cr_2O_7^{2-}\,(aq)}$$

As with the mixture of sugar and water, this mixture is also an aqueous solution. Its solutes, potassium and dichromate ions, remain individually dispersed among the solvent (water) molecules.



Figure 6.6.1: When potassium dichromate ($K_2Cr_2O_7$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott)

Link to Learning

Visit this virtual lab to view simulations of the dissolution of common covalent and ionic substances (sugar and salt) in water.

Water is used so often as a solvent that the word solution has come to imply an aqueous solution to many people. However, almost any gas, liquid, or solid can act as a solvent. Many alloys are solid solutions of one metal dissolved in another; for example, US five-cent coins contain nickel dissolved in copper. Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and several other gases. Oxygen (a gas), alcohol (a liquid), and sugar (a solid) all dissolve in water (a liquid) to form liquid solutions. Table 6.6.1 gives examples of several different solutions and the phases of the solutes and solvents.

Table 6.6.1: Different Types of Solutions

Solution	Solute	Solvent
air	$O_2(g)$	$N_2(g)$
soft drinks[1]	$CO_2(g)$	$H_2O(l)$
hydrogen in palladium	$H_2(g)$	Pd(s)
rubbing alcohol	$H_2O(l)$	$C_3H_8O(l)$ (2-propanol)
saltwater	NaCl(s)	$H_2O(l)$
brass	Zn(s)	Cu(s)

Solutions exhibit these defining traits:

- They are homogeneous; after a solution is mixed, it has the same composition at all points throughout (its composition is uniform).
- The physical state of a solution—solid, liquid, or gas—is typically the same as that of the solvent, as demonstrated by the examples in Table 6.6.1.
- The components of a solution are dispersed on a molecular scale; they consist of a mixture of separated solute particles (molecules, atoms, and/or ions) each closely surrounded by solvent species.
- The dissolved solute in a solution will not settle out or separate from the solvent.
- The composition of a solution, or the concentrations of its components, can be varied continuously (within limits determined by the *solubility* of the components, discussed in detail later in this chapter).

Intermolecular Forces and the Formation of Solutions

The formation of a solution is an example of a spontaneous process, a process that occurs under specified conditions without the requirement of energy from some external source. Sometimes a mixture is stirred to speed up the dissolution process, but this is not necessary; a homogeneous solution will form eventually.

Three types of intermolecular attractive forces are relevant to the dissolution process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in Figure 6.6.3: , the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as solvation). The relative magnitudes of the energy changes associated with these stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation. **For simplicity in this course, we will assume that solute-solvent interactions dictate whether or not a solution forms and ignore the other effects.** It's not perfect, but it's good enough for now. We will discuss solute-solvent interactions in greater detail later.

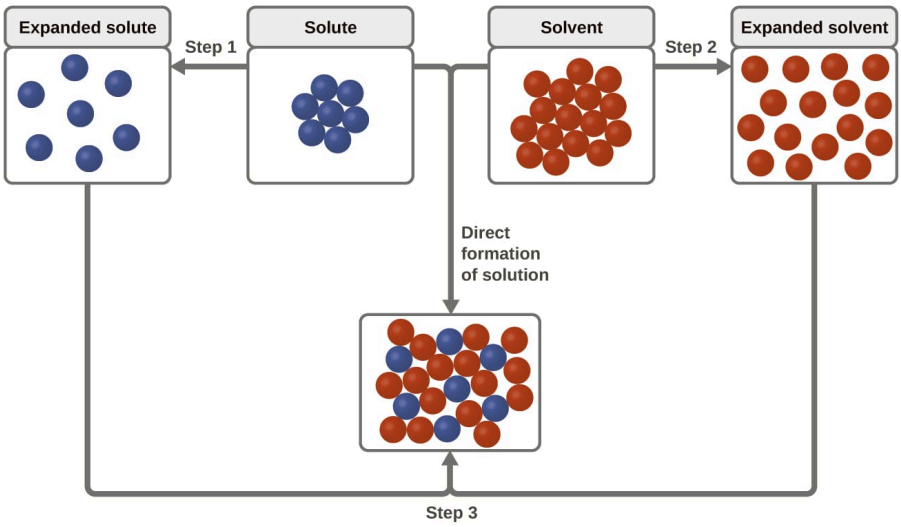


Figure 6.6.3: This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation (Step 3).

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6.7: Dissolution of Electrolytes

Learning Objectives

By the end of this section, you will be able to:

- Identify the dominant intermolecular force between molecules in a pure substance or **in a mixture.**
- Predict the result of mixing two substances on the basis of intermolecular forces.

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called electrolytes. Substances that do not yield ions when dissolved are called nonelectrolytes. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a strong electrolyte. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a weak electrolyte.

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 6.7.1).

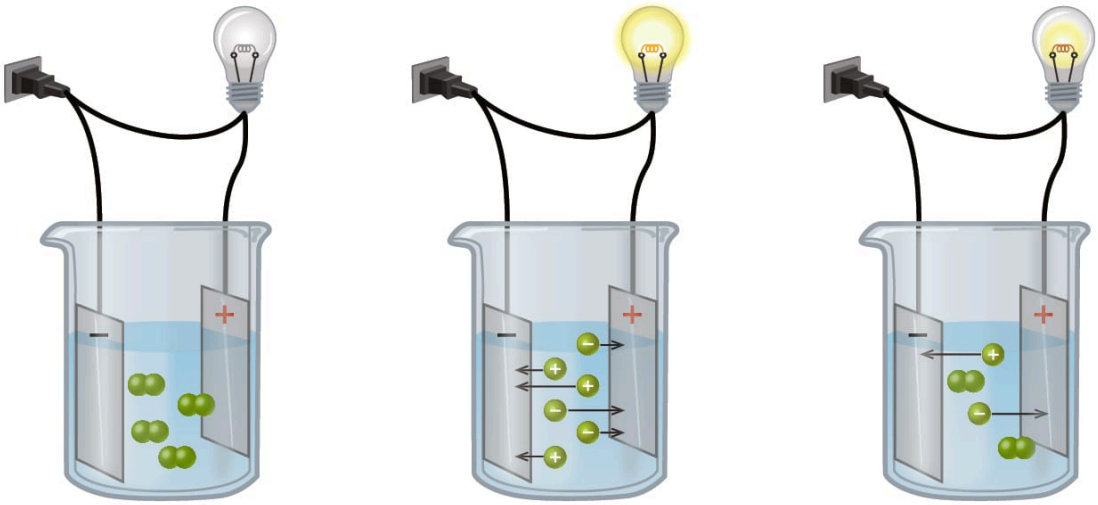


Figure 6.7.1: Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 6.7.2. The electrostatic attraction between an ion and a molecule with a dipole is called an **ion-dipole attraction.** These generally favorable attractions attractions play an important role in the dissolution of ionic compounds in water.

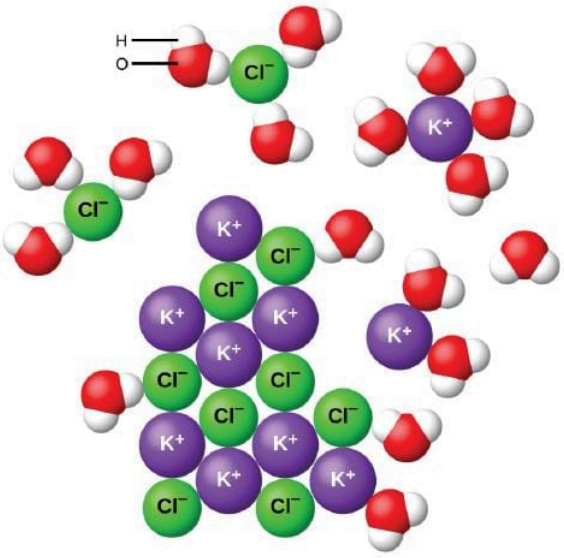


Figure 6.7.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

On the other hand, ions interact unfavorably with unpolar ions. This interaction is called an **ion-induced dipole** force. One such example occurs when sodium chloride (NaCl) added to the nonpolar solvent benzene (C_6H_6). Since benzene lacks a dipole, it does not have positive regions to attract chloride ion (Cl^-) or negative regions to attract sodium ion (Na^+). Since these interactions are not favorable, sodium chloride will not dissolve in benzene and we instead would see solid flakes in a clump at the bottom of a container filled with liquid.

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6.8: Solubility

Learning Objectives

By the end of this section, you will have the background information to be able to:

- Predict the result of mixing two substances on the basis of intermolecular forces.

Imagine adding a small amount of sugar to a glass of water, stirring until all the sugar has dissolved, and then adding a bit more. You can repeat this process until the sugar concentration of the solution reaches its natural limit, a limit determined primarily by the relative strengths of the solute-solute, solute-solvent, and solvent-solvent attractive forces discussed in the previous two modules of this chapter. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved sugar remains. The concentration of sugar in the solution at this point is known as its solubility.

The **solubility** of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is *at equilibrium*.

When a solute's concentration is equal to its solubility, the solution is said to be **saturated** with that solute. If the solute's concentration is less than its solubility, the solution is said to be **unsaturated**. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.

Link to Learning

Use this interactive simulation to prepare various saturated solutions.

Solutions may be prepared in which a solute concentration *exceeds* its solubility. Such solutions are said to be supersaturated, and they are interesting examples of *nonequilibrium* states (a detailed treatment of this important concept is provided in the text chapters on equilibrium). For example, the carbonated beverage in an open container that has not yet "gone flat" is supersaturated with carbon dioxide gas; given time, the CO_2 concentration will decrease until it reaches its solubility.

Link to Learning

Watch this impressive video showing the precipitation of sodium acetate from a supersaturated solution.

Solutions of Liquids in Liquids

Some liquids may be mixed in any proportions to yield solutions; in other words, they have infinite mutual solubility and are said to be **miscible**. Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in Figure 6.8.6) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline, mixtures of which are used as lubricating fuels for various types of outdoor power equipment (chainsaws, leaf blowers, and so on).



Figure 6.8.6: Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: “dno1967”/Wikimedia commons)

Miscible liquids are typically those with very similar polarities. Consider, for example, liquids that are polar or capable of hydrogen bonding. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom “like dissolves like.”

Two liquids that do not mix to an appreciable extent are called **immiscible**. Separate layers are formed when immiscible liquids are poured into the same container. Gasoline, oil (Figure 6.8.7), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. Relatively weak attractive forces between the polar water molecules and the nonpolar liquid molecules are not adequate to overcome much stronger hydrogen bonding between water molecules. The distinction between immiscibility and miscibility is really one of extent, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.



Figure 6.8.7: Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: “Yortw”/Flickr)

Two liquids, such as bromine and water, that are of *moderate* mutual solubility are said to be **partially miscible**. Two partially

miscible liquids usually form two layers when mixed. In the case of the bromine and water mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer (Figure 6.8.8).



Figure 6.8.8: Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers)

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6.9: Colligative Properties

Learning Objectives

By the end of this section, you will have the background information to be able to:

- Determine the freezing point or boiling point of a solution that contains a non-volatile solute.

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These **colligative properties** include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity (*M*) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction, X, of a component is the ratio of its molar amount to the total number of moles of all solution components:

$$X_A = \frac{molA}{\text{total mol of all components}}$$

By this definition, the sum of mole fractions for all solution components (the solvent and all solutes) is equal to one.

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

$$m = \frac{\text{mol solute}}{kg \text{ solvent}}$$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter module.

Example 6.9.1: Calculating Mole Fraction and Molality

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water, with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol, $C_2H_4(OH)_2$, in a solution prepared from 2.22 \times 10^{3} g of ethylene glycol and 2.00 \times 10^{3} g of water (approximately 2 L of glycol and 2 L of water)?

Solution

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the definition of mole fraction.

$$molC_2H_4(OH)_2 = 2.22 \times 10^3 g \times \frac{1 molC_2H_4(OH)_2}{62.07 gC_2H_4(OH)_2} = 35.8 molC_2H_4(OH)_2$$

$$molH_2O = 2.00 \times 10^3 g \times \frac{1 molH_2O}{18.02 gH_2O} = 111 molH_2O$$

$$X_{\text{ethylene glycol}} = \frac{35.8 molC_2H_4(OH)_2}{(35.8 + 111)\text{ mol total}} = 0.244$$

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) Derive moles of solute and mass of solvent (in kg).

First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

$$2.22 \times 10^3 gC_2H_4(OH)_2 \left(\frac{molC_2H_2(OH)_2}{62.07 g}\right) = 35.8 molC_2H_4(OH)_2$$

Then, convert the mass of the water from grams to kilograms:

$$2.00 \times 10^3 gH_2O \left(\frac{1 kg}{1000 g}\right) = 2.00 kgH_2O$$

Finally, calculate molality per its definition:

$$\begin{aligned}\text{molality} &= \frac{\text{mol solute}}{\text{kg solvent}} \\ &= \frac{35.8 molC_2H_4(OH)_2}{2 kgH_2O} \\ &= 17.9 m\end{aligned}$$

Exercise 6.9.1

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia, NH_3, dissolved in 125 g of water?

Answer available at the end of this section.

Example 6.9.2: Converting Mole Fraction and Molal Concentrations

Calculate the mole fraction of solute and solvent in a 3.0 *m* solution of sodium chloride.

Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case, both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

$$\frac{3.0 molNaCl}{1 kgH_2O}$$

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

$$1.0 kg H_2O \left(\frac{1000 g}{1 kg}\right)\left(\frac{mol H_2O}{18.02 g}\right) = 55 mol H_2O$$

and then substituting these molar amounts into the definition for mole fraction.

$$\begin{aligned} X_{H_2O} &= \frac{mol H_2O}{mol NaCl + mol H_2O} \\ &= \frac{55 mol H_2O}{3.0 mol NaCl + 55 mol H_2O} \\ &= 0.95 \\ &= \frac{mol NaCl}{mol NaCl + mol H H_2O} \\ &= \frac{3.0 mol NaCl}{3.0 mol NaCl + 55 mol H_2O} \\ &= 0.052 \end{aligned}$$

Exercise 6.9.2

The mole fraction of iodine, I_2, dissolved in dichloromethane, CH_2Cl_2, is 0.115. What is the molal concentration, *m*, of iodine in this solution?

Answer available at the end of this section.

Example 6.9.3: Molality and Molarity Conversions

Intravenous infusion of a 0.556 *M* aqueous solution of glucose (density of 1.04 g/mL) is part of some post-operative recovery therapies. What is the molal concentration of glucose in this solution?

Solution

The provided molal concentration may be explicitly written as:

$$M = 0.556 mol \text{ glucose } / 1 L \text{ solution}$$

Consider the definition of molality:

$$m = \text{ mol solute } / kg \text{ solvent}$$

The amount of glucose in 1-L of this solution is 0.556 mol, so the mass of water in this volume of solution is needed.

First, compute the mass of 1.00 L of the solution:

$$(1.0 L \text{ soln })(1.04 g/mL)(1000 mL/1 L)(1 kg/1000 g) = 1.04 kg \text{ soln}$$

This is the mass of both the water and its solute, glucose, and so the mass of glucose must be subtracted. Compute the mass of glucose from its molar amount:

$$(0.556 mol \text{ glucose })(180.2 g/1 mol) = 100.2 g \text{ or } 0.1002 kg$$

Subtracting the mass of glucose yields the mass of water in the solution:

$$1.04 kg \text{ solution } - 0.1002 kg \text{ glucose } = 0.94 kg \text{ water}$$

Finally, the molality of glucose in this solution is computed as:

$$m = \frac{0.556 \text{ mol glucose}}{0.94 \text{ kg water}} = 0.59\ m$$

Exercise 6.9.3

Nitric acid, $\mathrm{HNO_3\,(aq)}$, is commercially available as a 33.7 m aqueous solution (density = 1.35 g/mL). What is the molarity of this solution?

Answer available at the end of this section.

Boiling Point Elevation

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapor pressure is equal to ambient atmospheric pressure. Since the vapor pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Vapor pressure increases with temperature, and so a solution will require a higher temperature than will pure solvent to achieve any given vapor pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent, ΔT_b, is called **boiling point elevation** and is directly proportional to the molal concentration of solute species:

$$\Delta T_b = K_b m$$

where K_b is the boiling point elevation constant, or the *ebullioscopic constant* and m is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of K_b for several solvents are listed in Table 6.9.1.

Table 6.9.1: Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents

Solvent	Boiling Point (°C at 1 atm)	K_b (°Cm^{-1})	Freezing Point (°C at 1 atm)	K_f (°Cm^{-1})
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	−63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

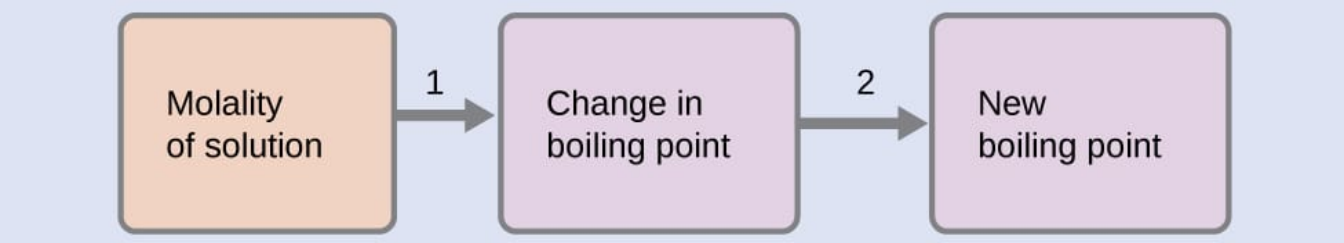
The extent to which the vapor pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1 *m* aqueous solution of sucrose (342 g/mol) and a 1 *m* aqueous solution of ethylene glycol (62 g/mol) will exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

Example 6.9.5: Calculating the Boiling Point of a Solution

Assuming ideal solution behavior, what is the boiling point of a 0.33 *m* solution of a nonvolatile solute in benzene?

Solution

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.



Step 1: Calculate the change in boiling point.

$$\Delta T_b = K_b m = 2.53^\circ C m^{-1} \times 0.33 m = 0.83^\circ C$$

Step 2: Add the boiling point elevation to the pure solvent's boiling point.

$$\text{Boiling temperature } = 80.1^\circ C + 0.83^\circ C = 80.9^\circ C$$

Exercise 6.9.1

Assuming ideal solution behavior, what is the boiling point of the antifreeze described in Example 6.9.1?

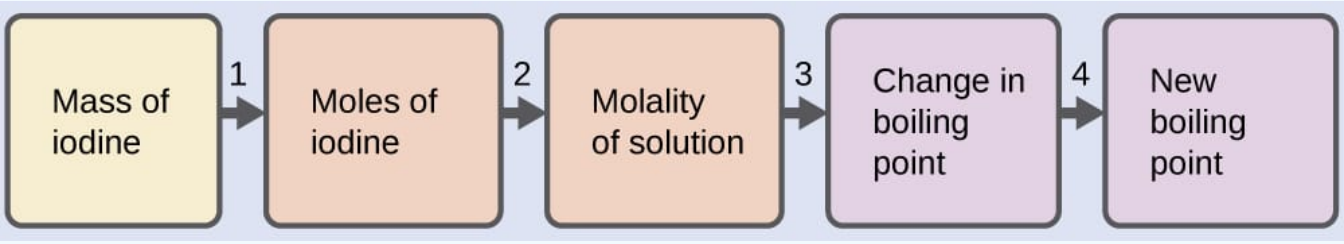
Answer available at the end of this section.

Example 6.9.6: The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine, I_2, in 800.0 g of chloroform, $CHCl_3$, assuming that the iodine is nonvolatile and that the solution is ideal.

Solution

A four-step approach to solving this problem is outlined below.



Step 1. *Convert from grams to moles of I_2 using the molar mass of I_2 in the unit conversion factor.*

Result: 0.363 mol

Step 2. *Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms.*

Result: 0.454 *m*

Step 3. *Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes.*

Result: 1.65 °C

Step 4. *Determine the new boiling point from the boiling point of the pure solvent and the change.*

Result: 62.91 °C

Check each result as a self-assessment.

Exercise 6.9.5

What is the boiling point of a solution of 1.0 g of glycerin, $C_3H_5(OH)_3$, in 47.8 g of water? Assume an ideal solution.

Answer available at the end of this section.

Freezing Point Depression

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in "de-icing" schemes that use salt (Figure 6.9.4), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an "antifreeze" in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).



Figure 6.9.4: Rock salt (NaCl), calcium chloride ($CaCl_2$), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

The decrease in freezing point of a dilute solution compared to that of the pure solvent, ΔT_f, is called the **freezing point depression** and is directly proportional to the molal concentration of the solute

$$\Delta T_f = K_f m$$

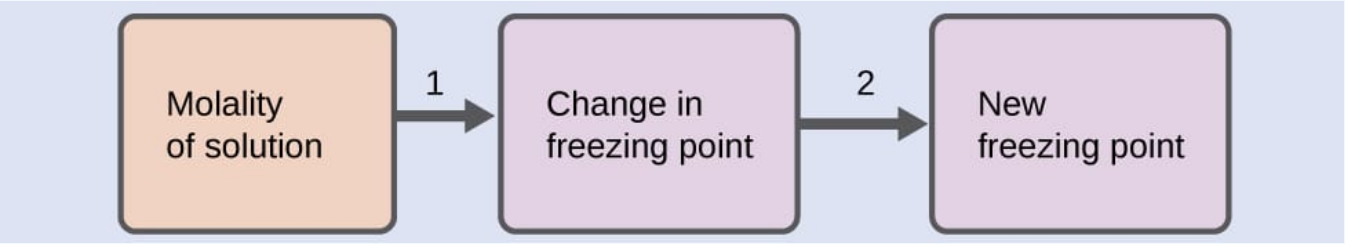
where *m* is the molal concentration of the solute and K_f is called the freezing point depression constant (or *cryoscopic constant*). Just as for boiling point elevation constants, these are characteristic properties whose values depend on the chemical identity of the solvent. Values of K_f for several solvents are listed in Table 6.9.1.

Example 6.9.7: Calculation of the Freezing Point of a Solution

Assuming ideal solution behavior, what is the freezing point of the 0.33 *m* solution of a nonvolatile nonelectrolyte solute in benzene described in Example 6.9.2?

Solution

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



Step 1: Calculate the change in freezing point.

$$\Delta T_f = K_f m = 5.12^{\circ}C m^{-1} \times 0.33 m = 1.7^{\circ}C$$

Step 2: Subtract the freezing point change observed from the pure solvent's freezing point.

$$\text{Freezing Temperature } = 5.5^{\circ}C - 1.7^{\circ}C = 3.8^{\circ}C$$

Exercise 6.9.1

Assuming ideal solution behavior, what is the freezing point of a 1.85 *m* solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

Answer available at the end of this section.

Chemistry in Everyday Life: Colligative Properties and De-Icing

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride ("rock salt") for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft (Figure 6.9.5).



Figure 6.9.5: Freezing point depression is exploited to remove ice from (a) roadways and (b) the control surfaces of aircraft.

Determination of Molar Masses

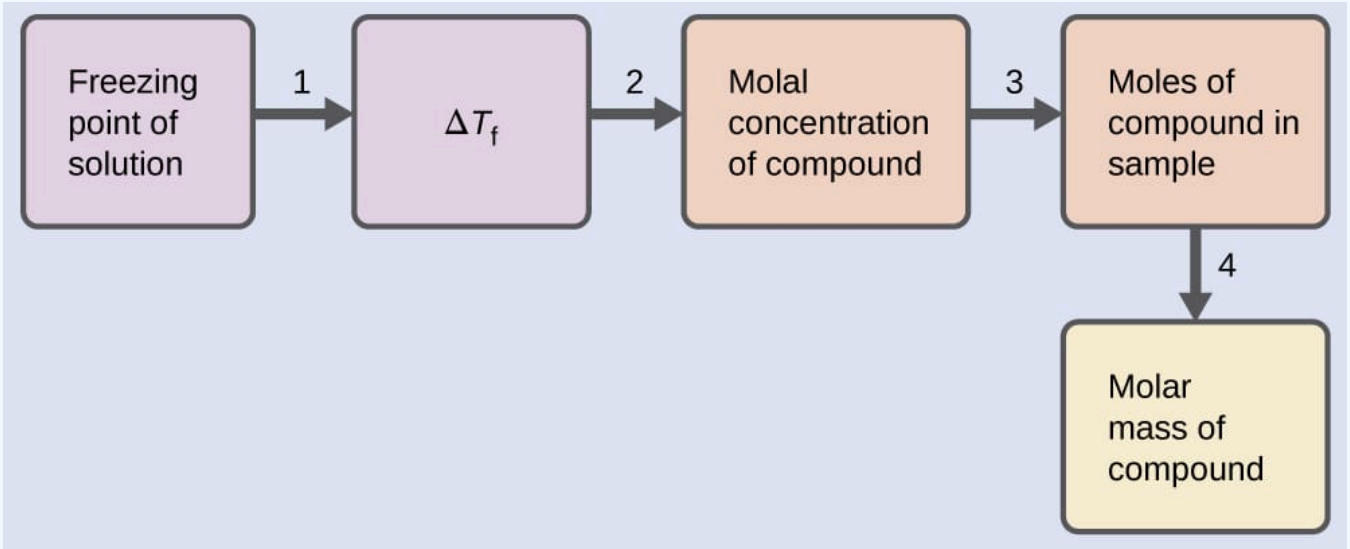
Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the number of solute species present in a given amount of solution. Consequently, measuring one of these properties for a solution prepared using a known mass of solute permits determination of the solute's molar mass.

Example 6.9.9: Determination of a Molar Mass from a Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. Assuming ideal solution behavior, what is the molar mass of this compound?

Solution

Solve this problem using the following steps.



Step 1. Determine the change in freezing point from the observed freezing point and the freezing point of pure benzene (Table 6.9.1.

$$\Delta T_f = 5.5^\circ C - 2.32^\circ C = 3.2^\circ C$$

Step 2. Determine the molal concentration from Kf, the freezing point depression constant for benzene (Table 6.9.1), and ΔT_f .

$$\Delta T_f = K_f m$$

$$m = \frac{\Delta T_f}{K_f} = \frac{3.2^\circ C}{5.12^\circ C m^{-1}} = 0.63 m$$

Step 3. Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution.

$$\text{Moles of solute } = \frac{0.63 \text{ mol solute}}{1.00 \cancel{\text{ kg solvent}}} \times 0.0550 \cancel{\text{ kg solvent}} = 0.035 mol$$

Step 4. Determine the molar mass from the mass of the solute and the number of moles in that mass.

$$\text{Molar mass } = \frac{4.00 \text{ g}}{0.035 \text{ mol}} = 1.1 \times 10^2 \text{ g / mol}$$

Exercise 6.9.9

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5 °C. Assuming ideal solution behavior, what is the molar mass of this compound?

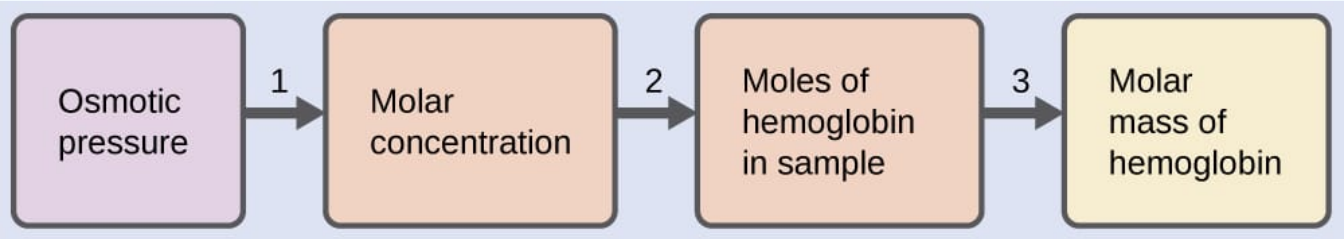
Answer available at the end of this section.

Example 6.9.10: Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. Assuming ideal solution behavior, what is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



Step 1. Convert the osmotic pressure to atmospheres, then determine the molar concentration from the osmotic pressure.

$$\Pi = \frac{5.9 \text{ torr } \times 1 atm}{760 \text{ torr}} = 7.8 \times 10^{-3} atm$$

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3} atm}{(0.08206 L atm/mol K)(295 K)} = 3.2 \times 10^{-4} M$$

Step 2. Determine the number of moles of hemoglobin in the solution from the concentration and the volume of the solution.

$$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4} mol}{1 \cancel{\text{L solution}}} \times 0.500 \cancel{\text{L solution}} = 1.6 \times 10^{-4} \text{ mol}$$

Step 3. Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.

$$\text{molar mass} = \frac{10.0 \text{ g}}{1.6 \times 10^{-4} \text{ mol}} = 6.2 \times 10^{4} \text{ g / mol}$$

Exercise 6.9.10

Assuming ideal solution behavior, what is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

Answer available at the end of this section.

Colligative Properties of Electrolytes

As noted previously in this module, the colligative properties of a solution depend only on the number, not on the identity, of solute species dissolved. The concentration terms in the equations for various colligative properties (freezing point depression, boiling point elevation, osmotic pressure) pertain to *all solute species present in the solution*. For the solutions considered thus far in this chapter, the solutes have been nonelectrolytes that dissolve physically without dissociation or any other accompanying process. Each molecule that dissolves yields one dissolved solute molecule. The dissolution of an electroyte, however, is not this simple, as illustrated by the two common examples below:

$$\begin{aligned} &\text{dissociation} && NaCl(s) \longrightarrow Na^{+}(aq) + Cl^{-}(aq) \\ &\text{ionization} && HCl(aq) + H_2O(l) \longrightarrow Cl^{-}(aq) + H3O^{+}(aq) \end{aligned}$$

Considering the first of these examples, and assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 2.0 mole of ions (1.0 mol Na^+ and 1.0 mol Cl^-) per each kilogram of water, and its freezing point depression is expected to be

$$\Delta T_f = 2.0 mol \text{ ions } / kg \text{ water } \times 1.86^{\circ} C kg \text{ water } / mol \text{ ion } = 3.7^{\circ} C.$$

When this solution is actually prepared and its freezing point depression measured, however, a value of 3.4 °C is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honor of Nobel Prize-winning German chemist Jacobus Henricus van 't Hoff is used. The van 't Hoff factor (i) is defined as the ratio of solute particles in solution to the number of formula units dissolved:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

Values for measured van 't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in Table 6.9.2.

Table 6.9.2: Predicated and Measured van't Hoff Factors for Several 0.050 m Aqueous Solutions

Formula unit	Classification	Dissolution products	*i* (predicted)	*i* (measured)
$C_{12}H_{22}O_{11}$ (glucose)	Nonelectrolyte	$C_{12}H_{22}O_{11}$	1	1.0
NaCl	Strong electrolyte	Na^+, Cl^-	2	1.9
HCl	Strong electrolyte (acid)	H_3O^+, Cl^-	2	1.9

Formula unit	Classification	Dissolution products	*i* (predicted)	*i* (measured)
$MgSO_4$	Strong electrolyte	Mg^{2+}, SO_4^{2-},	2	1.3
$MgCl_2$	Strong electrolyte	Mg^{2+}, $2Cl^-$	3	2.7
$FeCl_3$	Strong electrolyte	Fe^{3+}, $3Cl^-$	4	3.4

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles (Figure 6.9.11). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the activity, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in Table 6.9.2 are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.

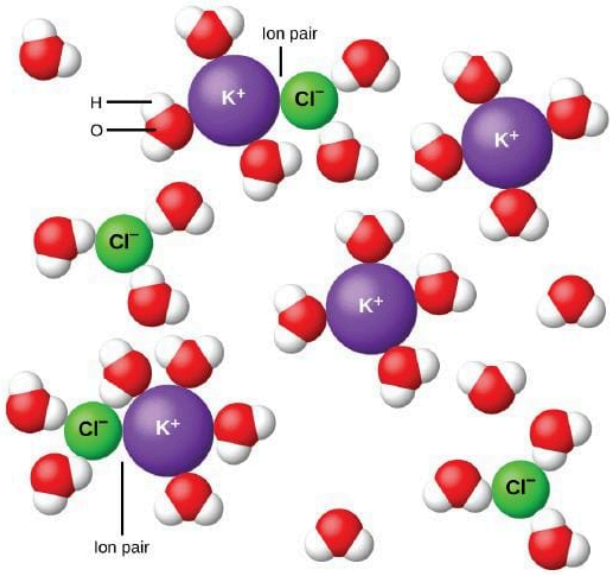


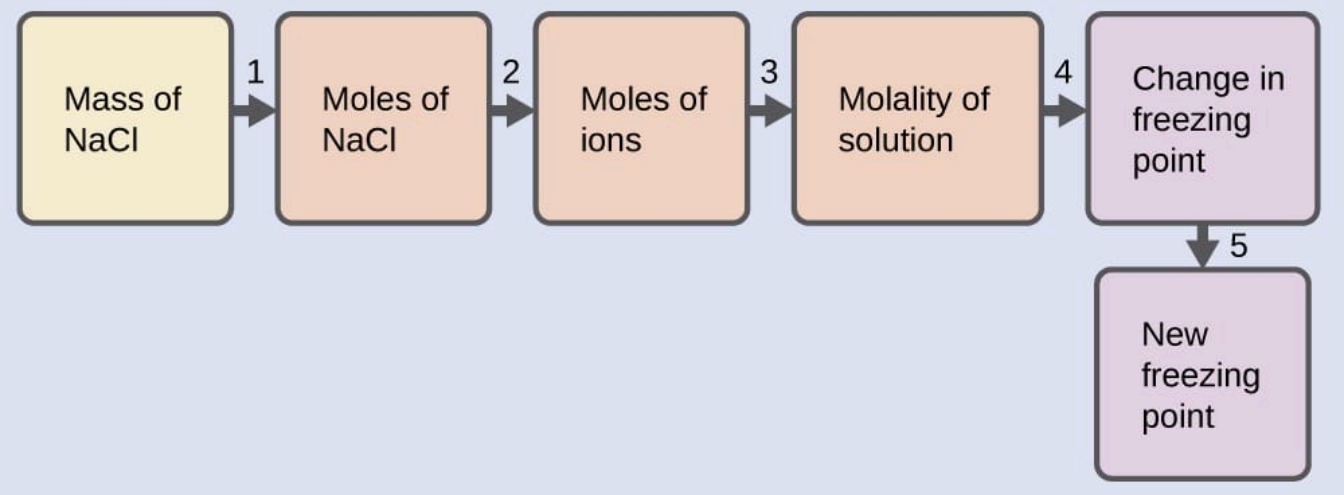
Figure 6.9.11: Dissociation of ionic compounds in water is not always complete due to the formation of ion pairs.

Example 6.9.11: The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Use this information and a predicted value for the van't Hoff factor (Table 6.9.2) to determine the freezing temperature the solution (assume ideal solution behavior).

Solution

Solve this problem using the following series of steps.



1. Step 1. *Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor.*
   Result: 0.072 mol NaCl
2. Step 2. *Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl).*
   Result: 0.14 mol ions
3. Step 3. *Determine the molality of the ions in the solution from the number of moles of ions and the mass of solvent, in kilograms.*
   Result: 1.2 *m*
4. Step 4. *Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes.*
   Result: 2.1 °C
5. Step 5. *Determine the new freezing point from the freezing point of the pure solvent and the change.*
   Result: −2.1 °C

Check each result as a self-assessment, taking care to avoid rounding errors by retaining guard digits in each step's result for computing the next step's result.

Exercise 6.9.11

Assuming complete dissociation and ideal solution behavior, calculate the freezing point of a solution of 0.724 g of $CaCl_2$ in 175 g of water.

Answer available at the end of this section.

Answers

Exercise 6.9.1
7.14 \times 10^{−3}; 0.399 *m*

Exercise 6.9.2
1.50 *m*

Exercise 6.9.3
14.6 M

Exercise 6.9.1
109.2 °C

Exercise 6.9.5
100.12 °C

Exercise 6.9.1
−9.3 °C

Exercise 6.9.9

1.8 \times 10^{2} g/mol

Exercise 6.9.10

3 \times 10^{4} g/mol

Exercise 6.9.11

−0.208 °C

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7: THE GAS PHASE IS DIFFERENT

7.1: Overview and Objectives

7.2: Gas Pressure

7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

7.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

7.5: The Kinetic-Molecular Theory

7.6: Effusion and Diffusion of Gases

7.7: Non-Ideal Gas Behavior

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7.1: Overview and Objectives

> Gases are distinguished from other forms of matter, not only by their power of indefinite expansion so as to fill any vessel, however large, and by the great effect heat has in dilating them, but by the uniformity and simplicity of the laws which regulate these changes. (James Clerk Maxwell)

Maxwell had the right of it: gases are surprisingly easy to describe. Let's take a look at the laws that govern their behavior, the theory that explains that behavior (and deviations from it), and how all of this relates back to stoichiometry.

Chapter Objectives

- Combine gas laws (Boyle's, Charles's, Combined, Ideal, Dalton's) with stoichiometry to determine the moles, pressure or volume of gas present at a specific temperature.
- Apply the principles of kinetic-molecular theory to describe the relative effusion rates of gases and the deviations of gases from ideal.

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7.2: Gas Pressure

Learning Objectives

By the end of this section, you will have the background information to help you to be able to:

- Describe the pressure of a gas.

In general, **pressure** is defined as the force exerted on a given area: \(P=\frac{F}{A}). Note that pressure is directly proportional to force and inversely proportional to area. Thus, pressure can be increased either by increasing the amount of force or by decreasing the area over which it is applied; pressure can be decreased by decreasing the force or increasing the area.

Let's apply this concept to determine which exerts a greater pressure in Figure 7.2.2 —the elephant or the figure skater? A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:

Even though the elephant is more than one hundred-times heavier than the skater on two blades, it exerts less than one-half of the pressure. On the other hand, if the skater removes their skates and stands with bare feet (or regular footwear) on the ice, the larger area over which their weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot } = 120\frac{lb}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30in^2} = 2lb/in^2$$

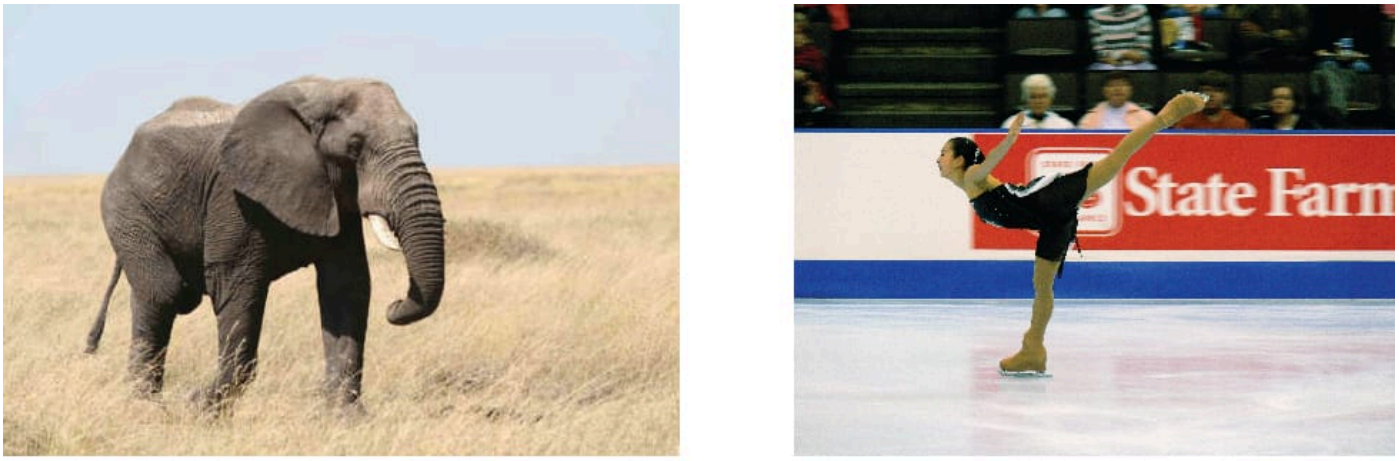


Figure 7.2.2: Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of the skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi)

The SI unit of pressure is the **pascal (Pa)**, with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or **bar** (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—**pounds per square inch (psi)**—for example, in car tires. Pressure can also be measured using the unit **atmosphere** (atm), which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table 7.2.1 provides some information on these and a few other common units for pressure measurements

Table 7.2.1: Pressure Units

Unit Name and Abbreviation	Definition or Relation to Other Unit
pascal (Pa)	1 Pa = 1 N/m^2 recommended IUPAC unit
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi
atmosphere (atm)	1 atm = 101,325 Pa = 760 torr air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly) commonly used in meteorology
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa used by aviation industry, also some weather reports
torr/millimeters of mercury (mm Hg)	named after Evangelista Torricelli, inventor of the barometer 1 mm Hg = 1 torr 760 torr = 1 atm

Example 7.2.1: Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

a. torr
b. atm
c. kPa
d. mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 7.2.1.

a. $$29.2 \text{ in } Hg_g \times \frac{25.4mm}{1in} \times \frac{1 \text{ torr}}{1mmHg_g} = 742 \text{ torr}$$

b. $$742 \text{ torr } \times \frac{1atm}{760 \text{ torr}} = 0.976atm$$

c. $$742 \text{ torr } \times \frac{101.325kPa}{760 \text{ torr}} = 98.9kPa$$

d. $$98.9kPa \times \frac{1000Pa}{1kPa} \times \frac{1bar}{100,000Pa} \times \frac{1000mbar}{1bar} = 989mbar$$

Gas pressures are measured using a device called a **manometer**. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. The distance between the liquid levels in the two arms of the tube (*h* in the diagram) is proportional to the pressure of the gas in the container. An open-end manometer (Figure 7.2.4) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.

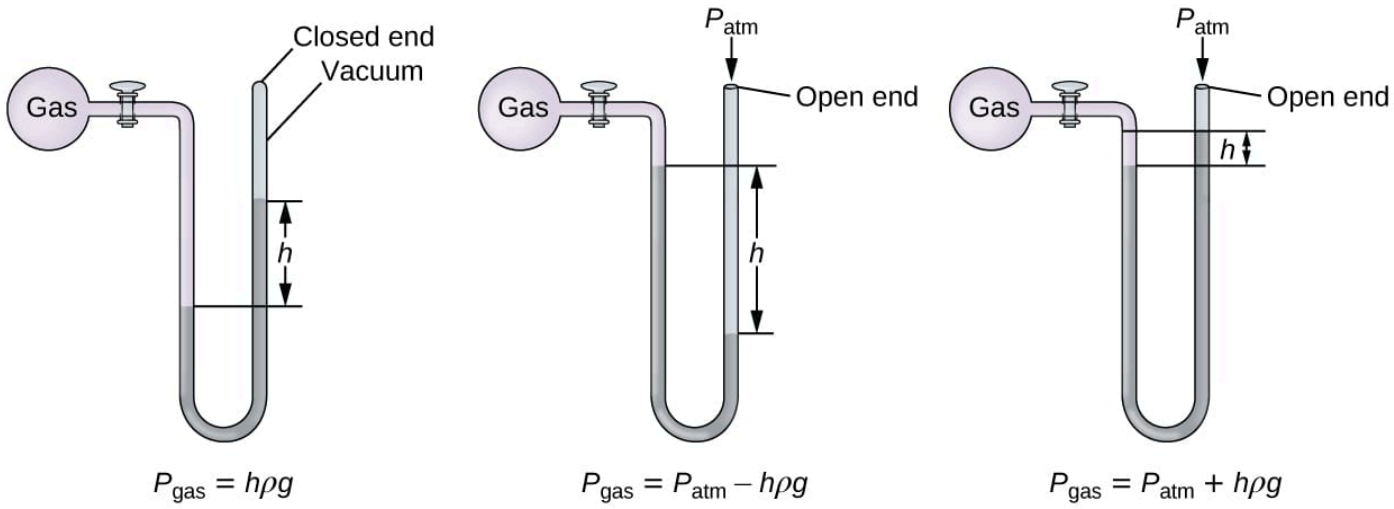


Figure 7.2.4: A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (*h*) is a measure of the pressure. Mercury is usually used because of its large density.

Chemistry in Everyday Life: Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = "pulse"). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure 7.2.5). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff's pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart's ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).

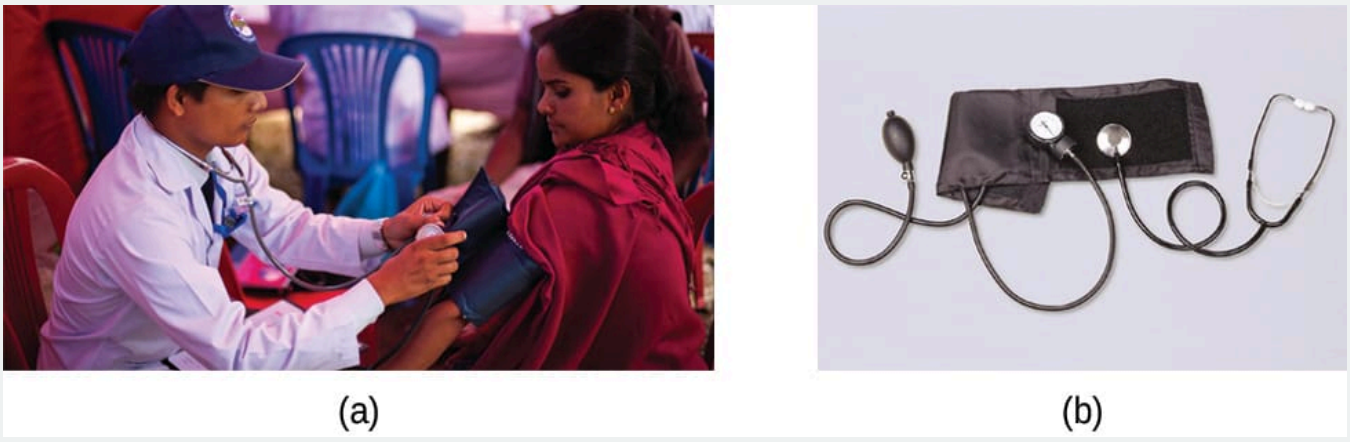


Figure 7.2.5: (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

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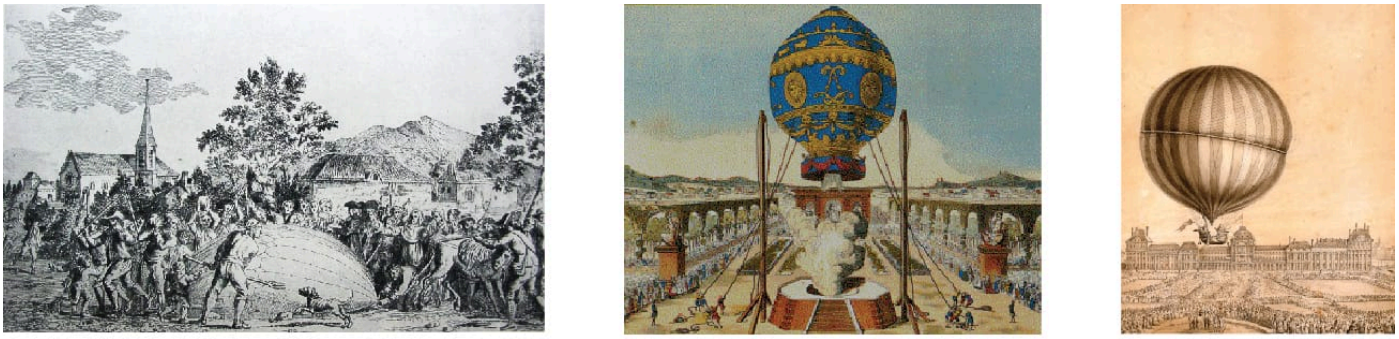
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

Learning Objectives

By the end of this section, you will have the background information to help you to be able to:

- Combine gas laws (Boyle's, Charles's, Combined, Ideal, Dalton's) with stoichiometry to determine the moles, pressure or volume of gas present at a specific temperature.

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (Figure 7.3.1), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.



(a) (b) (c)

Figure 7.3.1: In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

Pressure and Temperature: Amontons's Law

If you have rigid (constant-volume) container filled with gas that is sealed so no matter can get in our out (constant-moles), then cooling the container results in a decrease in pressure. On the other hand, heating the container results in an increase in pressure. This relationship between temperature and pressure is observed for any sealed sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in Figure 7.3.3. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then P and T are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
−100	173	36.0
−50	223	46.4
0	273	56.7
50	323	67.1
100	373	77.5
150	423	88.0

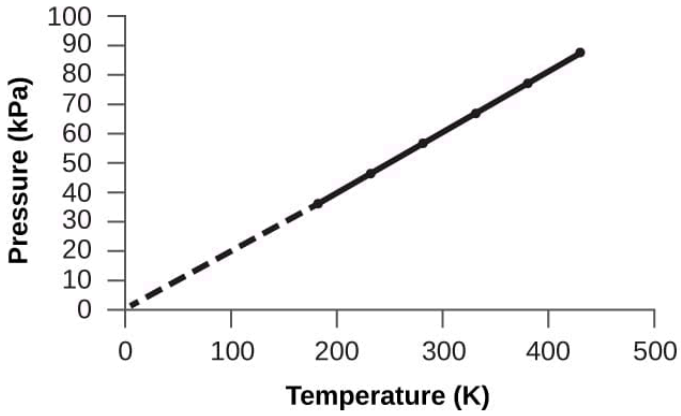


Figure 7.3.3: For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at –273 °C, which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the *P*-*T* relationship for gases is known as either **Amontons's law** or **Gay-Lussac's law**. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written as

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}.$$

This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called **absolute zero**). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Example 7.3.1: Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

a. On the can is the warning "Store only at temperatures below 120 °F (48.8 °C). Do not incinerate." Why?
b. The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

Solution

(a) The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)

(b) We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons's/Gay-Lussac's law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting °C to K, we have:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360 \text{ kPa}}{297 \text{ K}} = \frac{P_2}{323 \text{ K}}$$

Rearranging and solving gives:

$$P_2 = \frac{360 \text{ kPa} \times 323 \cancel{\text{K}}}{297 \cancel{\text{K}}} = 390 \text{ kPa}$$

Exercise 7.3.1

A sample of nitrogen, N_2, occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Answer available at the end of this section.

Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

Link to Learning

This video shows how cooling and heating a gas causes its volume to decrease or increase, respectively.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in Figure 9.12.

Temperature (°C)	Temperature (K)	Volume (L)
–3	270	22
–23	250	21
–53	220	18
–162	111	9

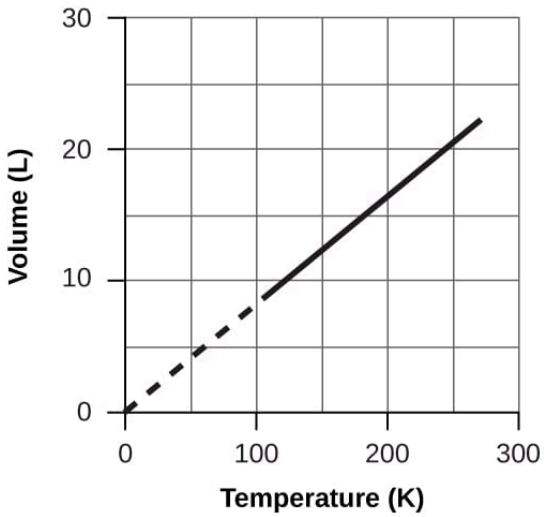


Figure 9.12 The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. **Charles's law** states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant*.

Mathematically, this can be written as:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}. \tag{7.3.1}$$

Example 7.3.2: Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO_2, occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300L}{283K} = \frac{V_2}{303K}$$

Rearranging and solving gives:

$$V_2 = \frac{0.300L \times 303 \cancel{K}}{283 \cancel{K}} = 0.321 \text{ L}$$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Exercise 7.3.2

A sample of oxygen, O_2, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at –70 °C and the same pressure?

Answer available at the end of this section.

Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in Figure 7.3.4.

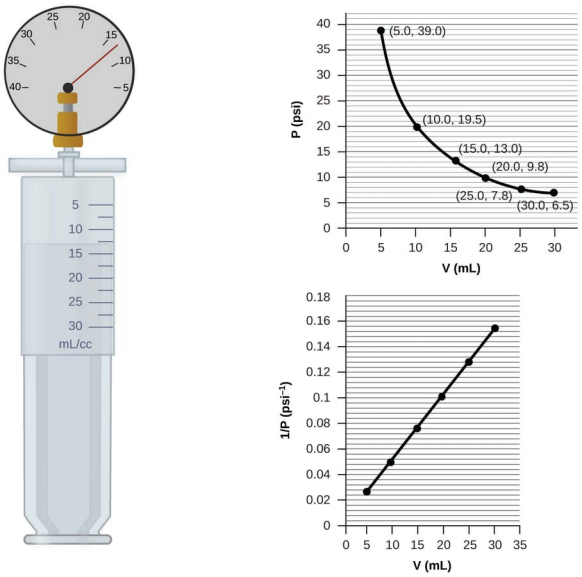


Figure 7.3.4: When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since *P* and *V* are inversely proportional, a graph of $\frac{1}{P}$ vs. *V* is linear.

Unlike the *P*-*T* and *V*-*T* relationships, pressure and volume are not directly proportional to each other. Instead, *P* and *V* exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P_1V_1 = P_2V_2 \tag{7.3.2}$$

Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure

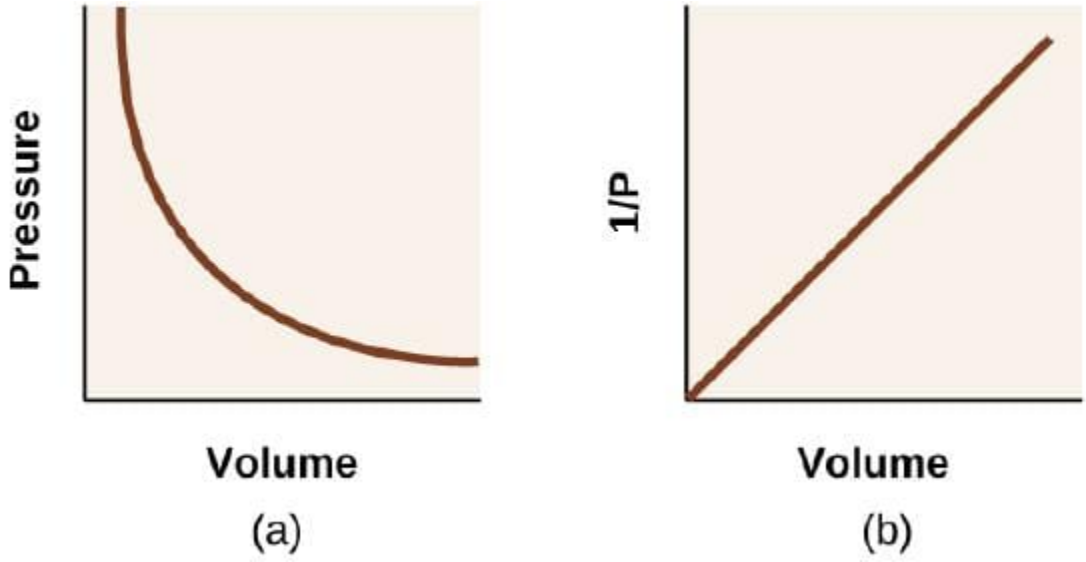


Figure 7.3.5: The relationship between pressure and volume is inversely proportional. (a) The graph of *P* vs. *V* is a hyperbola, whereas (b) the graph of $\frac{1}{P}$ vs. *V* is linear.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

Example 7.3.4: Volume of a Gas Sample

The sample of gas in Figure 7.3.4: has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

a. the *P*-*V* graph in Figure 7.3.5
b. the $\frac{1}{P}$ vs. V graph in Figure 7.3.5
c. the Boyle's law equations (Equations ??? - 7.3.2)

Comment on the likely accuracy of each method.

Solution

(a) Estimating from the *P*-*V* graph gives a value for *P* somewhere around 27 psi.

(b) Estimating from the \frac{1}{P}\) versus V graph give a value of about 26 psi.

(c) From Boyle's law, we know that the product of pressure and volume (*PV*) for a given sample of gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$.

Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_1\ V_1 = P_2\ V_2$$
$$(13.0\ \text{psi}) \times (15.0\ \text{mL} = P_2 \times (7.5\ \text{mL})$$

Solving:

$$P_2 = \frac{13.0\ \text{psi} \times 15.0\ \cancel{\text{mL}}}{7.5\ \cancel{\text{mL}}} = 26\ \text{psi}$$

It was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

Exercise 7.3.4

The sample of gas in Figure 7.3.4 has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 psi, using:

a. the *P*-*V* graph in Figure 7.3.5
b. the $\frac{1}{P}$ vs. \(*V*\) graph in Figure 7.3.5
c. the Boyle's law equations (??? - 7.3.2)

Comment on the likely accuracy of each method.

Answer available at the end of this section.

Chemistry in Everyday Life: Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When

you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure 7.3.6).

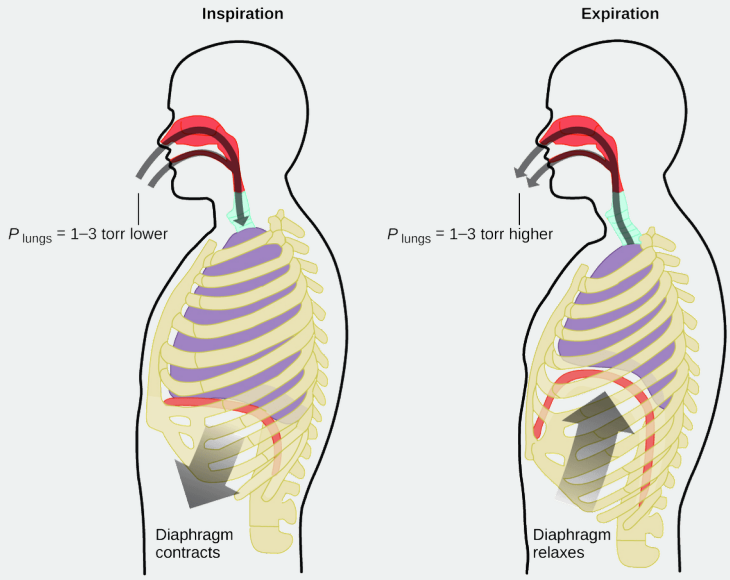


Figure 7.3.6: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by **Avogadro's law**: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant.*

In equation form, this is written as:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \tag{7.3.3}$$

Mathematical relationships can also be determined for the other variable pairs, such as *P* versus *n*, and *n* versus *T*.

Link to Learning

Visit this interactive PhET simulation to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).

The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: PV = constant at constant *T* and *n*
- Amontons's law: $\frac{P}{T}$ = constant at constant *V* and *n*
- Charles's law: $\frac{V}{T}$ = constant at constant *P* and *n*
- Avogadro's law: $\frac{V}{n}$ = constant at constant *P* and *T*

Combining these four laws yields the **ideal gas law**, a relation between the pressure, volume, temperature, and number of moles of a gas. This equation is shown below. **You must memorize this equation.**

$$PV = nRT$$

where *P* is the pressure of a gas, *V* is its volume, *n* is the number of moles of the gas, *T* is its temperature on the kelvin scale, and *R* is a constant called the **ideal gas constant** or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol^{-1} K^{-1} and 8.314 kPa L mol^{-1} K^{-1}.

Gases whose properties of *P*, *V*, and *T* are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an **ideal gas**. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant *R* and the variable properties *P*, *V*, *n*, and *T*. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Example 7.3.5: Using the Ideal Gas Law

Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of this much methane at 25 °C and 745 torr?

Solution

We must rearrange *PV* = *nRT* to solve for *V*:

$$V = \frac{nRT}{P}$$

If we choose to use *R* = 0.08206 L atm mol^{-1} K^{-1}, then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the "right" units:

$$n = 655 \text{ g } \cancel{CH_4} \times \frac{1 \text{ mol}}{16.043 \text{ g } \cancel{CH_4}} = 40.8 \text{ mol}$$

$$T = 25^{\circ}C + 273 = 298 \text{ K}$$

$$P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$$

$$V = \frac{nRT}{P} = \frac{(40.8 \cancel{\text{mol}}) \left(0.08206 \text{ L } \cancel{\text{atm mol}^{-1}\text{K}^{-1}}\right) (298 \cancel{\text{K}})}{0.980 \cancel{\text{atm}}} = 1.02 \times 10^3 \text{ L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

Exercise 7.3.5

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Answer available at the end of this section.

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the **combined gas law** is obtained. **This is a really good equation to memorize.**

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

using units of atm, L, and K. Both sets of conditions are equal to the product of *n R* (where *n* = the number of moles of the gas and *R* is the ideal gas law constant).

Example 7.3.6: Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (Figure 7.3.7). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?

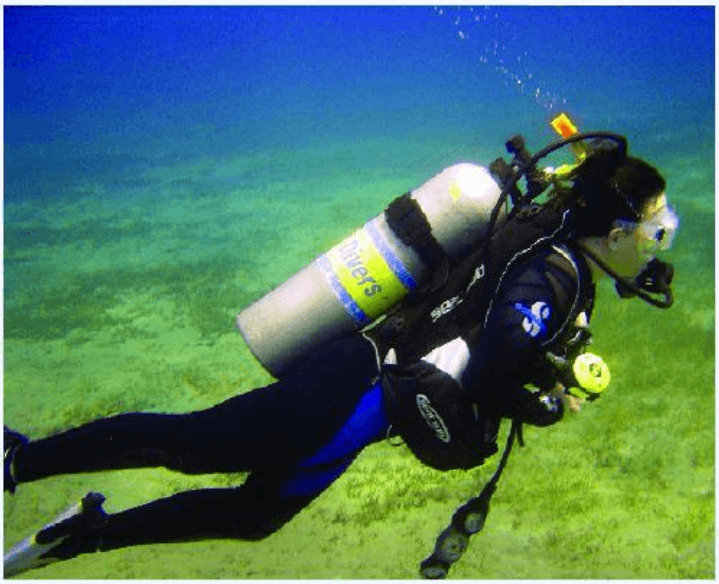


Figure 7.3.7: Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)

Letting *1* represent the air in the scuba tank and *2* represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \rightarrow \frac{(153atm)(13.2L)}{(300K)} = \frac{(3.13atm)\,(V_2)}{(310K)}$$

Solving for V_2:

$$V_2 = \frac{(153 \text{ atm })(13.2L)(310K)}{(300K)(3.13 \text{ atm })} = 667L$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good "ballpark" estimate.)

Exercise 7.3.6

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Answer available at the end of this section.

Chemistry in Everyday Life: The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 7.3.8) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.



Figure 7.3.8: Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor)

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as “atmospheres absolute” or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body’s air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in their BCD expands because of lower pressure according to Boyle’s law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and they begin to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a **standard temperature and pressure (STP)** for reporting properties of gases: 273.15 K and 1 atm (101.325 kPa).[1] At STP, one mole of an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume** (Figure 7.3.9).

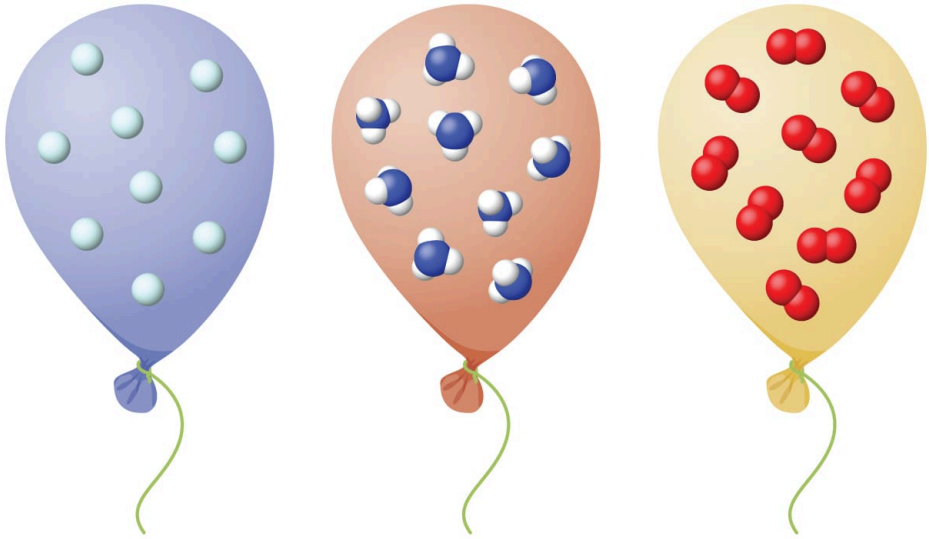


Figure 7.3.9: Regardless of its chemical identity, one mole of gas behaving ideally occupies a volume of ~22.4 L at STP.

Footnotes

- 1The IUPAC definition of standard pressure was changed from 1 atm to 1 bar (100 kPa) in 1982, but the prior definition remains in use by many literature resources and will be used in this text.

Answers

Exercise 7.3.1

400 torr

Exercise 7.3.2

21.6 mL

Exercise 7.3.4

(a) about 17–18 mL; (b) ~18 mL; (c) 17.7 mL; it was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

Exercise 7.3.5

350 bar

Exercise 7.3.6

0.193 L

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7.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

Learning Objectives

By the end of this section, you will have the background information to help you to be able to:

- Combine gas laws (Boyle's, Charles's, Combined, Ideal, Dalton's) with stoichiometry to determine the moles, pressure or volume of gas present at a specific temperature.

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask "How much?" The essential property involved in such use of stoichiometry is the amount of substance, typically measured in moles (*n*). For gases, molar amount can be derived from convenient experimental measurements of pressure, temperature, and volume. Therefore, these measurements are useful in assessing the stoichiometry of pure gases, gas mixtures, and chemical reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts already discussed.

Gas Density and Molar Mass

The ideal gas law described previously in this chapter relates the properties of pressure *P*, volume *V*, temperature *T*, and molar amount *n*. This law is universal, relating these properties in identical fashion regardless of the chemical identity of the gas:

$$PV = nRT$$

The density *d* of a gas, on the other hand, is determined by its identity. As described in another chapter of this text, the density of a substance is a characteristic property that may be used to identify the substance.

$$d = \frac{m}{V}$$

Rearranging the ideal gas equation to isolate *V* and substituting into the density equation yields

$$d = \frac{mP}{nRT} = \left(\frac{m}{n}\right)\frac{P}{RT}$$

The ratio *m*/*n* is the definition of molar mass, M:

$$\mathcal{M} = \frac{m}{n}$$

The density equation can then be written

$$d = \frac{\mathcal{M}P}{RT}$$

This relation may be used for calculating the densities of gases of known identities at specified values of pressure and temperature as demonstrated in Example 7.4.1.

Example 7.4.1: Measuring Gas Density

What is the density of molecular nitrogen gas at STP?

Solution

The molar mass of molecular nitrogen, N_2, is 28.01 g/mol. Substituting this value along with standard temperature and pressure into the gas density equation yields

$$d = \frac{\mathscr{M}P}{RT} = \frac{(28.01\ \text{g/mol}\ )(1.00\ \text{atm})}{\left(0.0821\ \text{L}\cdot\text{atm}\cdot\text{mol}^{-1}\text{K}^{-1}\right)(273\ \text{K})} = 1.25\ \text{g}\ /\ \text{L}$$

Exercise 7.4.1

What is the density of molecular hydrogen gas at 17.0 °C and a pressure of 760 torr?

Answer available at the end of this section.

When the identity of a gas is unknown, measurements of the mass, pressure, volume, and temperature of a sample can be used to calculate the molar mass of the gas (a useful property for identification purposes). Combining the ideal gas equation

$$PV = nRT$$

and the definition of molar mass

$$\mathscr{M} = \frac{m}{n}$$

yields the following equation:

$$\mathscr{M} = \frac{mRT}{PV}$$

Determining the molar mass of a gas via this approach is demonstrated in Example 7.4.2.

Example 7.4.2: Determining the Molecular Formula of a Gas from its Molar Mass and Empirical Formula

Cyclopropane, a gas once used with oxygen as a general anesthetic, is composed of 85.7% carbon and 14.3% hydrogen by mass. Find the empirical formula. If 1.56 g of cyclopropane occupies a volume of 1.00 L at 0.984 atm and 50 °C, what is the molecular formula for cyclopropane?

Solution

First determine the empirical formula of the gas. Assume 100 g and convert the percentage of each element into grams. Determine the number of moles of carbon and hydrogen in the 100-g sample of cyclopropane. Divide by the smallest number of moles to relate the number of moles of carbon to the number of moles of hydrogen.

$$85.7\ \text{g}\ C \times \frac{1\ \text{mol}\ C}{12.01\ \text{g}\ C} = 7.136\ \text{mol}\ C$$

$$14.3\ \text{g}\ H \times \frac{1\ \text{mol}\ H}{1.01\ \text{g}\ H} = 14.158\ \text{mol}\ H$$

In the last step, realize that the smallest whole number ratio is the empirical formula:

$$\frac{7.136}{7.136} = 1.00\ \text{mol}\ C$$

$$\frac{14.158}{7.136} = 1.98\ \text{mol}\ H$$

Empirical formula is CH_2 [empirical mass (EM) of 14.03 g/empirical unit].

Next, use the provided values for mass, pressure, temperature and volume to compute the molar mass of the gas:

$$\mathscr{M} = \frac{mRT}{PV} = \frac{(1.56\text{ g})\left(0.0821\text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\text{K}^{-1}\right)(323\text{ K})}{(0.984\text{ atm})(1.00\text{ L})} = 42.0\text{ g/mol}$$

Comparing the molar mass to the empirical formula mass shows how many empirical formula units make up a molecule:

$$\frac{\mathscr{M}}{EM} = \frac{42.0\text{ g/mol}}{14.0\text{ g/mol}} = 3$$

The molecular formula is thus derived from the empirical formula by multiplying each of its subscripts by three:

$$(\text{CH}_2)_3 = \text{C}_3\text{H}_6$$

Exercise 7.4.2

Acetylene, a fuel used welding torches, is composed of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies of volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Answer available at the end of this section.

Example 7.4.3: Determining the Molar Mass of a Volatile Liquid

The approximate molar mass of a volatile liquid can be determined by:

1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (see Figure 7.4.1)

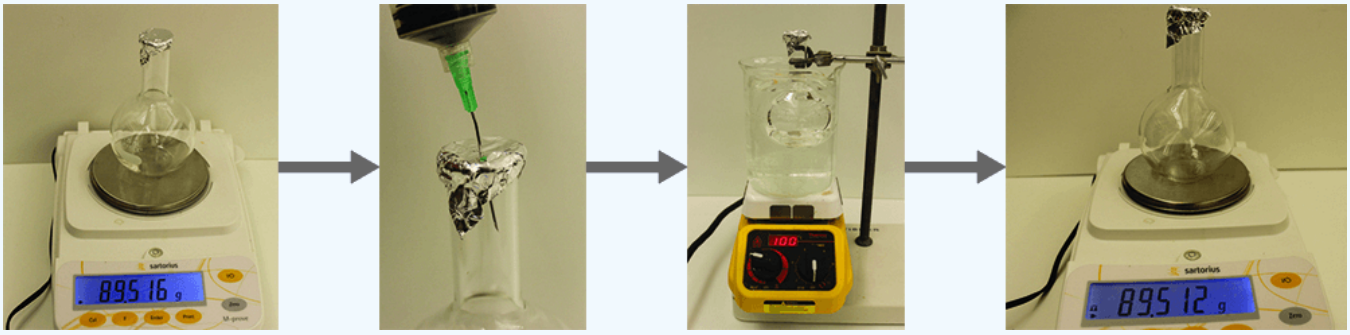


Figure 7.4.1: When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott)

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm^3 at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

Since $\mathscr{M} = \frac{m}{n}$ and $n = \frac{PV}{RT}$ substituting and rearranging gives $\mathscr{M} = \frac{mRT}{PV}$,

then

$$\mathscr{M} = \frac{mRT}{PV} = \frac{(0.494\text{ g}) \times 0.08206\text{ L}\cdot\text{atm/mol K} \times 372.8\text{ K}}{0.976\text{ atm} \times 0.129\text{ L}} = 120\text{ g/mol}$$

Exercise 7.4.3

A sample of phosphorus that weighs 3.243×10^{-2} g exerts a pressure of 31.89 kPa in a 56.0-mL bulb at 550 °C. What are the molar mass and molecular formula of phosphorus vapor?

Answer available at the end of this section.

The Pressure of a Mixture of Gases: Dalton's Law

Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other's pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it were present alone in the container (Figure 7.4.2). The pressure exerted by each individual gas in a mixture is called its **partial pressure**. This observation is summarized by **Dalton's law of partial pressures**: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases*:

$$P_{\text{Total}} = P_A + P_B + P_C + \ldots = \sum_i P_i$$

In the equation P_{Total} is the total pressure of a mixture of gases, P_A is the partial pressure of gas A; P_B is the partial pressure of gas B; P_C is the partial pressure of gas C; and so on.

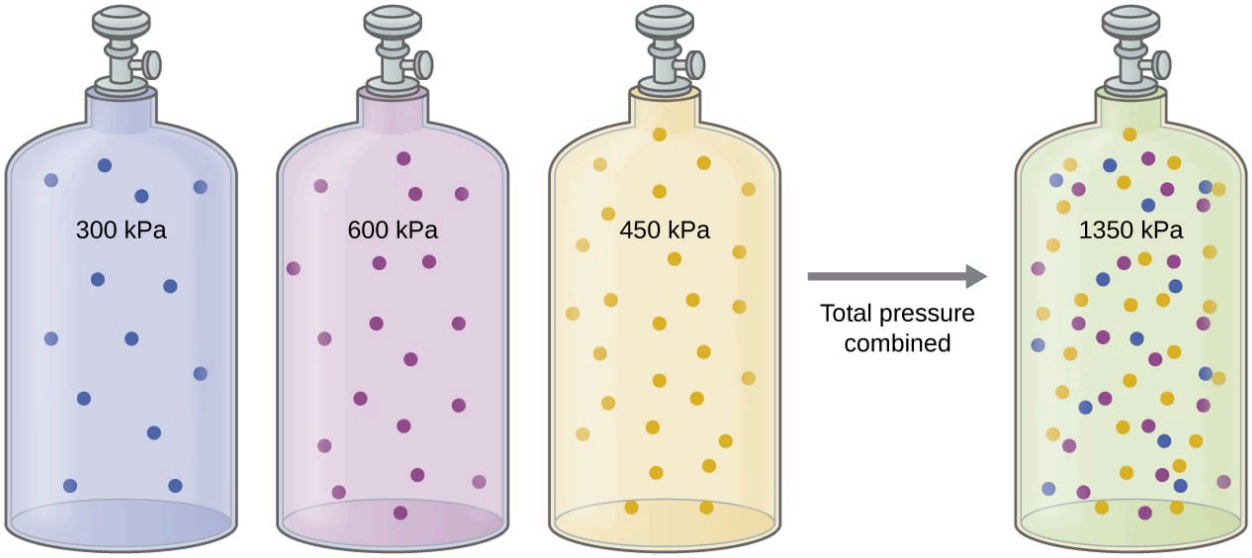


Figure 7.4.2: If equal-volume cylinders containing gasses at pressures of 300 kPa, 450 kPa, and 600 kPa are all combined in the same-size cylinder, the total pressure of the gas mixture is 1350 kPa.

The partial pressure of gas A is related to the total pressure of the gas mixture via its **mole fraction** (X), a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components:

$$P_A = X_A \times P_{\text{Total}}$$

where

$$X_A = \frac{n_A}{n_{\text{Total}}}$$

where P_A, X_A, and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

Example 7.4.4: The Pressure of a Mixture of Gases

A 10.0-L vessel contains $2.50\ 10^{-3}$ mol of H_2, $1.00\ 10^{-3}$ mol of He, and $3.00\ 10^{-4}$ mol of Ne at 35 °C.

a. What are the partial pressures of each of the gases?
b. What is the total pressure in atmospheres?

Solution

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = \frac{nRT}{V}$:

$$P_{H_2} = \frac{\left(2.50 \times 10^{-3}\ \cancel{\text{mol}}\right)\left(0.08206\ \cancel{L}\ \text{atm}\ \cancel{\text{mol}^{-1}\ \text{K}^{-1}}\right)(308\ \cancel{\text{K}})}{10.0\ \cancel{L}} = 6.32 \times 10^{-3}\ \text{atm}$$

$$= \frac{\left(1.00 \times 10^{-3}\ \cancel{\text{mol}}\right)\left(0.08206\ \cancel{L}\ \text{atm}\ \cancel{\text{mol}^{-1}\ \text{K}^{-1}}\right)(308\ \cancel{\text{K}})}{10.0\ \cancel{L}} = 2.53 \times 10^{-3}\ \text{atm}$$

$$= \frac{\left(3.00 \times 10^{-4}\ \cancel{\text{mol}}\right)\left(0.08206\ \cancel{L}\ \text{atm}\ \cancel{\text{mol}^{-1}\ \text{K}^{-1}}\right)(308\ \cancel{\text{K}})}{10.0\ \cancel{L}} = 7.58 \times 10^{-4}\ \text{atm}$$

The total pressure is given by the sum of the partial pressures:

$$P_T = P_{H_2} + P_{He} + P_{Ne} = (0.00632 + 0.00253 + 0.00076)\ \text{atm} = 9.61 \times 10^{-3}\ \text{atm}$$

Exercise 7.4.4

A 5.73-L flask at 25 °C contains 0.0388 mol of N_2, 0.147 mol of CO, and 0.0803 mol of H_2. What is the total pressure in the flask in atmospheres?

Answer available at the end of this section.

Here is another example of this concept, but dealing with mole fraction calculations.

Example 7.4.5: The Pressure of a Mixture of Gases

A gas mixture used for anesthesia contains 2.83 mol oxygen, O_2, and 8.41 mol nitrous oxide, N_2O. The total pressure of the mixture is 192 kPa.

a. What are the mole fractions of O_2 and N_2O?
b. What are the partial pressures of O_2 and N_2O?

Solution

The mole fraction is given by $X_A = \frac{n_A}{n_{\text{Total}}}$ and the partial pressure is $P_A = X_A P_{Total}$.

For O_2,

$$X_{O_2} = \frac{n_{O_2}}{n_{\text{Total}}} = \frac{2.83 mol}{(2.83 + 8.41) mol} = 0.252$$

and $P_{O_2} = X_{O_2} \times P_{\text{Total}} = 0.252 \times 192 kPa = 48.4 kPa$

For N_2O,

$$X_{N_2O} = \frac{n_{N_2O}}{n_{\text{Total}}} = \frac{8.41mol}{(2.83 + 8.41)mol} = 0.748$$

and

$$P_{N_2O} = X_{N_2O} \times P_{\text{Total}} = 0.748 \times 192kPa = 144kPa$$

Exercise 7.4.5

What is the pressure of a mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

Answer available at the end of this section.

Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure 7.4.3), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

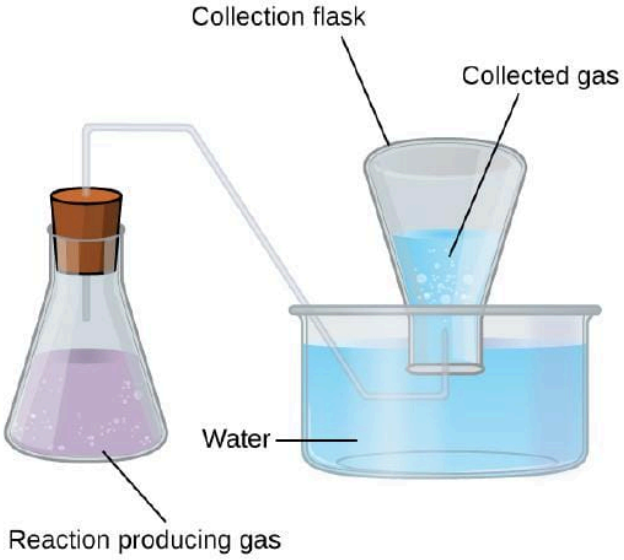


Figure 7.4.3: When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapor. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapor) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapor and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapor. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapor—this is referred to as the “dry” gas pressure, that is, the pressure of the gas only, without water vapor. The **vapor pressure of water**, which is the pressure exerted by water vapor in equilibrium with liquid water in a closed container, depends on the temperature (Figure 7.4.4); more detailed information on the temperature dependence of water vapor can be found in Table 7.4.1, and vapor pressure will be discussed in more detail in the next chapter on liquids.

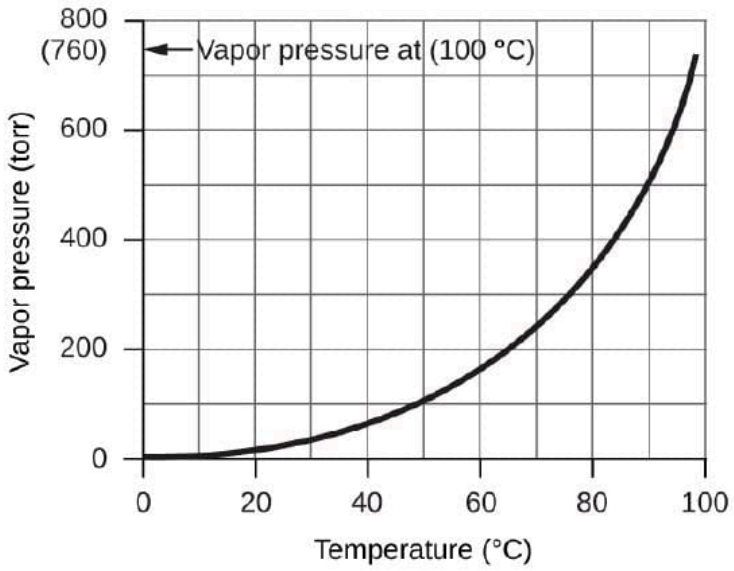


Figure 7.4.4: This graph shows the vapor pressure of water at sea level as a function of temperature.

Table 7.4.1: Vapor Pressure of Ice and Water in Various Temperatures at Sea Level

Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)
–10	1.95	18	15.5	30	31.8
–5	3.0	19	16.5	35	42.2
–2	3.9	20	17.5	40	55.3
0	4.6	21	18.7	50	92.5
2	5.3	22	19.8	60	149.4
4	6.1	23	21.1	70	233.7
6	7.0	24	22.4	80	355.1
8	8.0	25	23.8	90	525.8
10	9.2	26	25.2	95	633.9
12	10.5	27	26.7	99	733.2
14	12.0	28	28.3	100.0	760.0
16	13.6	29	30.0	101.0	787.6

Example 7.4.6: Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in Figure 7.4.3, what is the partial pressure of argon?

Solution

According to Dalton's law, the total pressure in the bottle (750 torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

$$P_T = P_{Ar} + P_{H_2O}$$

Rearranging this equation to solve for the pressure of argon gives:

$$P_{Ar} = P_T - P_{H_2O}$$

The pressure of water vapor above a sample of liquid water at 26 °C is 25.2 torr (Appendix E), so:

$$P_{Ar} = 750 \text{ torr } - 25.2 \text{ torr } = 725 \text{ torr}$$

Exercise 7.4.6

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 torr has a volume of 0.560 L. What volume would the dry oxygen from this sample have under the same conditions of temperature and pressure?

Answer available at the end of this section.

Chemical Stoichiometry and Gases

Chemical stoichiometry describes the quantitative relationships between reactants and products in chemical reactions.

We have previously measured quantities of reactants and products using masses for solids and volumes in conjunction with the molarity for solutions; now we can also use gas volumes to indicate quantities. If we know the volume, pressure, and temperature of a gas, we can use the ideal gas equation to calculate how many moles of the gas are present. If we know how many moles of a gas are involved, we can calculate the volume of a gas at any temperature and pressure.

Example 7.4.7: Reaction of Gases

Propane, $\mathrm{C_3H_8\,(g)}$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

The ratio of the volumes of C_3H_8 and O_2 will be equal to the ratio of their coefficients in the balanced equation for the reaction:

$$\underset{\mathrm{C_3H_8\,(g)+5\,O_2\,(g)}}{1 \text{ volume } + 5 \text{ volumes}} \longrightarrow \underset{\mathrm{3\,CO_2\,(g)+4\,H_2O\,(l)}}{3 \text{ volumes } + 4 \text{ volumes}}$$

From the equation, we see that one volume of $\mathrm{C_3H_8}$ will react with five volumes of $\mathrm{O_2}$:

$$2.7 \cancel{\text{ L}}\ \mathrm{C_3H_8} \times \frac{5 \text{ L } \mathrm{O_2}}{1\ \cancel{\text{L}}\mathrm{C_3H_8}} = 13.5 \text{ L } \mathrm{O_2}$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8.

Exercise 7.4.7

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at 0 °C and 1 atm. How many tanks of oxygen, each providing 7.00×10^3 L of O_2 at 0 °C and 1 atm, will be required to burn the acetylene?

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$

Answer available at the end of this section.

Example 7.4.8: Volumes of Reacting Gases

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of $H_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2?

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g)}$$

Solution

Because equal volumes of H_2 and NH_3 contain equal numbers of molecules and each three molecules of H_2 that react produce two molecules of NH_3, the ratio of the volumes of H_2 and NH_3 will be equal to 3:2. Two volumes of NH_3, in this case in units of billion ft^3, will be formed from three volumes of H_2:

$$683 \text{ billion } ft^3 NH_3 \times \frac{3 \text{ billion } ft^3 H_2}{2 \text{ billion } ft^3 NH_3} = 1.02 \times 10^3 \text{ billion } ft^3 H_2$$

The manufacture of 683 billion ft^3 of NH_3 required 1020 billion ft^3 of H_2. (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

Exercise 7.4.8

What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, $C_2H_4(g)$, measured under the same conditions of temperature and pressure? The products are CO_2 and water vapor.

Answer available at the end of this section.

Example 7.4.9: Volume of Gaseous Product

What volume of hydrogen at 27 °C and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?

$$\mathrm{2\,Ga\,(s) + 6\,HCl\,(aq) \longrightarrow 2\,GaCl_3\,(aq) + 3\,H_2\,(g)}$$

Solution

Convert the provided mass of the limiting reactant, Ga, to moles of hydrogen produced:

$$8.88 \ \cancel{\text{g Ga}} \times \frac{1 \ \cancel{\text{mol Ga}}}{69.723 \ \cancel{\text{g Ga}}} \times \frac{3 \text{ mol H}_2}{2 \ \cancel{\text{mol Ga}}} = 0.191 \text{ mol H}_2$$

Convert the provided temperature and pressure values to appropriate units (K and atm, respectively), and then use the molar amount of hydrogen gas and the ideal gas equation to calculate the volume of gas:

$$V = \left(\frac{nRT}{P}\right) = \frac{0.191 \ \cancel{\text{mol}} \times 0.08206 \text{ L } \cancel{\text{atm mol}}^{-1}\text{K}^{-1} \times 300 \text{ K}}{0.951 \ \cancel{\text{atm}}} = 4.94 \text{ L}$$

Exercise 7.4.9

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at 343 °C and 1.21 atm is produced by burning 1.00 kg of sulfur in excess oxygen?

Answer available at the end of this section.

How Sciences Interconnect: Greenhouse Gases and Climate Change

The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost $\frac{1}{3}$ is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. Most if this IR radiation, however, is absorbed by certain atmospheric gases, effectively trapping heat within the atmosphere in a phenomenon known as the greenhouse effect. This effect maintains global temperatures within the range needed to sustain life on earth. Without our atmosphere, the earth's average temperature would be lower by more than 30 °C (nearly 60 °F). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth's climate (Figure 7.4.6).

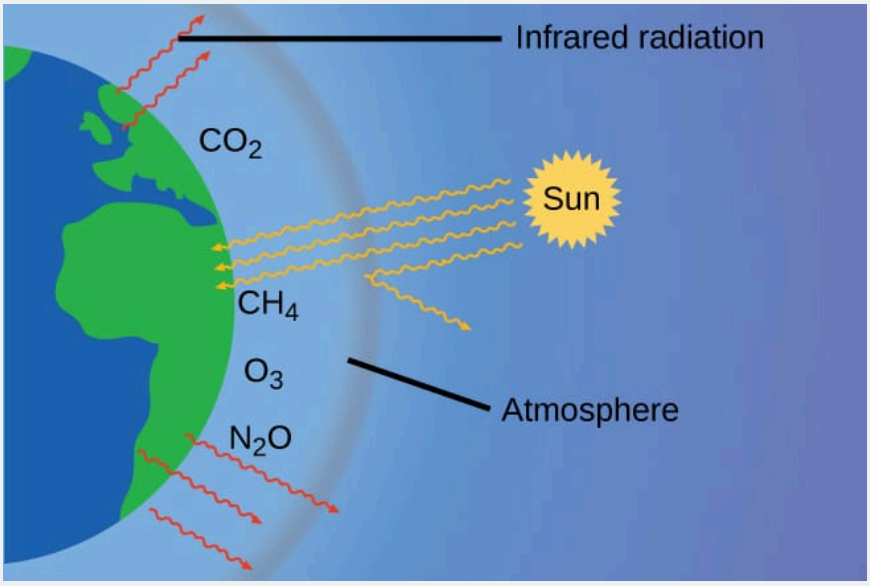


Figure 7.4.6: Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events.

There is strong evidence from multiple sources that higher atmospheric levels of CO2 are caused by human activity, with fossil fuel burning accounting for about $\frac{3}{4}$ of the recent increase in CO2. Reliable data from ice cores reveals that CO2 concentration in the atmosphere is at the highest level in the past 800,000 years; other evidence indicates that it may be at its highest level in 20 million years. In recent years, the CO2 concentration has increased preindustrial levels of ~280 ppm to more than 400 ppm today (Figure 7.4.7).

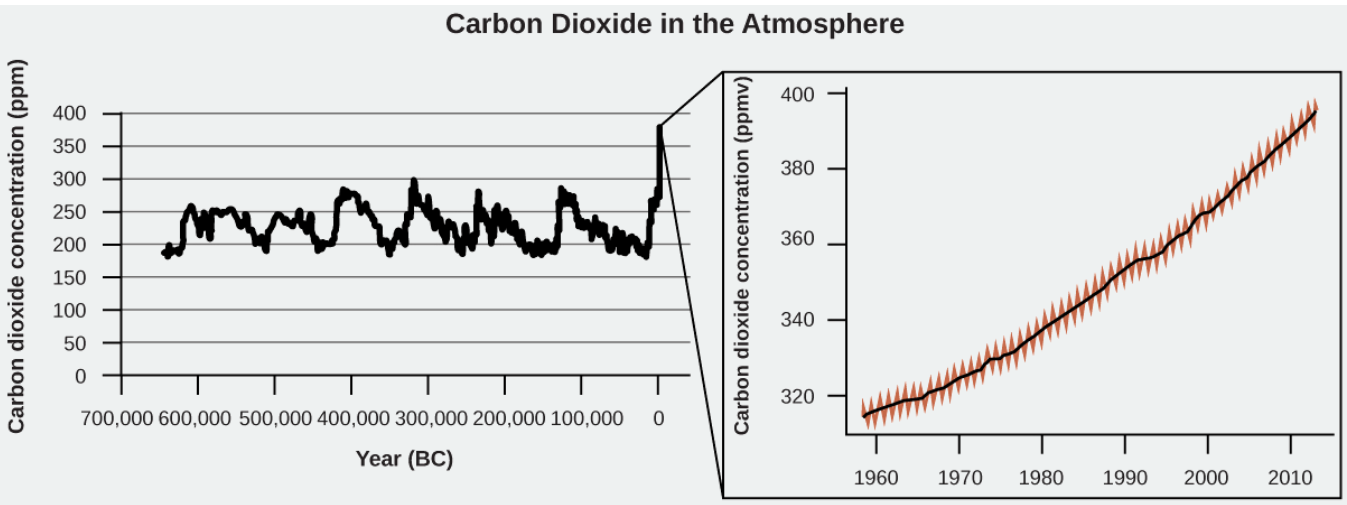


Figure 7.4.7: CO_2 levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years.

Link to Learning

Click here to see a 2-minute video explaining greenhouse gases and global warming.

Portrait of a Chemist: Susan Solomon

Atmospheric and climate scientist Susan Solomon (Figure 7.4.8) is the author of one of *The New York Times* books of the year (*The Coldest March*, 2001), one of Time magazine's 100 most influential people in the world (2008), and a working group leader of the Intergovernmental Panel on Climate Change (IPCC), which was the recipient of the 2007 Nobel Peace Prize. She helped determine and explain the cause of the formation of the ozone hole over Antarctica, and has authored many important papers on climate change. She has been awarded the top scientific honors in the US and France (the National Medal of Science and the Grande Medaille, respectively), and is a member of the National Academy of Sciences, the Royal Society, the French Academy of Sciences, and the European Academy of Sciences. Formerly a professor at the University of Colorado, she is now at MIT, and continues to work at NOAA.



Figure 7.4.8: Susan Solomon's research focuses on climate change and has been instrumental in determining the cause of the ozone hole over Antarctica. (credit: National Oceanic and Atmospheric Administration)

For more information, watch this video about Susan Solomon.

Footnotes

- 2"Quotations by Joseph-Louis Lagrange," last modified February 2006, accessed February 10, 2015, www-history.mcs.st-andrews.ac.../Lagrange.html

Answers

Exercise 7.4.1

d = 0.0847 g/L

Exercise 7.4.2

Empirical formula, CH; Molecular formula, C_2H_2

Exercise 7.4.3

124 g/mol P_4

Exercise 7.4.4

1.137 atm

Exercise 7.4.5

1.87 atm

Exercise 7.4.6

0.537 L

Exercise 7.4.7

3.34 tanks (2.34×10^4 L)

Exercise 7.4.8

51.0 L

Exercise 7.4.9

1.30×10^3 L

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7.5: The Kinetic-Molecular Theory

Learning Objectives

By the end of this section, you will have the background information to help you to be able to:

- Apply the principles of kinetic-molecular theory to describe the relative effusion rates of gases and the deviations of gases from ideal.

The **kinetic molecular theory** (KMT) is a simple microscopic model that effectively explains the origin of the gas laws described in previous sections of this chapter. This theory is based on the following five postulates described here. (Note: The term "molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, traveling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increases. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container. Therefore, pressure increases.
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease the both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume volume of a given amount of gas at a given temperature is decreased (that is, if the gas is *compressed*), the molecules will be exposed to a decreased container wall area. Collisions with the container wall will therefore occur more frequently and the pressure exerted by the gas will increase (Figure 7.5.1).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions (Figure 7.5.1).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.

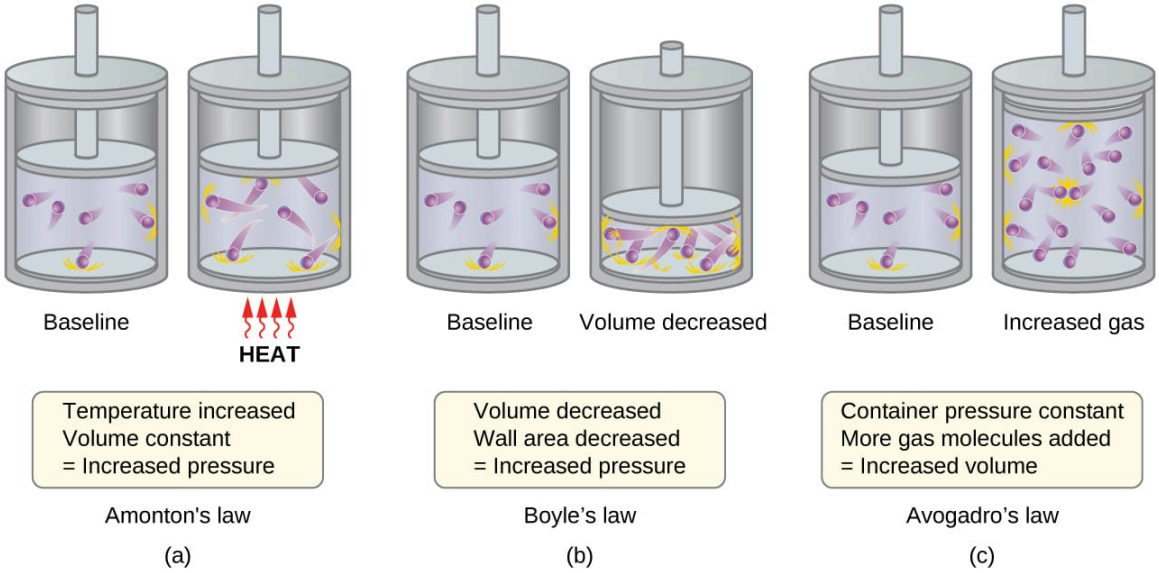


Figure 7.5.1: (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

Molecular Speeds and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at speeds and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed (Figure 7.5.2).

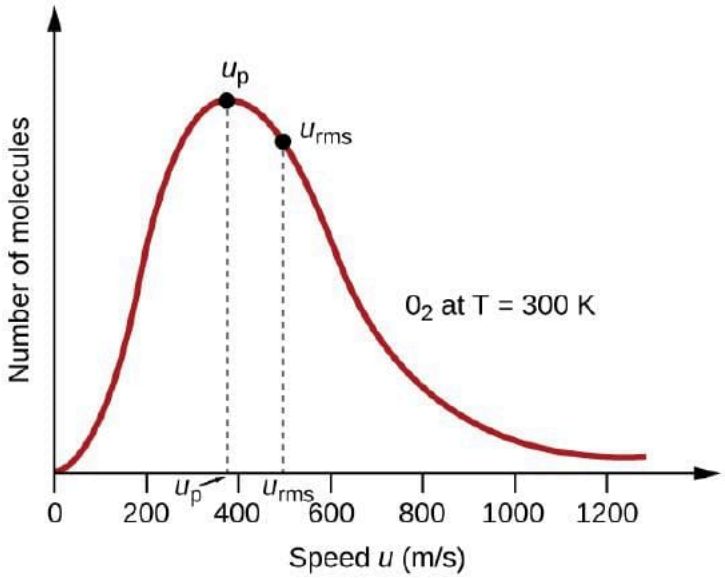


Figure 7.5.2: The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p, is a little less than 400 m/s, while the root mean square speed, u_{rms}, is closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:

$$KE = \frac{1}{2}mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules (J = kg m^2 s^{-2}). To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the root mean square speed of a particle, u_{rms}, is defined as the square root of the average of the squares of the speeds with n = the number of particles:

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \ldots}{n}}$$

The average kinetic energy for a mole of particles, KE_{avg}, is then equal to:

$$KE_{avg} = \frac{1}{2}Mu_{rms}^2$$

where M is the molar mass expressed in units of kg/mol. The KE_{avg} of a mole of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

$$KE_{avg} = \frac{3}{2}RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J/mol · K (8.314 kg $m^2s^{-2}mol^{-1}K^{-1}$). These two separate equations for KE_{avg} may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\frac{1}{2}Mu_{rms}^2 = \frac{3}{2}RT$$

with

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

Example 7.5.1: Calculation of u_{rms}

Calculate the root-mean-square speed for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

$$30^{\circ}C + 273 = 303K$$

Determine the molar mass of nitrogen in kilograms:

Extra close brace or missing open brace

Replace the variables and constants in the root-mean-square speed equation, replacing Joules with the equivalent kg m^2s^{-2}:

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$u_{rms} = \sqrt{\frac{3(8.314J/molK)(303K)}{(0.028kg/mol)}} = \sqrt{2.70 \times 10^5 m^2 s^{-2}} = 519m/s$$

Exercise 7.5.1

Calculate the root-mean-square speed for a mole of oxygen molecules at –23 °C.

Answer available at the end of this section.

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behavior is illustrated for nitrogen gas in Figure 7.5.3.

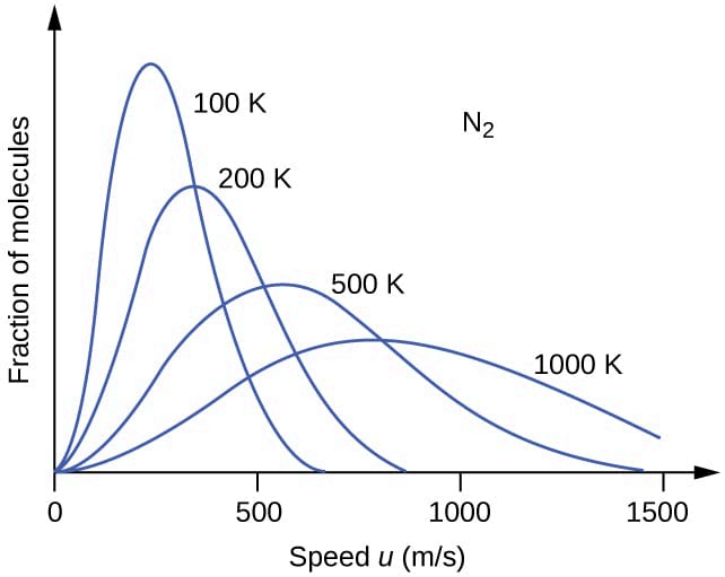


Figure 7.5.3: The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms}, with a speed distribution that peaks at relatively higher speeds. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms}, and a speed distribution that peaks at relatively lower speeds. This trend is demonstrated by the data for a series of noble gases shown in Figure 7.5.4.

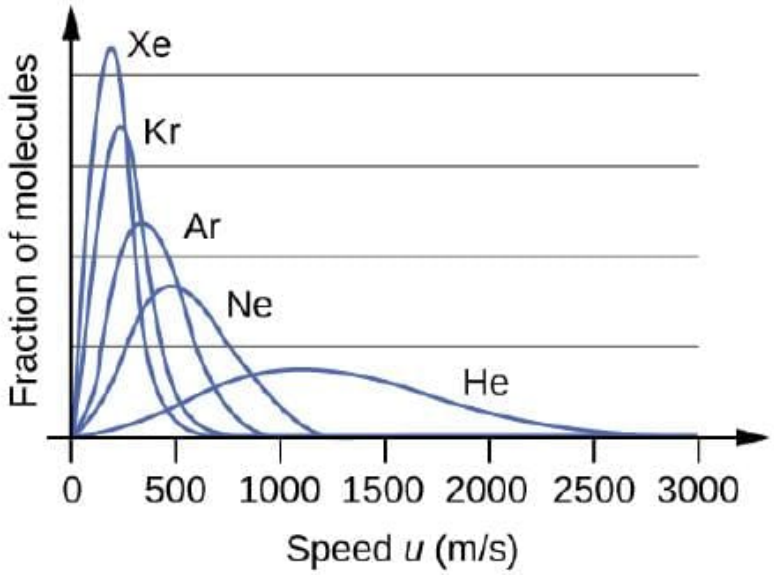


Figure 7.5.4: molecular speed is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

Link to Learning

The gas simulator may be used to examine the effect of temperature on molecular speeds. Examine the simulator's "energy histograms" (molecular speed distributions) and "species information" (which gives average speed values) for molecules of different masses at various temperatures.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II

According to Graham's law, the molecules of a gas are in rapid motion and the molecules themselves are small. The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates.

The rate of effusion of a gas depends directly on the (average) speed of its molecules:

$$\text{effusion rate } \propto u_{\text{rms}}$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$M = \frac{3RT}{u_{rms}^2} = \frac{3RT}{\bar{u}^2}$$

$$\frac{\text{effusion rate } A}{\text{effusion rate } B} = \frac{u_{rmsA}}{u_{rmsB}} = \frac{\sqrt{\frac{3RT}{M_A}}}{\sqrt{\frac{3RT}{M_B}}} = \sqrt{\frac{M_B}{M_A}}$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham's law.

Answers

Exercise 7.5.1

441 m/s

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7.6: Effusion and Diffusion of Gases

Learning Objectives

By the end of this section, you will have the background information to help you to be able to:

- Apply the principles of kinetic-molecular theory to describe the relative effusion rates of gases and the deviations of gases from ideal.

If you have ever been in a room when a piping hot pizza was delivered, you have been made aware of the fact that gaseous molecules can quickly spread throughout a room, as evidenced by the pleasant aroma that soon reaches your nose. Although gaseous molecules travel at tremendous speeds (hundreds of meters per second), they collide with other gaseous molecules and travel in many different directions before reaching the desired target. At room temperature, a gaseous molecule will experience billions of collisions per second. The **mean free path** is the average distance a molecule travels between collisions. The mean free path increases with decreasing pressure; in general, the mean free path for a gaseous molecule will be hundreds of times the diameter of the molecule

In general, we know that when a sample of gas is introduced to one part of a closed container, its molecules very quickly disperse throughout the container; this process by which molecules disperse in space in response to differences in concentration is called **diffusion** (shown in Figure 7.6.1). The gaseous atoms or molecules are, of course, unaware of any concentration gradient, they simply move randomly—regions of higher concentration have more particles than regions of lower concentrations, and so a net movement of species from high to low concentration areas takes place. In a closed environment, diffusion will ultimately result in equal concentrations of gas throughout, as depicted in Figure 7.6.1. The gaseous atoms and molecules continue to move, but since their concentrations are the same in both bulbs, the rates of transfer between the bulbs are equal (no *net* transfer of molecules occurs).

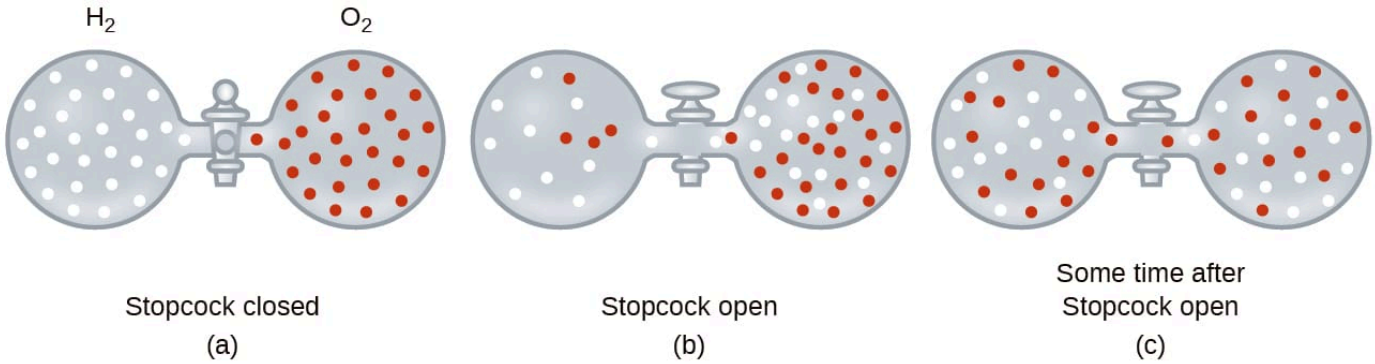


Figure 7.6.1: (a) Two gases, H_2 and O_2, are initially separated. (b) When the stopcock is opened, they mix together. The lighter gas, H_2, passes through the opening faster than O_2, so just after the stopcock is opened, more H_2 molecules move to the O_2 side than O_2 molecules move to the H_2 side. (c) After a short time, both the slower-moving O_2 molecules and the faster-moving H_2 molecules have distributed themselves evenly on both sides of the vessel.

We are often interested in the **rate of diffusion**, the amount of gas passing through some area per unit time:

$$\text{rate of diffusion} = \frac{\text{amount of gas passing through an area}}{\text{unit of time}}$$

The diffusion rate depends on several factors: temperature; the mass of the atoms or molecules; the concentration gradient (the increase or decrease in concentration from one point to another); the amount of surface area available for diffusion; and the distance the gas particles must travel. Note also that the time required for diffusion to occur is inversely proportional to the rate of diffusion, as shown in the rate of diffusion equation.

A process involving movement of gaseous species similar to diffusion is **effusion**, the escape of gas molecules through a tiny hole such as a pinhole in a balloon into a vacuum (Figure 7.6.2). Although diffusion and effusion rates both depend on the molar

mass of the gas involved, their rates are not equal; however, the ratios of their rates are the same.

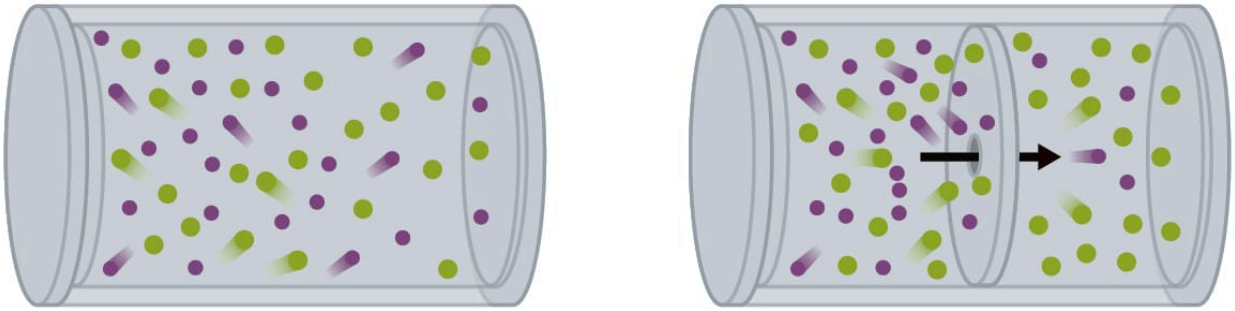


Figure 7.6.2: Diffusion involves the unrestricted dispersal of molecules throughout space due to their random motion. When this process is restricted to passage of molecules through very small openings in a physical barrier, the process is called effusion.

If a mixture of gases is placed in a container with porous walls, the gases effuse through the small openings in the walls. The lighter gases pass through the small openings more rapidly (at a higher rate) than the heavier ones (Figure 7.6.3). In 1832, Thomas Graham studied the rates of effusion of different gases and formulated **Graham's law of effusion**: *The rate of effusion of a gas is inversely proportional to the square root of the mass of its particles*:

$$\text{rate of effusion} \propto \frac{1}{\sqrt{M}}$$

This means that if two gases A and B are at the same temperature and pressure, the ratio of their effusion rates is inversely proportional to the ratio of the square roots of the masses of their particles:

$$\frac{\text{rate of effusion of } A}{\text{rate of effusion of } B} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$

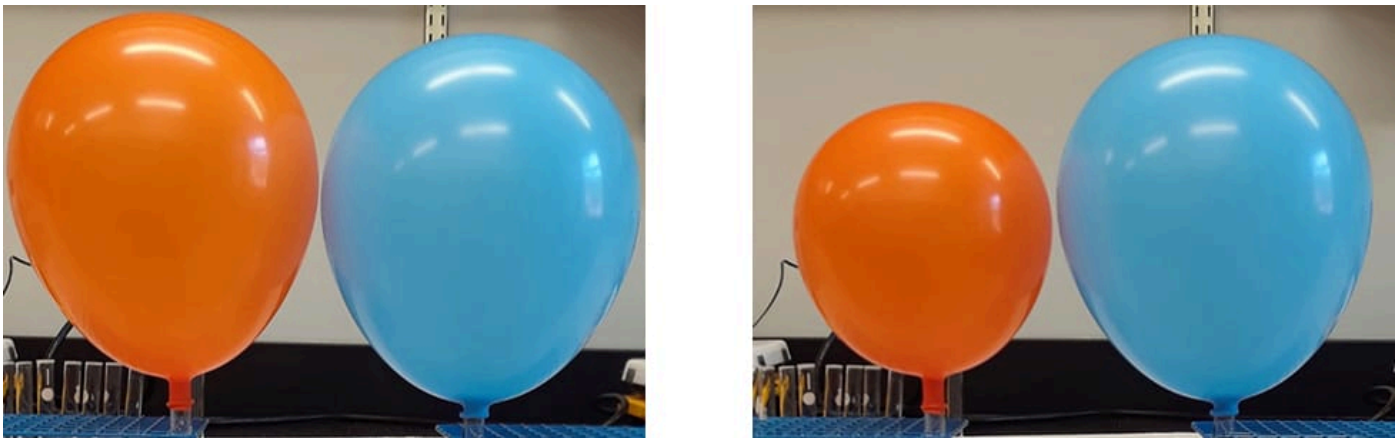


Figure 7.6.3: The left photograph shows two balloons inflated with different gases, helium (orange) and argon (blue).The right-side photograph shows the balloons approximately 12 hours after being filled, at which time the helium balloon has become noticeably more deflated than the argon balloon, due to the greater effusion rate of the lighter helium gas. (credit: modification of work by Paul Flowers)

Example 7.6.1: Applying Graham's Law to Rates of Effusion

Calculate the ratio of the rate of effusion of hydrogen to the rate of effusion of oxygen.

Solution

From Graham's law, we have:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{\sqrt{32 gmol^{-1}}}{\sqrt{2 gmol^{-1}}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

Hydrogen effuses four times as rapidly as oxygen.

Exercise 7.6.1

At a particular pressure and temperature, nitrogen gas effuses at the rate of 79 mL/s. Under the same conditions, at what rate will sulfur dioxide effuse?

Answer available at the end of this section.

Example 7.6.2: Effusion Time Calculations

It takes 243 s for 4.46 10^{-5} mol Xe to effuse through a tiny hole. Under the same conditions, how long will it take 4.46 10^{-5} mol Ne to effuse?

Solution

It is important to resist the temptation to use the times directly, and to remember how rate relates to time as well as how it relates to mass. Recall the definition of rate of effusion:

$$\text{rate of effusion } = \frac{\text{amount of gas transferred}}{\text{time}}$$

and combine it with Graham's law:

$$\frac{\text{rate of effusion of gas Xe}}{\text{rate of effusion of gas Ne}} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}}$$

To get:

$$\frac{\frac{\text{amount of Xe transferred}}{\text{time for Xe}}}{\frac{\text{amount of Ne transferred}}{\text{time for Ne}}} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}}$$

Noting that *amount of A = amount of B*, and solving for *time for Ne*:

$$\frac{\frac{\text{amount of } Xe}{\text{time for Xe}}}{\frac{\text{amount of } Ne}{\text{time for } Ne}} = \frac{\text{time for } Ne}{\text{time for Xe}} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}}$$

and substitute values:

$$\frac{\text{time for Ne}}{243 s} = \sqrt{\frac{20.2 \cancel{\text{ g mol}}}{131.3 \cancel{\text{ g mol}}}} = 0.392$$

Finally, solve for the desired quantity:

$$\text{time for } Ne = 0.392 \times 243 \text{ s} = 95.3 \text{ s}$$

Note that this answer is reasonable: Since Ne is lighter than Xe, the effusion rate for Ne will be larger than that for Xe, which means the time of effusion for Ne will be smaller than that for Xe.

Exercise 7.6.2

A party balloon filled with helium deflates to $\frac{2}{3}$ of its original volume in 8.0 hours. How long will it take an identical balloon filled with the same number of moles of air (M = 28.2 g/mol) to deflate to $\frac{1}{2}$ of its original volume?

Answer available at the end of this section.

Example 7.6.3: Determining Molar Mass Using Graham's Law

An unknown gas effuses 1.66 times more rapidly than CO_2. What is the molar mass of the unknown gas? Can you make a reasonable guess as to its identity?

Solution

From Graham's law, we have:

$$\frac{\text{rate of effusion of Unknown}}{\text{rate of effusion of } CO_2} = \frac{\sqrt{M_{CO_2}}}{\sqrt{M_{\text{Unknown}}}}$$

Plug in known data:

$$\frac{1.66}{1} = \frac{\sqrt{44.0 g/mol}}{\sqrt{M_{\text{Unknown}}}}$$

Solve:

$$M_{\text{Unknown}} = \frac{44.0 g/mol}{(1.66)^2} = 16.0 g/mol$$

The gas could well be CH_4, the only gas with this molar mass.

Exercise 7.6.3

Hydrogen gas effuses through a porous container 8.97-times faster than an unknown gas. Estimate the molar mass of the unknown gas.

Answer available at the end of this section.

How Sciences Interconnect: Use of Diffusion for Nuclear Energy Applications: Uranium Enrichment

Gaseous diffusion has been used to produce enriched uranium for use in nuclear power plants and weapons. Naturally occurring uranium contains only 0.72% of ^{235}U, the kind of uranium that is "fissile," that is, capable of sustaining a nuclear fission chain reaction. Nuclear reactors require fuel that is 2–5% ^{235}U, and nuclear bombs need even higher concentrations. One way to enrich uranium to the desired levels is to take advantage of Graham's law. In a gaseous diffusion enrichment plant, uranium hexafluoride (UF_6, the only uranium compound that is volatile enough to work) is slowly pumped through large cylindrical vessels called diffusers, which contain porous barriers with microscopic openings. The process is one of diffusion because the other side of the barrier is not evacuated. The $^{235}UF_6$ molecules have a higher average speed and diffuse through the barrier a little faster than the heavier $^{238}UF_6$ molecules. The gas that has passed through the barrier is slightly enriched in $^{235}UF_6$ and the residual gas is slightly depleted. The small difference in molecular weights between $^{235}UF_6$ and $^{238}UF_6$ only about 0.4% enrichment, is achieved in one diffuser (Figure 7.6.4). But by connecting many diffusers in a sequence of stages (called a cascade), the desired level of enrichment can be attained.

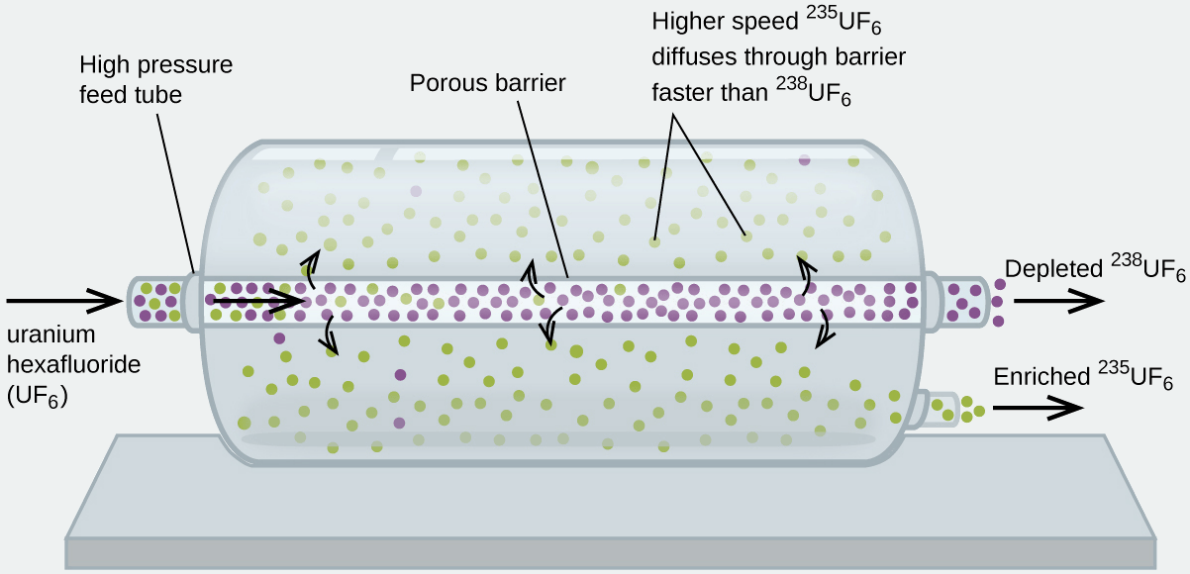


Figure 7.6.4: In a diffuser, gaseous UF_6 is pumped through a porous barrier, which partially separates $^{235}UF_6$ from $^{238}UF_6$ The UF_6 must pass through many large diffuser units to achieve sufficient enrichment in ^{235}U.

The large scale separation of gaseous $^{235}UF_6$ from $^{238}UF_6$ was first done during the World War II, at the atomic energy installation in Oak Ridge, Tennessee, as part of the Manhattan Project (the development of the first atomic bomb). Although the theory is simple, this required surmounting many daunting technical challenges to make it work in practice. The barrier must have tiny, uniform holes (about 10^{-6} cm in diameter) and be porous enough to produce high flow rates. All materials (the barrier, tubing, surface coatings, lubricants, and gaskets) need to be able to contain, but not react with, the highly reactive and corrosive UF_6.

Because gaseous diffusion plants require very large amounts of energy (to compress the gas to the high pressures required and drive it through the diffuser cascade, to remove the heat produced during compression, and so on), it is now being replaced by gas centrifuge technology, which requires far less energy. A current hot political issue is how to deny this technology to Iran, to prevent it from producing enough enriched uranium for them to use to make nuclear weapons.

Answers

Exercise 7.6.1
52 mL/s

Exercise 7.6.2
32 h

Exercise 7.6.3
163 g/mol

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7.7: Non-Ideal Gas Behavior

Learning Objectives

By the end of this section, you will have the background information to help you to be able to:

- Apply the principles of kinetic-molecular theory to describe the relative effusion rates of gases and the deviations of gases from ideal.

Thus far, the ideal gas law, $PV = nRT$, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

We use a ratio called the **compressibility factor** (Z) to describe whether or not a gas is ideal. This ratio is calculated as:

$$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{PV_m}{RT}\right)_{\text{measured}}$$

Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior. Figure 7.7.1 shows plots of Z over a large pressure range for several common gases.

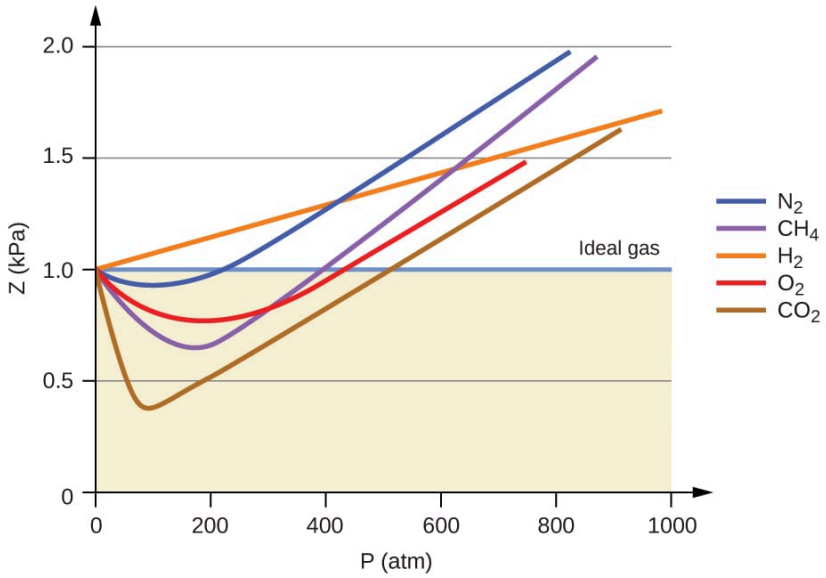


Figure 7.7.1: A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.

As is apparent from Figure 7.7.1, **the ideal gas law does not describe gas behavior well at relatively high pressures**. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other (Postulates 2 and 4 of kinetic molecular theory) In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas. The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) (Figure 7.7.2). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.

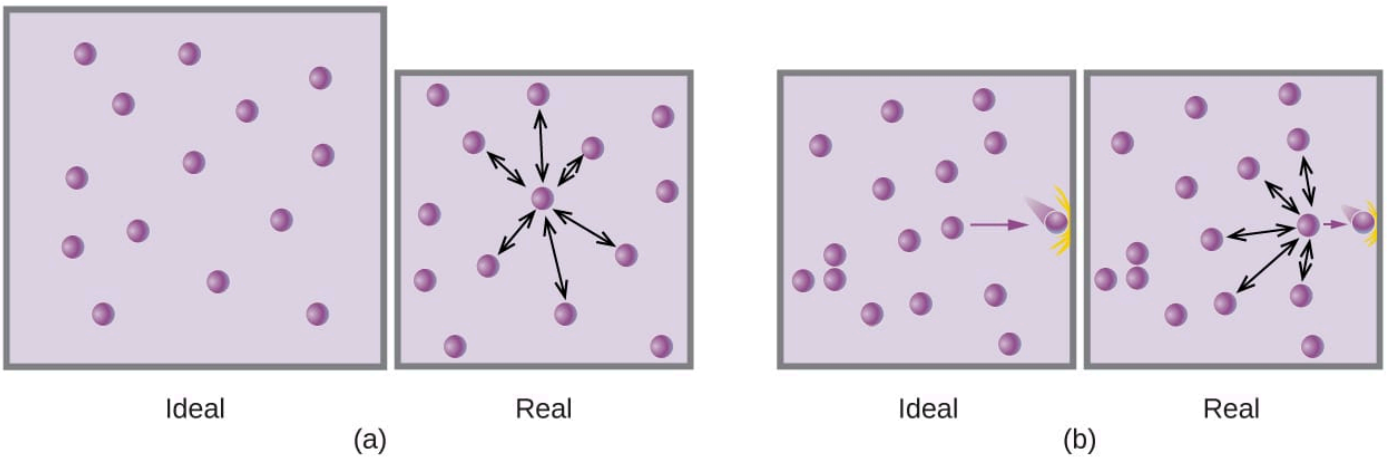


Figure 7.7.2: (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted at constant volume compared to an ideal gas.

There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The **van der Waals equation** improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$PV = nRT \longrightarrow \left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Correction for molecular attraction

Correction for volume of molecules

The constant *a* corresponds to the strength of the attraction between molecules of a particular gas, and the constant *b* corresponds to the size of the molecules of a particular gas. The "correction" to the pressure term in the ideal gas law is

Table 7.7.1: Values of van der Waals Constants for Some Common Gases

Gas	*a* (L^2 atm/mol^2)	*b* (L/mol)
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427
H_2O	5.46	0.0305
He	0.0342	0.0237
CCl_4	20.4	0.1383

At low pressures, the correction for intermolecular attraction, *a*, is more important than the one for molecular volume, *b*. At

high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by $PV = nRT$ over a small range of pressures. This behavior is reflected by the “dips” in several of the compressibility curves shown in Figure 7.7.1. The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing P). At very high pressures, the gas becomes less compressible (Z increases with P), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

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8: THERMODYNAMICS DESCRIBES THE FLOW OF ENERGY

8.1: Overview and Objectives

8.2: Energy Changes in Chemical Reactions

8.3: Enthalpy and Reactions

8.4: Thermodynamics and Work

8.5: The First Law of Thermodynamics

8.6: Direction of Heat Flow and Enthalpy of Reaction

8.7: Calorimetry

8.8: Hess's Law

8.9: Heats of Formation

8.10: The Second Law of Thermodynamics

8.11: Entropy Changes and the Third Law of Thermodynamics

8.12: Spontaneity is Related to Entropy

8.13: Entropy

8.14: Free Energy is a Good Predictor of Spontaneity

8.15: Temperature Dependence of Free Energy

8.16: Free Energy

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8.1: Overview and Objectives

> Zeroth: You must play the game.
> First: You can't win.
> Second: You can't break even.
> Third: You can't quit the game.
>
> (Common scientific joke summarizing the laws of thermodynamics)

The word *thermodynamics* contains within it the Greek roots *thermo*, regarding "heat," and *dynamis*, regarding "force" or "motion." This field of science grew up around the quest to build a better steam engine, with the hope of turbocharging technological advances that were driving the industrial revolution. Scientists were shocked and a more than a little frustrated to find that all of their experiments and theoretical underpinnings led to the inevitable conclusion that no matter how good their technology got, fundamental laws of the universe - particularly the Second Law of Thermodynamics - would prevent them from producing complete, 100% conversion of heat to work.

The same principles that describe the underlying physics of steam engines also govern chemical processes. In this chapter, we'll look at how heat flows from hot bodies to cold, and how we can take advantage of that to determine some fundamental properties of chemical processes.

Chapter Objectives

- Classify reactions as endothermic/exothermic (ΔH), entropically favored/entropically disfavored (ΔS), or spontaneous/nonspontaneous (ΔG) given relevant thermodynamic data, balanced chemical equations, and/or a reaction coordinate diagram.
- Use appropriate mathematical expressions (stoichiometry, Hess's Law) and relevant experimental data (bond energies, formation ΔH/ΔG, standard molar entropy, definition of free energy) to calculate ΔH, ΔS, and ΔG for a chemical reaction.
- Predict how changing temperature, pressure, and/or volume conditions will affect the spontaneity of a physical process or chemical reaction.

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8.2: Energy Changes in Chemical Reactions

Learning Objectives

By the end of this section, you will have background information that helps you to be able to:

- Use the 1st, 2nd, and 3rd laws of thermodynamics to explain key relationships between heat, work, and physical or chemical processes.

Because energy takes many forms, only some of which can be seen or felt, it is defined by its effect on matter. For example, microwave ovens produce energy to cook food, but we cannot see that energy. In contrast, we can see the energy produced by a light bulb when we switch on a lamp. In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 8.2.1). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. Radiant energy is carried by light, microwaves, and radio waves (the other forms of energy are thermal, chemical, nuclear, and electrical). Electrical energy results from the flow of electrically charged particles. The other four forms of energy are radiant, thermal, chemical, and nuclear. results from the flow of electrically charged particles. Nuclear energy is stored in the nucleus of an atom. Chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

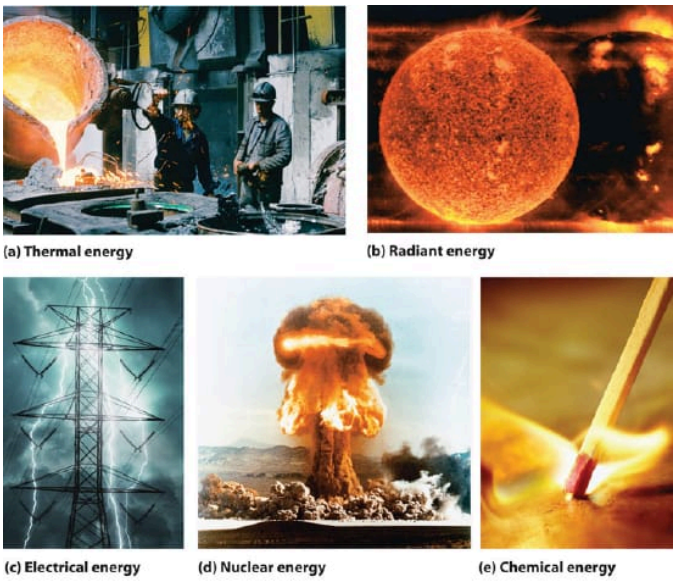


Figure 8.2.1 **Forms of Energy** *(a) Thermal energy results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) Radiant energy (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of electrical energy, which is due to the flow of electrically charged particles. (d) Nuclear energy is released when particles in the nucleus of the atom are rearranged. (e) Chemical energy results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds.*

Electrical energy, nuclear energy, and chemical energy are different forms of potential energy (*PE*)Energy stored in an object because of its relative position or orientation., which is energy stored in an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, kinetic energy (*KE*)Energy due to the motion of an object: $1/2\ mv^2$ where m is the mass of the object and v is its velocity. is energy due to the *motion* of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is then transferred to the object on the ground that it strikes. The electrostatic

attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure 8.2.2) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

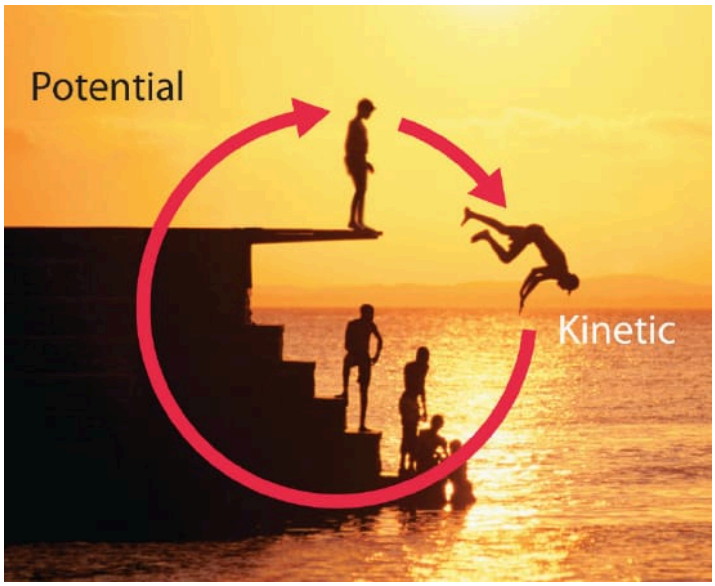


Figure 8.2.2 **Interconversion of Forms of Energy** *When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.*

Although energy can be converted from one form to another, ***the total amount of energy in the universe remains constant***. This is known as the law of conservation of energy or the **First Law of Thermodynamics.** The total amount of energy in the universe remains constant. Energy can be neither created nor destroyed, but it can be converted from one form to another..As you will learn in Chapter 18, the law of conservation of energy is also known as the first law of thermodynamics. ***Energy cannot be created or destroyed.***

Energy, Heat, and Work

One definition of energy is the capacity to do work. The easiest form of work to visualize is mechanical work. The energy required to move an object a distance *d* when opposed by a force *F*, (Figure 8.2.3), which is the energy required to move an object a distance *d* when opposed by a force *F*, such as gravity:

$$\begin{aligned} work &= force \times distance \\ w &= Fd \end{aligned} \tag{8.2.1}$$

Because the force (*F*) that opposes the action is equal to the mass (*m*) of the object times its acceleration (*a*), we can also write Equation 9.1.1 as follows:Recall from Chapter 1 that weight is a force caused by the gravitational attraction between two masses, such as you and Earth.

$$\begin{aligned} work &= mass \times acceleration \times distance \\ w &= mad \end{aligned} \tag{8.2.2}$$

Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an

elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the force of gravity. The amount of work done (*w*) and thus the energy required depends on three things: (1) the height of the second floor (the distance *d*); (2) your mass, which must be raised that distance against the downward acceleration due to gravity; and (3) your path, as you will learn in Section 9.2.

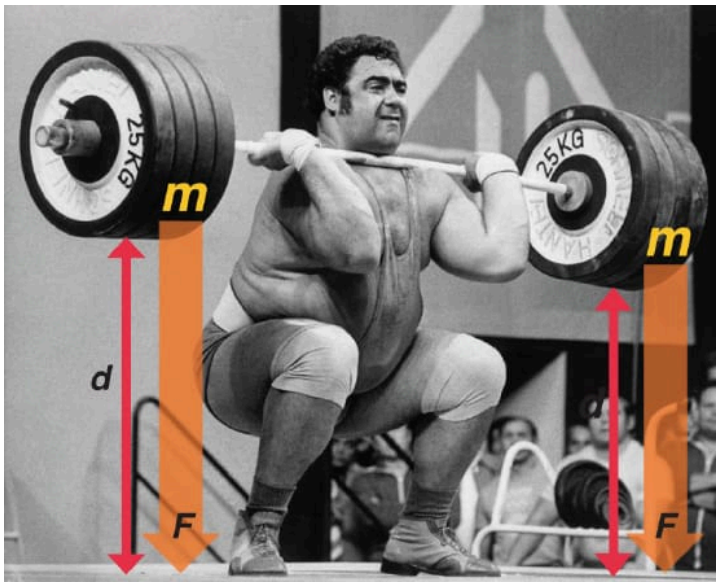


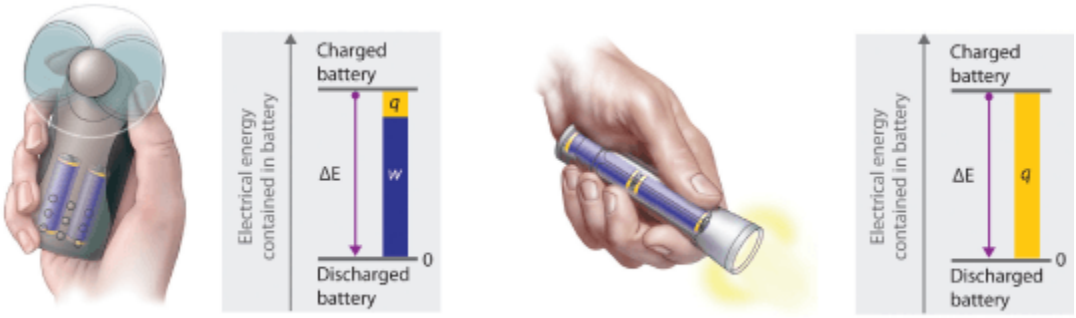
Figure 8.2.3 **An Example of Mechanical Work** *One form of energy is mechanical work, the energy required to move an object of mass m a distance d when opposed by a force F, such as gravity.*

In contrast, **heat (*q*)** is thermal energy that can be transformed from an object at one temperature to an object at another temperature. is thermal energy that can be transferred from an object at one temperature to an object at another temperature. The net transfer of thermal energy stops when the two objects reach the same temperature.

The energy of an object can be changed only by the transfer of energy to or from another object in the form of heat, As you learned, hot objects can also lose energy as radiant energy, such as heat or light. This energy is converted to heat when it is absorbed by another object. Hence radiant energy is equivalent to heat. work performed on or by the object, or some combination of heat and work. Consider, for example, the energy stored in a fully charged battery. As shown in Figure 8.2.4, this energy can be used primarily to perform work (e.g., running an electric fan) or to generate light and heat (e.g., illuminating a light bulb). When the battery is fully discharged in either case, the total change in energy is the same, even though the fraction released as work or heat varies greatly. The sum of the heat produced and the work performed equals the change in energy (ΔE):

$$\begin{aligned} EnergyChange(\Delta E) &= work + heat \\ \Delta E &= q + w \end{aligned} \tag{8.2.3}$$

Energy can be transferred only in the form of heat, work performed on or by an object, or some combination of heat and work.



(a) Energy (*E*) released as work (*w*) and heat (*q*)

(b) Energy (*E*) released as heat (*q*) and light

Figure 8.2.4 **Energy Transfer:** *Discharging a fully charged battery releases the same amount of energy whether the battery is used to run a fan (a) or illuminate a light bulb (b). In (a), most of the energy is used to perform work, which turns the blades of the fan and thus moves the air; only a small portion of the energy is released as heat by the electric motor. In (b), all the energy is released as heat and light; no work is done.*

Energy is an extensive property of matter—for example, the amount of **thermal energy** in an object is proportional to both its mass and its temperature. (For more information on the properties of matter, see Chapter 1) A water heater that holds 150 L of water at 50°C contains much more thermal energy than does a 1 L pan of water at 50°C. Similarly, a bomb contains much more chemical energy than does a firecracker. We now present a more detailed description of kinetic and potential energy.

Energy Units

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J). The joule is named after the British physicist James Joule (1818–1889), an early worker in the field of energy. is defined as 1 kilogram·meter^2/second^2 (kg·m^2/s^2). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10^3 J). For example, the kinetic energy of a 1360 kg car traveling at 26.8 m/s is 4.88 × 10^5 J or 4.88 × 10^2 kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.

Energy can also be expressed in the non-SI units of calories (cal)A non-SI unit of energy: 1 cal = 4.184 J exactly., where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5°C to 15.5°C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1°C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0°C–100°C. The name is derived from the Latin *calor*, meaning “heat.” Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$$1 \ \ cal = 4.184 \ \ Jexactly$$

$$1 \ \ J = 0.2390 \ \ cal$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information, addressed in Section 9.7 .

Contributors

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Modified by Joshua Halpern

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8.3: Enthalpy and Reactions

Learning Objectives

- To know the key features of a state function.
- To understand why enthalpy is an important state function.

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8.4: Thermodynamics and Work

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use the 1st, 2nd, and 3rd laws of thermodynamics to explain key relationships between heat, work, and physical or chemical processes.

Let's summarize some important concepts from previous sections of this chapter.

- A **system** is that part of the universe in which we are interested, such as a mixture of gases in a glass bulb or a solution of substances in a flask.
- The **surroundings** are everything else—the rest of the *universe*.
- We can therefore state the following: $$ system + surroundings = universe \tag{18.1.1}$$
- A **closed system**, such as the contents of a sealed jar, cannot exchange matter with its surroundings, whereas an **open system** can; in this case, we can convert a closed system (the jar) to an open system by removing the jar's lid.
- A **state function** is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Thus a change in a state function depends on only the difference between the initial and final states, not the pathway used to go from one to the other. To help understand the concept of a state function, imagine a person hiking up a mountain (Figure 18.1.1). If the person is well trained and fit, he or she may be able to climb almost vertically to the top (path A), whereas another less athletic person may choose a path that winds gradually to the top (path B). If both hikers start from the same point at the base of the mountain and end up at the same point at the top, their *net change in altitude* will be the same regardless of the path chosen. Hence altitude is a state function. On the other hand, a person may or may not carry a heavy pack and may climb in hot weather or cold. These conditions would influence changes in the hiker's fatigue level, which depends on the path taken and the conditions experienced. Fatigue, therefore, is not a state function. Thermodynamics is generally concerned with state functions and does not deal with how the change between the initial state and final state occurs.

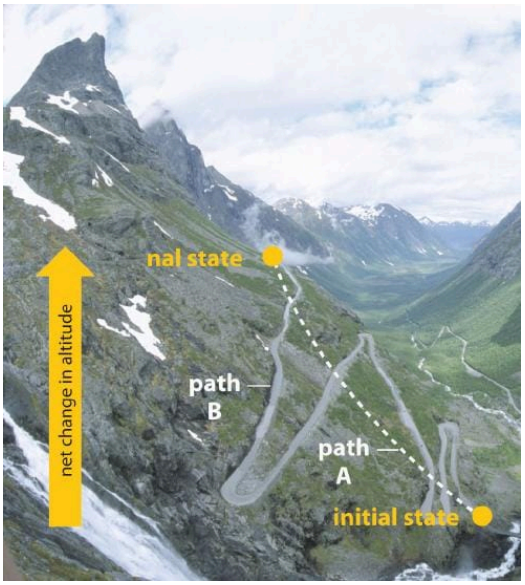


Figure 18.1.1 Altitude Is a State **Function.** When hiking up a mountain, a person may decide to take path A, which is almost vertical, or path B, which gradually winds up to the top. Regardless of the path taken, the net change in altitude going from the initial state (bottom of the climb) to the final state (top of the climb) is the same. Thus altitude is a state function.

The Connections among Work, Heat, and Energy

The internal energy (*E*)A state function that is the sum of the kinetic and potential energies of all a system's components. Although a closed system cannot exchange matter with its surroundings, it can exchange energy with its surroundings in two ways: by doing work or by releasing or absorbing heat—the flow of thermal energy. Work and heat are therefore two distinct ways of changing the internal energy of a system. We defined *work* (*w*) as a force *F* acting through a distance *d*:

$$w = Fd$$

Because work occurs only when an object, such as a person, or a substance, such as water, moves against an opposing force, work requires that a system and its surroundings be connected. In contrast, the flow of *heat*, the transfer of energy due to differences in temperature between two objects, represents a thermal connection between a system and its surroundings. Thus doing work causes a physical displacement, whereas the flow of heat causes a temperature change. The units of work and heat must be the same because both processes result in the transfer of energy. In the SI system, those units are joules (J), the same unit used for energy. There is no difference between an energy change brought about by doing work on a system and an equal energy change brought about by heating it.

The connections among work, heat, and energy were first described by Benjamin Thompson (1753–1814), an American-born scientist who was also known as Count Rumford. While supervising the manufacture of cannons, Rumford recognized the relationship between the amount of work required to drill out a cannon and the temperature of the water used to cool it during the drilling process (Figure 18.1.2). At that time, it was generally thought that heat and work were separate and unrelated phenomena. Hence Rumford's ideas were not widely accepted until many years later, after his findings had been corroborated in other laboratories.

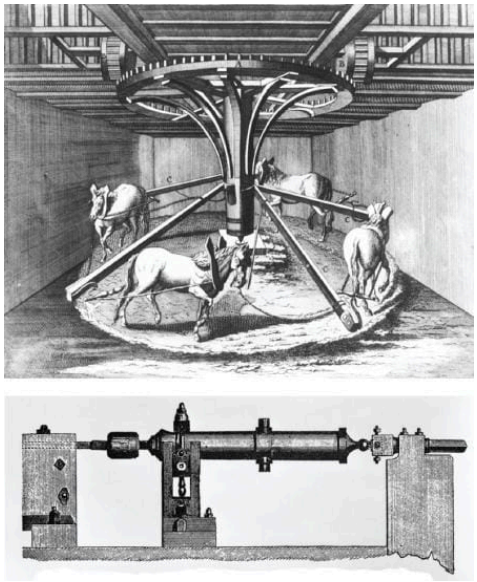


Figure 18.1.2 The Relationship between Heat and **Work** In the 1780s, an American scientist named Benjamin Thompson, also known as Count Rumford, was hired by the Elector of Bavaria to supervise the manufacture of cannons. During the manufacturing process, teams of horses harnessed to a large-toothed wheel supplied the power needed to drill a hole several inches in diameter straight down the center of a solid brass or bronze cylinder, which was cooled by water. Based on his observations, Rumford became convinced that heat and work are equivalent ways of transferring energy.

PV Work

There are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will consider only mechanical work, focusing on the work done during changes in the pressure or the volume of a gas. To describe this *pressure–volume work* (*PV* work), we will use such imaginary oddities as frictionless pistons, which involve no component of resistance, and ideal gases, which have no attractive or repulsive interactions.

Imagine, for example, an ideal gas, confined by a frictionless piston, with internal pressure P_{int} and initial volume V_i (Figure 18.1.3). If $P_{ext} = P_{int}$, the system is at equilibrium; the piston does not move, and no work is done. If the external pressure on

the piston (P_{ext}) is less than P_{int}, however, then the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings; that is, the final volume (V_f) will be greater than V_i. If $P_{ext} > P_{int}$, then the gas will be compressed, and the surroundings will perform work on the system.

If the piston has cross-sectional area A, the external pressure exerted by the piston is, by definition, the force per unit area: $P_{ext} = F/A$. The volume of any three-dimensional object with parallel sides (such as a cylinder) is the cross-sectional area times the height ($V = Ah$). Rearranging to give $F = P_{ext}A$ and defining the distance the piston moves (d) as Δh, we can calculate the magnitude of the work performed by the piston by substituting into Equation 18.1.2:

$$w = Fd = P_{ext}A\Delta h \tag{18.1.3}$$



Figure 18.1.3 *PV* **Work** Using a frictionless piston, if the external pressure is less than P_{int} (a), the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume (V_f) will be greater than V_i. Alternatively, if the external pressure is greater than P_{int} (b), the gas will be compressed, and the surroundings will perform work on the system.

The change in the volume of the cylinder (ΔV) as the piston moves a distance d is $\Delta V = A\Delta h$, as shown in Figure 18.1.4. The work performed is thus

$$w = P_{ext}\Delta V \tag{18.1.4}$$

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m^2) and volume has units of cubic meters, so

$$w = \left(\frac{F}{A}\right)\Delta V = \frac{newton}{m^2 \times m^3}$$

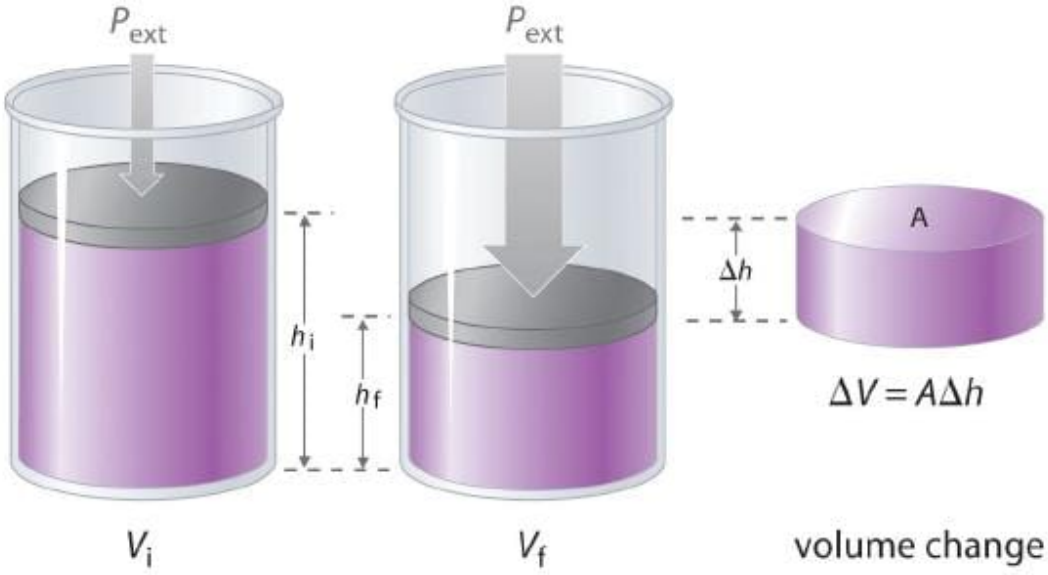


Figure 18.1.4 Work Performed with a Change in Volume The change in the volume (ΔV) of the cylinder housing a piston is $\Delta V = A\Delta h$ as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by $w = P_{ext}\Delta V$.

If we use atmospheres for P and liters for V, we obtain units of L·atm for work. These units correspond to units of energy, as shown

in the different values of the ideal gas constant *R*:

$$R = \frac{0.08206\ L \cdot atm}{mol \cdot K} = \frac{8.314\ J}{mol \cdot K}$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J. (For more information on the ideal gas law, see Chapter 10.)

Whether work is defined as having a positive sign or a negative sign is a matter of convention. In Chapter 9, we defined heat flow *from* a system *to* its surroundings as negative. Using that same sign convention, we define work done *by* a system *on* its surroundings as having a negative sign because it results in a transfer of energy from a system to its surroundings.This is an arbitrary convention and one that is not universally used. Some engineering disciplines are more interested in the work done *on* the surroundings than in the work done *by* the system and therefore use the opposite convention. Because $\Delta V > 0$ for an expansion, Equation 18.4 must be written with a negative sign to describe *PV* work done *by* the system as negative:

$$w = P_{ext}\Delta V$$

The work done by a gas expanding against an external pressure is therefore negative, corresponding to work done *by* a system *on* its surroundings. Conversely, when a gas is compressed by an external pressure, $\Delta V < 0$ and the work is positive because work is being done *on* a system *by* its surroundings.

Suppose, for example, that the system under study is a mass of steam heated by the combustion of several hundred pounds of coal and enclosed within a cylinder housing a piston attached to the crankshaft of a large steam engine. The gas is not ideal, and the cylinder is not frictionless. Nonetheless, as steam enters the engine chamber and the expanding gas pushes against the piston, the piston moves, so useful work is performed. In fact, *PV* work launched the Industrial Revolution of the 19th century and powers the internal combustion engine on which most of us still rely for transportation.

In contrast to internal energy, work is not a state function. We can see this by examining Figure 18.1.5, in which two different, two-step pathways take a gaseous system from an initial state to a final state with corresponding changes in temperature. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1); then its pressure is decreased while the volume remains constant (step 2). In pathway B, the order of the steps is reversed. The temperatures, pressures, and volumes of the initial and final states are identical in both cases, but the amount of work done, indicated by the shaded areas in the figure, is substantially different. As we can see, the amount of work done depends on the pathway taken from (V_1, P_1) to (V_2, P_2), which means that work is not a state function.

Example 18.1.1

A small high-performance internal combustion engine has six cylinders with a total nominal displacement (volume) of 2.40 L and a 10:1 compression ratio (meaning that the volume of each cylinder decreases by a factor of 10 when the piston compresses the air–gas mixture inside the cylinder prior to ignition). How much work in joules is done when a gas in one cylinder of the engine expands at constant temperature against an opposing pressure of 40.0 atm during the engine cycle? Assume that the gas is ideal, the piston is frictionless, and no energy is lost as heat.

Given: final volume, compression ratio, and external pressure

Asked for: work done

Strategy:

A Calculate the final volume of gas in a single cylinder. Then compute the initial volume of gas in a single cylinder from the compression ratio.

B Use Equation 18.1.5 to calculate the work done in liter-atmospheres. Convert from liter-atmospheres to joules.

Solution:

A To calculate the work done, we need to know the initial and final volumes. The final volume is the volume of one of the six cylinders with the piston all the way down: V_f = 2.40 L/6 = 0.400 L. With a 10:1 compression ratio, the volume of the same cylinder

with the piston all the way up is V_i = 0.400 L/10 = 0.0400 L. Work is done by the system on its surroundings, so work is negative.

$$w = -P_{ext}\Delta V = -\left(40.0\ atm\right)\left(0.400\ L - 0.0400\ L\right) = 14.4\ \ L \cdot atm$$

Converting from liter-atmospheres to joules,

$$w = -P_{ext}\Delta V = -\left(14.4\ \cancel{L \cdot atm}\right)\left[101.3J/\left(\cancel{L \cdot atm}\right)\right] = -1.46 \times 10^3\ \ J$$

In the following exercise, you will see that the concept of work is not confined to engines and pistons. It is found in other applications as well.

Exercise

Breathing requires work, even if you are unaware of it. The lung volume of a 70 kg man at rest changed from 2200 mL to 2700 mL when he inhaled, while his lungs maintained a pressure of approximately 1.0 atm. How much work in liter-atmospheres and joules was required to take a single breath? During exercise, his lung volume changed from 2200 mL to 5200 mL on each in-breath. How much additional work in joules did he require to take a breath while exercising?

Answer: –0.500 L·atm, or –50.7 J; –304 J; if he takes a breath every three seconds, this corresponds to 1.4 Calories per minute (1.4 kcal).

Summary

Thermodynamics is the study of the interrelationships among heat, work, and the energy content of a system at equilibrium. The sum of the potential energy and the kinetic energy of all the components of a system is the **internal energy (*E*)** of the system, which is a **state function**. When the pressure or the volume of a gas is changed, any mechanical work done is called *PV work*. Work done by a system on its surroundings is given a negative value, whereas work done on a system by its surroundings has a positive value.

Conceptual Problems

1. Thermodynamics focuses on the energetics of the reactants and products and provides information about the composition of the reaction system at equilibrium. What information on reaction systems is not provided by thermodynamics?

2. Given a system in which a substance can produce either of two possible products, A → B or A → C, which of the following can be predicted using chemical thermodynamics?

    1. At equilibrium, the concentration of product C is greater than the concentration of product B.
    2. Product C forms more quickly than product B.
    3. The reaction A → C is exothermic.
    4. Low-energy intermediates are formed in the reaction A → B.
    5. The reaction A → C is spontaneous.

3. In what two ways can a closed system exchange energy with its surroundings? Are these two processes path dependent or path independent?

4. A microwave oven operates by providing enough energy to rotate water molecules, which produces heat. Can the change in the internal energy of a cup of water heated in a microwave oven be described as a state function? Can the heat produced be described as a state function?

Answers

1. Thermodynamics tells us nothing about the rate at which reactants are converted to products.

2.

3. heat and work; path dependent
4.

Numerical Problems

1. Calculate the work done in joules in each process.
    1. compressing 12.8 L of hydrogen gas at an external pressure of 1.00 atm to 8.4 L at a constant temperature
    2. expanding 21.9 L of oxygen gas at an external pressure of 0.71 atm to 23.7 L at a constant temperature
2. How much work in joules is done when oxygen is compressed from a volume of 22.8 L and an external pressure of 1.20 atm to 12.0 L at a constant temperature? Was work done by the system or the surroundings?
3. Champagne is bottled at a CO_2 pressure of about 5 atm. What is the force on the cork if its cross-sectional area is 2.0 cm^2? How much work is done if a 2.0 g cork flies a distance of 8.2 ft straight into the air when the cork is popped? Was work done by the system or the surroundings?
4. One mole of water is converted to steam at 1.00 atm pressure and 100°C. Assuming ideal behavior, what is the change in volume when the water is converted from a liquid to a gas? If this transformation took place in a cylinder with a piston, how much work could be done by vaporizing the water at 1.00 atm? Is work done by the system or the surroundings?
5. Acceleration due to gravity on the earth's surface is 9.8 m/s^2. How much work is done by a 175 lb person going over Niagara Falls (approximately 520 ft high) in a barrel that weighs 145 lb?
6. Recall that force can be expressed as mass times acceleration ($F = ma$). Acceleration due to gravity on the earth's surface is 9.8 m/s^2.
    1. What is the gravitational force on a person who weighs 52 kg?
    2. How much work is done if the person leaps from a burning building out of a window that is 20 m above the ground?
    3. If the person lands on a large rescue cushion fitted with a pressure-release valve that maintains an internal pressure of 1.5 atm, how much air is forced out of the cushion?
7. A gas is allowed to expand from a volume of 2.3 L to a volume of 5.8 L. During the process, 460 J of heat is transferred from the surroundings to the gas.
    1. How much work has been done if the gas expands against a vacuum?
    2. How much work has been done if the gas expands against a pressure of 1.3 atm?
    3. What is the change in the internal energy of the system?
8. One mole of an ideal gas is allowed to expand from an initial volume of 0.62 L to a final volume of 1.00 L at constant temperature against a constant external pressure of 1.0 atm. How much work has been done?

Answers

1.
2.
3.
4.
5. –230 kJ
6.
7.
    1. 0 J
    2. –460 J
    3. 0 J
8.

Contributors

- Anonymous

Modified by Joshua B. Halpern

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8.5: The First Law of Thermodynamics

Learning Objectives

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use the 1st, 2nd, and 3rd laws of thermodynamics to explain key relationships between heat, work, and physical or chemical processes.

The relationship between the energy change of a system and that of its surroundings is given by the first law of thermodynamics. A mathematical way of expressing the first law is that the energy of the universe is constant: $\mathbf{\Delta E_{universe} = \Delta E_{system} + \Delta E_{surroundings} = 0}$ Using Equation 18.1.1, we can also express this law mathematically as follows:

$$\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0$$

$$\Delta E_{sys} = -\Delta E_{surr}$$

where the subscripts *univ*, *sys*, and *surr* refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane/O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\Delta E_{sys} = q + w$$

Although q and w are not state functions on their own, their sum (ΔE_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed, as discussed in Section 18.5. Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

Note the Pattern

The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

Note the Pattern

Although q and w are not state functions, their sum (ΔE_{sys}) is independent of the path taken and therefore is a state function.

Example 18.2.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔE) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A Determine the sign of *q* to use in Equation 18.2.2.

B From Equation 18.1.5, calculate *w* from the values given. Substitute this value into Equation 18.2.2 to calculate ΔE.

Solution:

A From Equation 18.2.2, we know that $\Delta E = q + w$. We are given the magnitude of *q* (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, *q* is negative by convention.

B Because the gas is being compressed, we know that work is being done *on* the system, so *w* must be positive. From Equation 18.1.5,

$$w = -P_{ext}\Delta V = -\left(8.0\ \cancel{atm}\right)\left(0.0500\ \cancel{L} - 0.400\ \cancel{L}\right)\left(\frac{101.3\ J}{\cancel{L}\cdot\cancel{atm}}\right) = 284\ \ J$$

Thus

$$\Delta E = q + w = -140\ \ J + 284\ \ J = 144\ \ J$$

In this case, although work is done *on* the gas, increasing its internal energy, heat flows *from* the system *to* the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔE) of the gas in joules?

Answer: –216 J

Note the Pattern

By convention, both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Enthalpy

To further understand the relationship between heat flow (*q*) and the resulting change in internal energy (ΔE), we can look at two sets of limiting conditions: reactions that occur at constant volume and reactions that occur at constant pressure. We will assume that *PV* work is the only kind of work possible for the system, so we can substitute its definition from Equation 18.1.5 into Equation 18.7 to obtain the following:

$$\Delta E = q - p\Delta V$$

where the subscripts have been deleted.

If the reaction occurs in a closed vessel, the volume of the system is fixed, and ΔV is zero. Under these conditions, the heat flow (often given the symbol q_v to indicate constant volume) must equal ΔE:

$$\underset{constant\ volume}{q_v = \Delta E}$$

No *PV* work can be done, and the change in the internal energy of the system is equal to the amount of heat transferred from the system to the surroundings or vice versa.

Many chemical reactions are not, however, carried out in sealed containers at constant volume but in open containers at a more or less constant pressure of about 1 atm. The heat flow under these conditions is given the symbol q_p to indicate constant pressure. Replacing q in Equation 18.2.3 by q_p and rearranging to solve for q_p,

$$\underset{constant\ pressure}{q_p = \Delta E + P\Delta V}$$

Thus, at constant pressure, the heat flow for any process is equal to the change in the internal energy of the system plus the *PV* work done, as we stated in Chapter 9.

Because conditions of constant pressure are so important in chemistry, a new state function called enthalpy (*H*)A state function that is the sum of the system's internal energy E and the product of its pressure P and volume V. H=E+PV is defined as $H = E + PV$. At constant pressure, the change in the enthalpy of a system is as follows:

$$\Delta H = \Delta E + \Delta\left(PV\right) = \Delta E + P\Delta\left(V\right)$$

Comparing the previous two equations shows that at constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$. This expression is consistent with our definition of enthalpy in Section Section 9.1, where we stated that enthalpy is the heat absorbed or produced during any process that occurs at constant pressure.

Note the Pattern

At constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$.

Example 18.2.2

The molar enthalpy of fusion for ice at 0.0°C and a pressure of 1.00 atm is 6.01 kJ, and the molar volumes of ice and water at 0°C are 0.0197 L and 0.0180 L, respectively. Calculate ΔH and ΔE for the melting of ice at 0.0°C. (For more information on enthalpy, see Section 9.2.)

Given: enthalpy of fusion for ice, pressure, and molar volumes of ice and water

Asked for: ΔH and ΔE for ice melting at 0.0°C

Strategy:

A Determine the sign of q and set this value equal to ΔH.

B Calculate $\Delta(PV)$ from the information given.

C Determine ΔE by substituting the calculated values into Equation 18.2.6.

Solution:

A Because 6.01 kJ of heat is absorbed from the surroundings when 1 mol of ice melts, q = +6.01 kJ. When the process is carried out at constant pressure, $q = q_p = \Delta H$ = 6.01 kJ.

B To find ΔE using Equation 18.2.6, we need to calculate $\Delta(PV)$. The process is carried out at a constant pressure of 1.00 atm, so

$$\Delta PV = P\Delta V = P\left(V_f - V\right) = \left(1.00\ atm\right)\left(0.0180\ L - 0.0197\ lL\right)$$

$$= \left(-1.7 \times 10{-}3 \ \cancel{L \cdot atm}\right)\left(101.3 \ J/\cancel{L \cdot atm}\right)$$

C Substituting the calculated values of ΔH and $P\Delta V$ into Equation 18.2.6,

$$\Delta E = \Delta H - P\Delta V = -6010 \ \ J - (-0.0017 \ J) = 6010 \ \ J = 6.01 \ \ kJ$$

Exercise

At 298 K and 1 atm, the conversion of graphite to diamond requires the input of 1.850 kJ of heat per mole of carbon. The molar volumes of graphite and diamond are 0.00534 L and 0.00342 L, respectively. Calculate ΔH and ΔE for the conversion of C (graphite) to C (diamond) under these conditions.

Answer: ΔH = 1.85 kJ/mol; ΔE = 1.85 kJ/mol

The Relationship between ΔH and ΔE

If ΔH for a reaction is known, we can use the change in the enthalpy of the system (Equation 18.2.6) to calculate its change in internal energy. When a reaction involves only solids, liquids, liquid solutions, or any combination of these, the volume does not change appreciably (ΔV = 0). Under these conditions, we can simplify Equation 18.2.6 to $\Delta H = \Delta E$. If gases are involved, however, ΔH and ΔE can differ significantly. We can calculate ΔE from the measured value of ΔH by using the right side of Equation 18.11 together with the ideal gas law, $PV = nRT$. Recognizing that $\Delta(PV) = \Delta(nRT)$, we can rewrite Equation 18.2.6 as follows:

$$\Delta H = \Delta E + \Delta\left(PV\right) = \Delta E + \Delta\left(nRT\right)$$

At constant temperature, $\Delta(nRT) = RT\Delta n$, where Δn is the difference between the final and initial numbers of moles of gas. Thus

$$\Delta E = \Delta H - RT\Delta n$$

For reactions that result in a net production of gas, $\Delta n > 0$, so $\Delta E < \Delta H$. Conversely, endothermic reactions ($\Delta H > 0$) that result in a net consumption of gas have $\Delta n < 0$ and $\Delta E > \Delta H$. The relationship between ΔH and ΔE for systems involving gases is illustrated in Example 4.

Note the Pattern

For reactions that result in a net production of gas, $\Delta E < \Delta H$. For endothermic reactions that result in a net consumption of gas, $\Delta E > \Delta H$.

Example 18.2.3

The combustion of graphite to produce carbon dioxide is described by the equation C (graphite, s) + O_2(g) → CO_2(g). At 298 K and 1.0 atm, ΔH = –393.5 kJ/mol of graphite for this reaction, and the molar volume of graphite is 0.0053 L. What is ΔE for the reaction?

Given: balanced chemical equation, temperature, pressure, ΔH, and molar volume of reactant

Asked for: ΔE

Strategy:

A Use the balanced chemical equation to calculate the change in the number of moles of gas during the reaction.

B Substitute this value and the data given into Equation 18.2.8 to obtain ΔE.

Solution:

A In this reaction, 1 mol of gas (CO_2) is produced, and 1 mol of gas (O_2) is consumed. Thus $\Delta n = 1 - 1 = 0$.

B Substituting this calculated value and the given values into Equation 18.2.8,

$$\Delta E = \Delta H - RT\Delta n = (-393.5\ kJ/mol) - [8.314\ J/mol \cdot K]\,(298\ K)\,(0)$$

$$= (-393.5\ kJ/mol) - (0\ J/mol) = -393.5\ \ kJ$$

To understand why only the change in the volume of the gases needs to be considered, notice that the molar volume of graphite is only 0.0053 L. A change in the number of moles of gas corresponds to a volume change of 22.4 L/mol of gas at standard temperature and pressure (STP), so the volume of gas consumed or produced in this case is (1)(22.4 L) = 22.4 L, which is much, much greater than the volume of 1 mol of a solid such as graphite.

Exercise

Calculate ΔE for the conversion of oxygen gas to ozone at 298 K: $3O_2(g) \rightarrow 2O_3(g)$. The value of ΔH for the reaction is 285.4 kJ.

Answer: 288 kJ

As the exercise in Example 4 illustrates, the magnitudes of ΔH and ΔE for reactions that involve gases are generally rather similar, even when there is a net production or consumption of gases.

Summary

The **first law of thermodynamics** states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. At constant pressure, heat flow (q) and internal energy (E) are related to the system's **enthalpy (H)**. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔE.

Key Takeaway

- Enthalpy is a state function, and the change in enthalpy of a system is equal to the sum of the change in the internal energy of the system and the PV work done.

Key Equations

Internal energy change

Equation 18.2.2: $\Delta E_{sys} = q + w$

Enthalpy change

Equation 18.2.6: $\Delta H = \Delta E + \Delta(PV)$

Relationship between ΔH and ΔE for an ideal gas

Equation 18.2.8: $\Delta E = \Delta H - RT\Delta n$

Conceptual Problems

1. Describe how a swinging pendulum that slows with time illustrates the first law of thermodynamics.
2. When air is pumped into a bicycle tire, the air is compressed. Assuming that the volume is constant, express the change in internal energy in terms of q and w.
3. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant pressure?
4. An intrepid scientist placed an unknown salt in a small amount of water. All the salt dissolved in the water, and the temperature of the solution dropped several degrees.

1. What is the sign of the enthalpy change for this reaction?
2. Assuming the heat capacity of the solution is the same as that of pure water, how would the scientist calculate the molar enthalpy change?
3. Propose an explanation for the decrease in temperature.

5. For years, chemists and physicists focused on enthalpy changes as a way to measure the spontaneity of a reaction. What arguments would you use to convince them not to use this method?

6. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant volume?

7. The *enthalpy of combustion* (ΔH_{comb}) is defined thermodynamically as the enthalpy change for complete oxidation. The complete oxidation of hydrocarbons is represented by the following general equation: hydrocarbon + $O_2(g) \rightarrow CO_2(g) + H_2O(g)$. Enthalpies of combustion from reactions like this one can be measured experimentally with a high degree of precision. It has been found that the less stable the reactant, the more heat is evolved, so the more negative the value of ΔH_{comb}. In each pair of hydrocarbons, which member do you expect to have the greater (more negative) heat of combustion? Justify your answers.

   1. cyclopropane or cyclopentane
   2. butane or 2-methylpropane
   3. hexane or cyclohexane

8. Using a structural argument, explain why the *trans* isomer of 2-butene is more stable than the *cis* isomer. The enthalpies of formation of *cis*- and *trans*-2-butene are –7.1 kJ/mol and –11.4 kJ/mol, respectively.

9. Using structural arguments, explain why cyclopropane has a positive $\Delta H_f°$ (12.7 kJ/mol), whereas cyclopentane has a negative $\Delta H_f°$ (–18.4 kJ/mol). (Hint: consider bond angles.)

Answers

1.
2.

3. At constant pressure, $\Delta H = \Delta E + P\Delta V$.

4.
5.
6.
7.
8.

9. With bond angles of 60°, cyclopropane is highly strained, causing it to be less stable than cyclopentane, which has nearly ideal tetrahedral geometry at each carbon atom.

Numerical Problems

1. A block of CO_2 weighing 15 g evaporates in a 5.0 L container at 25°C. How much work has been done if the gas is allowed to expand against an external pressure of 0.98 atm under isothermal conditions? The enthalpy of sublimation of CO_2 is 25.1 kJ/mol. What is the change in internal energy (kJ/mol) for the sublimation of CO_2 under these conditions?

2. Zinc and HCl react according to the following equation:

   $Zn(s) + 2HCl(aq) \rightarrow Zn^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$

   When 3.00 g of zinc metal is added to a dilute HCl solution at 1.00 atm and 25°C, and this reaction is allowed to go to completion at constant pressure, 6.99 kJ of heat must be removed to return the final solution to its original temperature. What are the values of q and w, and what is the change in internal energy?

3. Acetylene torches, used industrially to cut and weld metals, reach flame temperatures as high as 3000°C. The combustion reaction is as follows:

$$2C_2H_2\,(g) + 5O_2\,(g) \rightarrow 4CO_2\,(g) + 2H_2O\,(l)\;\;\; \Delta H=-2599\;kJ$$

   Calculate the amount of work done against a pressure of 1.0 atm when 4.0 mol of acetylene are allowed to react with 10 mol of O_2 at 1.0 atm at 20°C. What is the change in internal energy for the reaction?

4. When iron dissolves in 1.00 M aqueous HCl, the products are $FeCl_2$(aq) and hydrogen gas. Calculate the work done if 30 g of Fe react with excess hydrochloric acid in a closed vessel at 20°C. How much work is done if the reaction takes place in an open vessel with an external pressure of 1.0 atm?

Answer

1. –350 J; 8.2 kJ
2.
3.
4.

Contributors

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Modified by Joshua B. Halpern

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8.6: Direction of Heat Flow and Enthalpy of Reaction

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use the 1st, 2nd, and 3rd laws of thermodynamics to explain key relationships between heat, work, and physical or chemical processes.
- Classify reactions as **endothermic/exothermic (ΔH)**, entropically favored/entropically disfavored (ΔS), or spontaneous/nonspontaneous (ΔG) given relevant thermodynamic data, balanced chemical equations, and/or a reaction coordinate diagram.
- Use appropriate mathematical expressions (stoichiometry, Hess's Law) and relevant experimental data (**calorimetry,** bond energies, formation ΔH/ΔG, standard molar entropy, definition of free energy) to calculate ΔH, ΔS, and ΔG for a chemical reaction.

Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (see chapter opening image). The balanced chemical equation for the reaction is as follows:

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s) \tag{8.6.1}$$

We can also write this chemical equation as

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s) + heat \tag{8.6.2}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (*q*) is transferred *from* a system *to* its surroundings is described as exothermicA process in which heat (*q*) is transferred *from* a system *to* its surroundings.. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$heat + H_2O\,(s) \rightarrow H_2O\,(l) \tag{8.6.3}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermicA process in which heat q>0 is transferred *to* a system *from* its surroundings.. By convention, $q > 0$ for an endothermic reaction.

Enthalpy of Reaction

We have stated that the change in energy (Δ*E*) is equal to the sum of the heat produced and the work performed (Equation 9.1.3). Work done by an expanding gas is called *pressure-volume work*, also called *PV work*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$Cu\,(s) + 4HNO_3\,(aq) \rightarrow Cu(NO_3)_2\,(aq) + 2H_2O\,(l) + 2NO_3\,(g) \tag{8.6.4}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure $8.6.3$). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of *PV* work done by multiplying the external pressure *P* by the change in volume caused by movement of the piston (Δ*V*). At a constant external pressure (here, atmospheric pressure)

$$w = -P\Delta V \tag{8.6.5}$$

The negative sign associated with *PV* work done indicates that the system loses energy. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

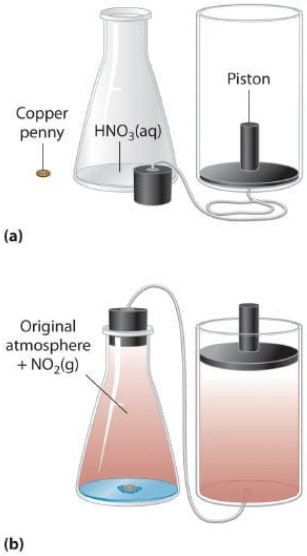


Figure 8.6.3 **An Example of Work Performed by a Reaction Carried Out at Constant Pressure***(a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.*

The symbol *E* in Equation 8.6.3 represents the internal energyThe sum of the kinetic and potential energies of all of a system's component. Internal energy is a state function. of a system, which is the sum of the kinetic energy and potential energy of all its components. Additionally, $\Delta E = q + w$, where q is the heat produced by the system and w is the work performed by the system. It is the change in internal energy that produces heat plus work. Substituting Equation 8.1.5 we find that

$$\Delta E = q - P\Delta V \tag{8.6.6}$$

Thus, if a reaction were carried out in a constant volume system (a pressure cooker for example)

$$\Delta E = q_v \tag{8.6.7}$$

Where the subscipt v in q_v indicates that the process is carried out at constant volume. Thus, if the volume is held constant, the change in internal energy is equal to the heat flowing into or out of the system. However, we live in a constant pressure world, not a constant volume one. The atmospheric pressure at the surface of the earth where we live is roughly constant allowing for variation in barometric pressure due to weather or altitude.

To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called enthalpy (*H*)The sum of a system's internal energy *E* and the product of its pressure *P* and volume *V* (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy *E* plus the product of its pressure *P* and volume *V*:

$$H = E + PV \tag{8.6.8}$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (for a given *P*, $\Delta P = 0$), the change in enthalpy (ΔH)At constant pressure, the amount of heat transferred from the surroundings to the system or $\Delta H = q$ is

$$\Delta H = \Delta(E + PV) = \Delta E + \Delta PV = \Delta E + P\Delta V \tag{8.6.9}$$

Substituting $q + w$ for ΔE (Equation 8.6.9) and $-w$ for $P\Delta V$ (Equation 8.6.5), we obtain

$$\Delta H = \Delta E + P\Delta V = q_p + w - w = q_p \tag{8.6.10}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 8.6.10 we see that at constant pressure the change in enthalpy, ΔH of the system, defined as $H_{final} - H_{initial}$, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} = q_p \tag{8.6.11}$$

Just as with ΔE, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. The enthalpy change is the same even if the process does *not* occur at constant pressure. Most importantly, the change in enthalpy for a reaction can be determined by measuring the flow of heat into or out of the system. As we will see below, there are also cases where we want to know the amount of heat generated by a reaction, as for example for combustion of fuel. In that case knowing the molar change in enthalpy provides the information needed.

Finally, looking at Equation 9.2.9 shows that for reactions where the volume does not change, or better put does not change much, $\Delta H_{rxn} \sim \Delta E_{rxn}$. As a practical matter, this includes all reactions where all the products and reactants are either in the solid, liquid or aqueous phases. This is not generally true when there are gases on either side of the equation, a question which we will discuss in the chapter on gases.

Note the Pattern

To find ΔH, measure q_p.

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn})The change in enthalpy that occurs during a chemical reaction., the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus $\Delta H_{rxn} < 0$ *for an exothermic reaction*, and $\Delta H_{rxn} > 0$ *for an endothermic reaction*. In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (part (a) in Figure 8.6.4). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (part (b) in Figure 8.6.4). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

Note the Pattern

Bond breaking requires an input of energy; bond making releases energy.

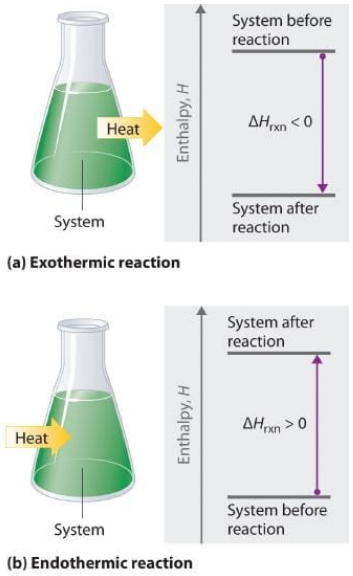


Figure \({8{.}6{.}\eatSpaces{4} \endSpaces}\) ***The Enthalpy of Reaction*** *Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill.*

- **Reversing a reaction or a process changes the sign of Δ*H*.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$heat + H_2O(s) \rightarrow H_2O(l) \quad \Delta H > 0 \tag{8.6.12}$$

$$H_2O(l) \rightarrow H_2O(s) + heat \quad \Delta H < 0 \tag{8.6.13}$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of Δ*H* for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 9.2.12, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

$$2Al\,(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s) + 815.5\ kJ \tag{8.6.14}$$

  Thus Δ*H* = −851.5 kJ/mol of Fe_2O_3. We can also describe Δ*H* for the reaction as −425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide −851.5 kJ by 2. When a value for Δ*H*, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 9.2.13, it is the value of Δ*H* corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

$$2Al\,(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s) \quad \Delta H_{rxn} = -851.5\ kJ \tag{8.6.15}$$

  If 4 mol of Al and 2 mol of Fe_2O_3 react, the change in enthalpy is 2 × (−851.5 kJ) = −1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{8.6.16}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 8.6.1.

Example 8.6.1

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction $H_2O(s) \rightarrow H_2O(l)$ at 0°C and constant pressure, how much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.

B Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given ΔH for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by ΔH (+6.01 kJ/mol):

$$\begin{aligned} moles\ H_2O &= 1.00 \times 10^6\ metric\ tons H_2O \left(\frac{1000\ \cancel{kg}}{1\ \cancel{metric\ ton}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right) \\ &= 5.55 \times 10^{10}\ mol H_2O \end{aligned}$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55 \times 10^{10}\ \cancel{mol\ H_2O}\right) = 3.34 \times 10^{11}\ \ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown in the table below.

Possible sources of the approximately 3.34×10^{11} kJ needed to melt a 1.00×10^6 metric ton iceberg
Combustion of 3.8×10^3 ft^3 of natural gas
Combustion of 68,000 barrels of oil
Combustion of 15,000 tons of coal
1.1×10^8 kilowatt-hours of electricity

Exercise 8.6.1

If 17.3 g of powdered aluminum are allowed to react with excess Fe_2O_3, how much heat is produced?

Answer available at the end of this section.

Key Equations

definition of enthalpy

Equation $8.6.6$: $H = E + PV$

pressure-volume work

Equation $8.6.5$: $w = -P\Delta V$

enthalpy change at constant pressure

Equation $8.6.8$: $\Delta H = \Delta E + P\Delta V$

Equation $8.6.9$: $\Delta H = q_p$

Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**.

Enthalpy is a state function used to measure the heat transferred from a system to its surroundings or vice versa at constant pressure. Only the **change in enthalpy (ΔH)** can be measured. A negative ΔH means that heat flows from a system to its surroundings; a positive ΔH means that heat flows into a system from its surroundings. For a chemical reaction, the **enthalpy of reaction (ΔH_{rxn})** is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}. The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion (ΔH_{fus})** and the **enthalpy of vaporization (ΔH_{vap})**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion (ΔH_{comb})** is the enthalpy change that occurs when a substance is burned in excess oxygen. The **enthalpy of formation (ΔH_f)** is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH^o_f) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH^o_{rxn}) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the "products minus reactants" rule. The **enthalpy of solution (ΔH_{soln})** is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Key Takeaway

- Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure.

Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Conceptual Problems.

1. Heat implies the flow of energy from one object to another. Describe the energy flow in an

   a. exothermic reaction.

b. endothermic reaction.

2. When a thermometer is suspended in an insulated thermos that contains a block of ice, the temperature recorded on the thermometer drops. Describe the direction of heat flow.

3. In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. State whether each process is endothermic or exothermic.

    1. Water is added to sodium hydroxide pellets, and the flask becomes hot.
    2. The body metabolizes glucose, producing carbon dioxide and water.
    3. Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.

4. In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. Determine whether each process is endothermic or exothermic.

    1. Concentrated acid is added to water in a flask, and the flask becomes warm.
    2. Water evaporates from your skin, causing you to shiver.
    3. A container of ammonium nitrate detonates.

5. Is Earth's environment an isolated system, an open system, or a closed system? Explain your answer.

6. Why is it impossible to measure the absolute magnitude of the enthalpy of an object or a compound?

7. Determine whether energy is consumed or released in each scenario. Explain your reasoning.

    1. A leaf falls from a tree.
    2. A motorboat maneuvers against a current.
    3. A child jumps rope.
    4. Dynamite detonates.
    5. A jogger sprints down a hill.

8. The chapter states that enthalpy is an extensive property. Why? Describe a situation that illustrates this fact.

9. The enthalpy of a system is affected by the physical states of the reactants and the products. Explain why.

10. Is the distance a person travels on a trip a state function? Why or why not?

11.

Contributors

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Modified by Joshua Halpern

Answers

Exercise 8.6.1

273 kJ

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8.7: Calorimetry

Learning Objectives

- By the end of this section, you will have background information that will help you to be able to:
- Use the 1st, 2nd, and 3rd laws of thermodynamics to explain key relationships between heat, work, and physical or chemical processes.
- Use appropriate mathematical expressions (stoichiometry, Hess's Law) and relevant experimental data (**calorimetry,** bond energies, formation ΔH/ΔG, standard molar entropy, definition of free energy) to calculate ΔH, ΔS, and ΔG for a chemical reaction.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes set of techniques used to measure enthalpy changes in chemical (reactions) and physical changes (melting for example) processes using devices called *calorimeters*.

To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

Heat Capacity

We have seen that the temperature of an object changes when it absorbs or loses thermal energy. The *magnitude* of the temperature change depends on both the *amount* of thermal energy transferred (q) and the *heat capacity* of the object. **Its heat capacity (C) is the amount of energy needed to raise the temperature of an object by 1°C**. The units of C are joules per degree Celsius (J/°C) and it is always a positive quantity.

Note that a degree Celsius is exactly the same as a Kelvin, so the heat capacities can be expresses equally well, and perhaps a bit more correctly in SI, as joules per Kelvin, J/K

The change in temperature (ΔT) is

$$\Delta T = \frac{q}{C} \tag{8.7.1}$$

where q is the amount of heat (in joules), C is the heat capacity (in joules per degree Celsius), and ΔT is $T_{final} - T_{initial}$ (in degrees Celsius). Note that ΔT is *always* written as the final temperature minus the initial temperature.

Since Kelvin and degrees Celcius are exactly the same the DIFFERENCE $\Delta T = T_{final} - T_{initial}$ is the same whether one uses Kelving (K) or Celcius (°C) for BOTH T_{final} and $T_{initial}$, but make sure not to mix these two temperature units.

Although C must be positive, ΔT and q can be either positive or negative, depending on the context. However, both ΔT and q have to have the same sign in any given context:

- If both ΔT and q are positive, then *heat flows from the surroundings into an object.*
- If both ΔT and q are negative, then *heat flows from an object into its surroundings*.

Specific Heat

An object's heat capacity *(C)* depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. It would be good to have a property of a substance that is not dependent on composition. in this context, we'll use **specific heat (C_s).** This is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C. Its units are thus J/(g·°C). We can relate the quantity of a substance, the amount of heat transferred, its heat capacity, and the temperature change in two ways:

$$q = nC_p\Delta T \tag{8.7.2}$$

$$q = mCs\Delta T \tag{8.7.3}$$

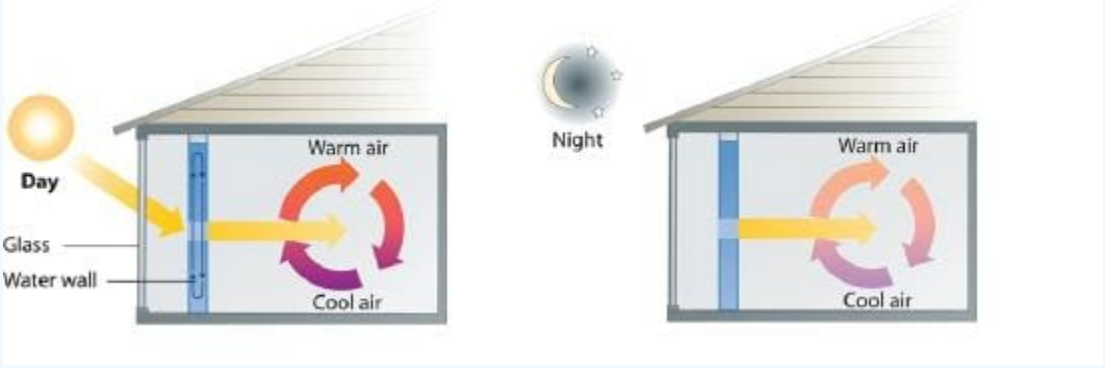
The specific heats of some common substances are given in Table 8.7.1 Note that the specific heat values of most solids are less than 1 J/(g·°C), whereas those of most liquids are about 2 J/(g·°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g·°C), is one of the highest known.

Table 8.7.1 Specific Heats of Selected Substances at 25°C

Compound	Specific Heat [J/(g·°C)]
$H_2O(l)$	4.184
$H_2O(g)$	2.062
CH_3OH (methanol)	2.531
CH_3CH_2OH (ethanol)	2.438
n-C_6H_{14} (*n*-hexane)	2.270
C_6H_6 (benzene)	1.745
C(s) (graphite)	0.709
C(s) (diamond)	0.509
Al(s)	0.897
Fe(s)	0.449
Cu(s)	0.385
Au(s)	0.129
Hg(l)	0.140
NaCl(s)	0.864
MgO(s)	0.921
SiO_2(s) (quartz)	0.742
$CaCO_3$(s) (calcite)	0.915

Example 8.7.1

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0°C. During the course of the day, the temperature of the water rises to 38.0°C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0°C is 0.998 g/mL.)



Passive solar system. *During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.*

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A Use the density of water at 22.0°C to obtain the mass of water (*m*) that corresponds to 400 L of water. Then compute Δ*T* for the water.

B Determine the amount of heat absorbed by substituting values for *m*, C_s, and Δ*T* into Equation 8.7.1

Solution:

A The mass of water is

$$mass\ of\ H_2O = 400\ \cancel{L}\left(\frac{1000\ \cancel{mL}}{1\ \cancel{L}}\right)\left(\frac{0.998\ g}{1\ \cancel{mL}}\right) = 3.99 \times 10^5 g\ H_2O$$

The temperature change (Δ*T*) is 38.0°C – 22.0°C = +16.0°C.

B From Table 8.7.1, the specific heat of water is 4.184 J/(g·°C). From Equation 8.7.3 the heat absorbed by the water is thus

$$q = mC_s\Delta T = \left(3.99X10^5\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)\left(16.0\ \cancel{^oC}\right) = 2.67 \times 10^7 J = 2.67 \times 10^4 kJ$$

Both *q* and Δ*T* are positive, consistent with the fact that the water has absorbed energy.

Exercise 8.7.1

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 2500 kg of sandstone rocks, what amount of energy is stored if the temperature of the rocks increases from 20.0°C to 34.5°C during the day? Assume that the specific heat of sandstone is the same as that of quartz (SiO_2) in Table 8.7.1.

Answer available at the end of this section.

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this process so that the heat lost by one object is equal to the heat gained by the other object:

$$q_{cold} = -q_{hot} \tag{8.7.4}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

Example 8.7.2

If a 30.0 g piece of copper pipe at 80.0°C is placed in 100.0 g of water at 27.0°C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass and initial temperature of two objects

Asked for: final temperature

Strategy:

Using Equation 8.7.6 and writing ΔT as $T_{final} - T_{initial}$ for both the copper and the water, substitute the appropriate values of m, C_s, and $T_{initial}$ into the equation and solve for T_{final}.

Solution:

We can adapt Equation 8.7.7 to solve this problem, remembering that ΔT is defined as $T_{final} - T_{initial}$:

$$\left[mC_s\left(T_{final} - T_{initial}\right)\right]_{Cu} + \left[mC_s\left(T_{final} - T_{initial}\right)\right]_{H_2O} = 0$$

Substituting the data provided in the problem and Table 8.7.1 gives

$$\left[(30\ g)\ (0.385\ J)\left(T_{final} - T_{initial}\right)\right]_{Cu} + \left[mC_s\left(T_{final} - T_{initial}\right)\right]_{H_2O} = 0$$

$$T_{final}\left(11.6\ J/^oC\right) - 924\ J + T_{final}\left(418.4\ J/^oC\right) - 11,300\ J$$

$$T_{final}\left(430\ J/\left(g\cdot^o C\right)\right) = -12,224\ J$$

$$T_{final} = -28.4\ ^oC$$

Exercise (a)

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0°C, what is the final temperature if no heat is transferred to the surroundings?

Exercise 8.7.2

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0°C. If the final temperature of the water is 24.0°C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer available at the end of this section.

Measuring Heat Flow

The thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter.

- If the reaction releases heat ($q_{rxn} < 0$), then heat is absorbed by the calorimeter ($q_{calorimeter} > 0$) and its temperature increases.
- Conversely, if the reaction absorbs heat ($q_{rxn} > 0$), then heat is transferred from the calorimeter to the system ($q_{calorimeter} < 0$) and the temperature of the calorimeter decreases.
- In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.

Constant-Pressure Calorimetry

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C). Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mC_s\Delta T \tag{8.7.5}$$

The use of a constant-pressure calorimeter is illustrated in Example 3.

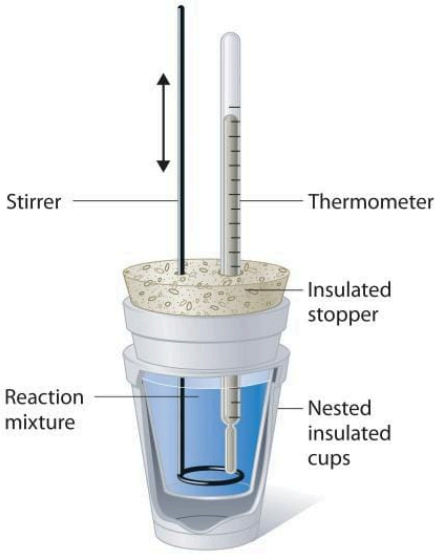


Figure 8.7.2 **A Coffee-Cup Calorimeter** *This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.*

Example 8.7.3

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.

B Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 8.7.8.

C Use the molar mass of KOH to calculate ΔH_{soln}.

Solution:

A To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$(100.0\ mL\ H2O)\left(0.9969\ g/\cancel{mL}\right) + 5.03\ g\ KOH = 104.72\ g$$

The temperature change is (34.7°C − 23.0°C) = +11.7°C.

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$q_{calorimater} = mC_s\Delta T = \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)(11.7\ ^oC) = 5130\ J = 5.13\ lJ$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 8.7.1, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\ kJ$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln}—the heat released when dissolving 1 mol of KOH:

$$\Delta H_{soln} = \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right) = -57.2\ kJ/mol$$

Exercise 8.7.3

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 9, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer available at the end of this section.

Constant-Volume Calorimetry

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the "bomb"). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

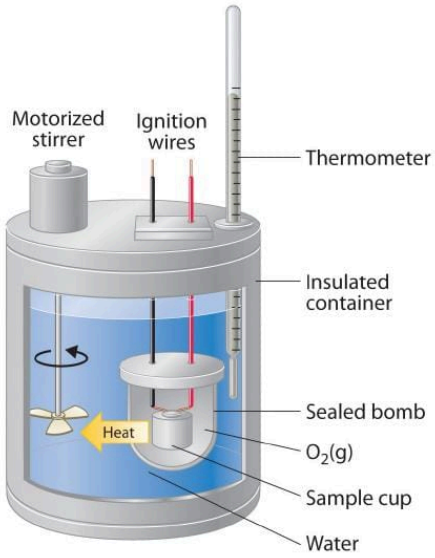


Figure 9.6.3 A Bomb Calorimeter *After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.*

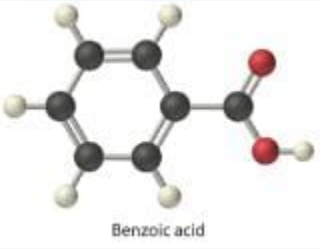
Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔE) rather than the enthalpy change (ΔH); ΔE is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta E < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 8.7.9, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{8.7.6}$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its ΔH_{comb} = −26.38 kJ/g). This value and the measured increase in temperature of the calorimeter can be used in Equation 8.7.9 to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example 10.

Example 8.7.4

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?


Benzoic acid

Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.

B Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 8.7.9 and the information obtained from the combustion of benzoic acid to calculate C_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$qcomb = \left(0.579\ \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) = -15.3\ kJ$$

From Equation 8.7.9,

$$-Cbomb = \frac{q_{comb}}{\Delta T} = \frac{-15.3\ kJ}{2.08\ ^oC} = -7.34\ kJ/^oC$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$q_{comb} = -C_{bomb}\Delta T = (-7.34\ kJ/^oC)\,(3.64\ ^oC) = -26.7\ kJ$$

Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\Delta H_{comb} = \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) = -2780\ kJ/mol = 2.78 \times 10^3\ kJ/mol$$

This result is in good agreement (< 1% error) with the value of ΔH_{comb} = −2803 kJ/mol that calculated using enthalpies of formation.

Exercise 8.7.4

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64°C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Answer available at the end of this section.

Key Equations

relationship of quantity of a substance, heat capacity, heat flow, and temperature change

Equation 8.7.2 : $q = nC_p\Delta T$

Equation 8.7.3 : $q = mC_s\Delta T$

constant-pressure calorimetry

Equation 8.7.8 : $\Delta H_{rxn} = q_{rxn} = -q_{calorimeter} = -mC_s\Delta T$

constant-volume calorimetry

Equation 8.7.9 : $\Delta H_{comb} < q_{comb} = -q_{calorimeter} = -C_{bomb}\Delta T$

Summary

Calorimetry is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (*C*)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat (C_s)** of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity (C_p)** is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C.

Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives ΔH values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

Key Takeaway

- Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system.

Conceptual Problems

1. Can an object have a negative heat capacity? Why or why not?
2. What two factors determine the heat capacity of an object? Does the specific heat also depend on these two factors? Explain your answer.
3. Explain why regions along seacoasts have a more moderate climate than inland regions do.
4. Although soapstone is more expensive than brick, soapstone is frequently the building material of choice for fireplaces, particularly in northern climates with harsh winters. Propose an explanation for this.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Numerical Problems.

1. Using Equation $8.7.2$ and Equation $8.7.3$, derive a mathematical relationship between C_s and C_p.
2. Complete the following table for 28.0 g of each element at an initial temperature of 22.0°C.

Element	q (J)	C_p [J/(mol·K)]	Final T (°C)
nickel	137	26.07	
silicon		19.789	3.0
zinc	603		77.5
mercury	137		57

3. Using Table 9.6.1, how much heat is needed to raise the temperature of a 2.5 g piece of copper wire from 20°C to 80°C? How much heat is needed to increase the temperature of an equivalent mass of aluminum by the same amount? If you were using one of these metals to channel heat away from electrical components, which metal would you use? Once heated, which metal will cool faster? Give the specific heat for each metal.
4. Gold has a molar heat capacity of 25.418 J/(mol·K), and silver has a molar heat capacity of 23.350 J/(mol·K).
    1. If you put silver and gold spoons of equal mass into a cup of hot liquid and wait until the temperature of the liquid is constant, which spoon will take longer to cool down when removed from the hot liquid?
    2. If 8.00 g spoons of each metal at 20.0°C are placed in an insulated mug with 50.0 g of water at 97.0°C, what will be the final temperature of the water after the system has equilibrated? (Assume that no heat is transferred to the surroundings.)
5. In an exothermic reaction, how much heat would need to be evolved to raise the temperature of 150 mL of water 7.5°C? Explain how this process illustrates the law of conservation of energy.
6. How much heat must be evolved by a reaction to raise the temperature of 8.0 oz of water 5.0°C? What mass of lithium iodide would need to be dissolved in this volume of water to produce this temperature change?

7. A solution is made by dissolving 3.35 g of an unknown salt in 150 mL of water, and the temperature of the water rises 3.0°C. The addition of a silver nitrate solution results in a precipitate. Assuming that the heat capacity of the solution is the same as that of pure water, use the information in Table 9.5.1 and solubility rules to identify the salt.

8. Using the data in Table 9.8.2, calculate the change in temperature of a calorimeter with a heat capacity of 1.78 kJ/°C when 3.0 g of charcoal is burned in the calorimeter. If the calorimeter is in a 2 L bath of water at an initial temperature of 21.5°C, what will be the final temperature of the water after the combustion reaction (assuming no heat is lost to the surroundings)?

9. A 3.000 g sample of TNT (trinitrotoluene, $C_7H_5N_3O_6$) is placed in a bomb calorimeter with a heat capacity of 1.93 kJ/°C; the ΔH_{comb} of TNT is −3403.5 kJ/mol. If the initial temperature of the calorimeter is 19.8°C, what will be the final temperature of the calorimeter after the combustion reaction (assuming no heat is lost to the surroundings)? What is the ΔH_f of TNT?

Answers

1. $C_p = C_s \times$ (molar mass)

2.

3. For Cu: q = 58 J; For Al: q = 130 J; Even though the values of the molar heat capacities are very similar for the two metals, the specific heat of Cu is only about half as large as that of Al, due to the greater molar mass of Cu versus Al: C_s = 0.385 and 0.897 *J*/(g·K) for Cu and Al, respectively. Thus loss of one joule of heat will cause almost twice as large a decrease in temperature of Cu versus Al.

4.

5. 4.7 kJ

6.

7. ΔH_{soln} = −0.56 kJ/g; based on reaction with $AgNO_3$, salt contains halide; dividing ΔH_{soln} values in Table 5.2 by molar mass of salts gives lithium bromide as best match, with −0.56 kJ/g.

8.

9. T_{final} = 43.1°C; the combustion reaction is

$$4C_7H_5N_3O_{6(s)} + 21O_{2(g)} \rightarrow 28CO_{2(g)} + 10H_2O_{(g)} + 6N_{2(g)}$$

with

$$\Delta^o_f H(TNT) = -65.5\ kJ/mol$$

Contributors

- Anonymous

Modified by Joshua Halpern

Answers

Exercise 8.7.1

2.7 × 10^4 kJ (Even though the mass of sandstone is more than six times the mass of the water in Example 7, the amount of thermal energy stored is the same to two significant figures.)

Exercise 8.7.2

80.0°C

Exercise 8.7.3

16.6 kJ/mol

Exercise 8.7.4

−1.30 × 10^3 kJ/mol

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8.8: Hess's Law

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use appropriate mathematical expressions (stoichiometry, **Hess's Law**) and relevant experimental data (calorimetry, bond energies, formation ΔH/ΔG, standard molar entropy, definition of free energy) to calculate ΔH, ΔS, and ΔG for a chemical reaction.

Hess's Law

Because enthalpy is a state function, the enthalpy change for a reaction depends on *only* two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does *not* depend on the path by which reactants are converted to products. This means that if we add two or more balanced chemical equations to obtain a net chemical equation, ΔH *for the net reaction is the sum of the* ΔH *values for the individual reactions*. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate Δ*H* values for reactions that are difficult to carry out directly by adding together the known Δ*H* values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 9.3.1 can be viewed as occurring in three distinct steps with known Δ*H* values. As shown in Figure $8.8.1$, the first reaction produces 1 mol of solid aluminum oxide (Al_2O_3) and 2 mol of liquid iron at its melting point of 1758°C (part (a) in Equation $8.8.1$); the enthalpy change for this reaction is –732.5 kJ/mol of Fe_2O_3.

The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (part (b) in Equation 9.3.1); the enthalpy change for this reaction is –13.8 kJ/mol of Fe (–27.6 kJ per 2 mol Fe).

In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (part (c) in Equation $8.8.1$); the enthalpy change for this reaction is –45.5 kJ/mol of Fe (–91.0 kJ per 2 mol Fe).

As you can see in Figure $8.8.1$, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding parts (a), (b), and (c) in Equation $8.8.1$ gives the overall reaction, shown in part (d):

$$\begin{array}{ccccc} 2Al\,(s,\ 25^oC) + 2Fe_2O_3\,(s,\ 25^oC) & \rightarrow & 2Fe\,(l,\ 1758^oC) + 2Al_2O_3\,(s,\ 1758^oC) & \Delta H = -732.5\ kJ & (a) \\ 2Fe\,(l,\ 1758^oC) & \rightarrow & 2Fe\,(s,\ 1758^oC) & \Delta H = -\ 27.6\ kJ & (b) \\ 2Fe\,(s,\ 1758^oC) + 2Al_2O_3\,(s,\ 1758^oC) & \rightarrow & 2Fe\,(l,\ 25^oC) + 2Al_2O_3\,(s,\ 25^oC) & \Delta H = -\ 91.0\ kJ & (c) \\ 2Al\,(s,\ 25^oC) + 2Fe_2O_3\,(s,\ 25^oC) & \rightarrow & 2Al_2O_3\,(s,\ 25^oC) + 2Fe_2O_3\,(s,\ 25^oC) & \Delta H = -852.2\ kJ & (d) \end{array} \tag{8.8.1}$$

The net reaction in part (d) in Equation $8.8.1$ is identical to Equation $8.8.1$ the sum of parts (a) + (b) +(c). By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure $8.8.1$.

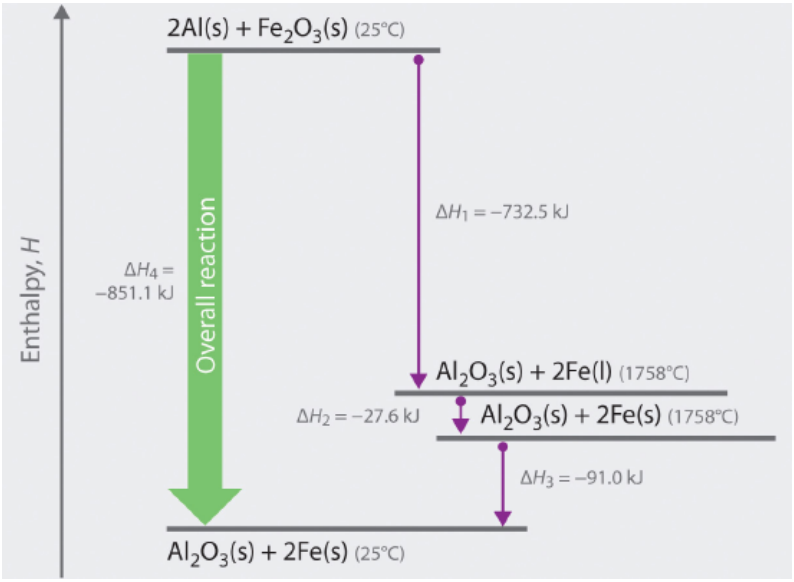


Figure 8.8.1 **Energy Changes Accompanying the Thermite Reaction** *Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid Al_2O_3 and liquid iron (ΔH_1), solid iron at 1758°C (ΔH_2), and solid iron at 25°C (ΔH_3). Thus $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, as stated by Hess's law.*

Comparing parts (a) and (d) in Equation 8.8.1 also illustrates an important point: *The magnitude of* ΔH *for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution).* When the product is liquid iron at its melting point (part (a) in Equation 8.8.1), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is solid iron at 25°C (part (d) in Equation 9.3.1). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

When using Hess's law to calculate the value of Δ*H* for a reaction, follow this procedure:

1. Identify the equation whose Δ*H* value is unknown and write individual reactions with known Δ*H* values that, when added together, will give the desired equation.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of Δ*H* for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its Δ*H* value by that same factor.
4. Add together the individual reactions and their corresponding Δ*H* values to obtain the reaction of interest and the unknown Δ*H*.

We illustrate how to use this procedure in Example 8.8.1

Example 8.8.1

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

\(\left (1 \right) \;2C\left (s \right) + O_{2}\left (g \right) \rightarrow 2CO\left (g \right) \; \;\ \; \Delta H=-221.0 \; kJ \]

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

$$(2)\ C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5\ kJ \tag{8.8.2}$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2.

Given: two balanced chemical equations and their Δ*H* values

Asked for: enthalpy change for a third reaction

Strategy:

A After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH.)

B Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:

$$(3)\ \ CO\,(g) + \frac{1}{2}O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H_{rxn} = ? \tag{8.8.3}$$

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in Equation 3, is a product in Equation 1, we can reverse Equation (1) to give

$$2CO\,(g) \rightarrow 2C\,(s) + O_2\,(g) \quad \Delta H = +221.0\ kJ \tag{8.8.4}$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use Equation 2 as written because its product, CO_2, is the product we want in Equation 3:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(s) \quad \Delta H = -393.5\ kJ \tag{8.8.5}$$

B Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$2C\,(s) + 2O_2\,(g) \rightarrow 2CO_2\,(s) \quad \Delta H = -787.0\ kJ \tag{8.8.6}$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{array}{rcccccccc} 2CO\,(g) & \rightarrow & \cancel{2C\,(s)} + \cancel{O_2\,(g)} & \Delta H & = & -\Delta H_1 & = & +221.0\ kJ \\ \cancel{2C\,(s)} + \cancel{2}O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H & = & -\Delta 2H_2 & = & -787.0\ kJ \\ 2CO\,(g) + O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H & = & -566.0\ kJ & & \end{array} \tag{8.8.7}$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with O_2, and the problem asks for the amount *per mole of CO*. Consequently, we must divide both sides of the final equation *and the magnitude of* ΔH by 2:

$$CO\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = -283.0\ kJ \tag{8.8.8}$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$\begin{array}{rcccccccc} (A) & 2C\,(s) + O_2\,(g) & \rightarrow & \cancel{2CO\,(g)} & \Delta H_A & = & \Delta H_1 & = & +221.0\ kJ \\ (B) & \cancel{2CO\,(g)} + O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H_B & & & = & ? \\ (C) & 2C\,(s) + 2O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H & = 2\Delta H_2 & = 2 \times (-393.5\ kJ) & = -787.0\ kJ & \end{array} \tag{8.8.9}$$

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give CO_2. From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given ΔH for reactions A and C. Substituting the appropriate values gives

$$\begin{array}{c} -221.0\ kJ + \Delta H_B = -787.0\ kJ \\ \Delta H_B = -566.0 \end{array} \tag{8.8.10}$$

This is again the enthalpy change for the conversion of 2 mol of CO to CO_2. The enthalpy change for the conversion of 1 mol of CO to CO_2 is therefore –566.0 ÷ 2 = –283.0 kJ/mol of CO, which is the same result we obtained earlier. As you can see, *there may be more than one correct way to solve a problem*.

Exercise 8.8.1

The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$\begin{aligned} C_2H_2\,(g) + H_2\,(g) &\rightarrow C_2H_4\,(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2 \\ C_2H_2\,(g) + 2H_2\,(g) &\rightarrow C_2H_6\,(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2 \end{aligned} \tag{8.8.11}$$

What is ΔH for the reaction of C_2H_4 with H_2 to form C_2H_6?

Answer available at the end of this section.

Note the Pattern

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Summary

For a chemical reaction, the **enthalpy of reaction (ΔH_{rxn})** is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}. The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion (ΔH_{fus})** and the **enthalpy of vaporization (ΔH_{vap})**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion (ΔH_{comb})** is the enthalpy change that occurs when a substance is burned in excess oxygen.

Key Takeaway

- Hess's law: The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions:

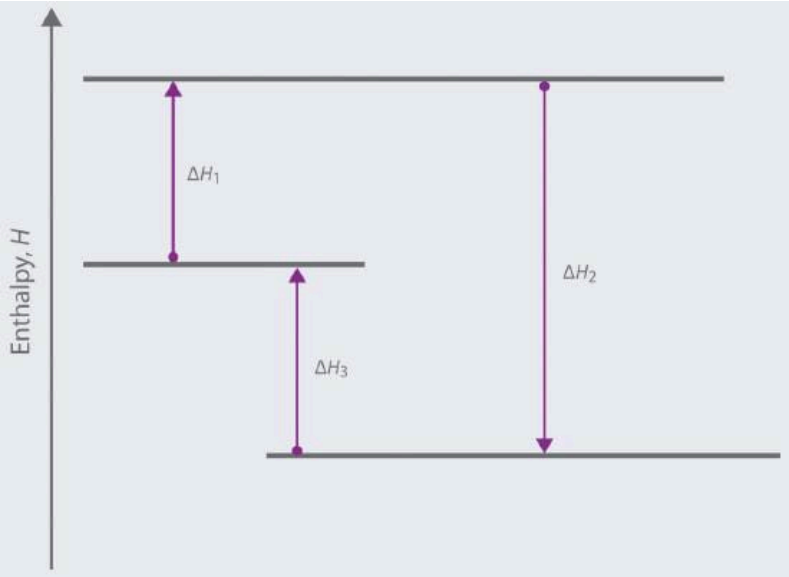
Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Conceptual Problems.

1. Based on the following energy diagram,

   a. write an equation showing how the value of ΔH_2 could be determined if the values of ΔH_1 and ΔH_3 are known.

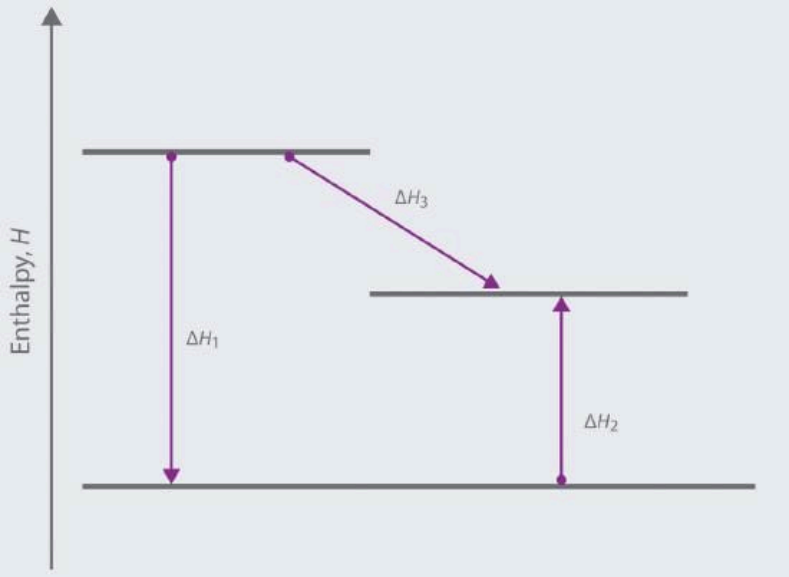
   b; identify each step as being exothermic or endothermic.



2. Based on the following energy diagram,

   a. write an equation showing how the value of ΔH_3 could be determined if the values of ΔH_1 and ΔH_2 are known.

   b. identify each step as being exothermic or endothermic.



3. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.

4. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?

   1. the melting of a solid
   2. the conversion of a gas to a liquid
   3. the solidification of a liquid
   4. the dissolution of a solid into water

5. In their elemental form, A_2 and B_2 exist as diatomic molecules. Given the following reactions, each with an associated $\Delta H°$, describe how you would calculate ΔH^{o}_{f} for the compound AB_2.

$$\begin{array}{rcll} 2AB & \rightarrow & A_2 + B_2 & \Delta H_1^o \\ 3AB & \rightarrow & AB_2 + A_2B & \Delta H_2^o \\ 2A_2B & \rightarrow & 2A_2 + B_2 & \Delta H_3^o \end{array} \tag{8.8.12}$$

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Numerical Problems.

1. Methanol is used as a fuel in Indianapolis 500 race cars. Use the following table to determine whether methanol or 2,2,4-trimethylpentane (isooctane) releases more energy per liter during combustion.

Fuel	$\Delta H^\circ_{combustion}$(kJ/mol)	Density (g/mL)
methanol	−726.1	0.791
2,2,4-trimethylpentane	−5461.4	0.692

2. a. Use the enthalpies of combustion given in the following table to determine which organic compound releases the greatest amount of energy per gram during combustion.

Fuel	$\Delta H^\circ_{combustion}$(kJ/mol)
methanol	−726.1
1-ethyl-2-methylbenzene	−5210.2
n-octane	−5470.5

   b. Calculate the standard enthalpy of formation of 1-ethyl-2-methylbenzene.

3. Given the enthalpies of combustion, which organic compound is the best fuel per gram?

Fuel	ΔH°_f(kJ/mol)
ethanol	−1366.8
benzene	−3267.6
cyclooctane	−5434.7

Answers

1.

2.

a. To one decimal place

methanol: ΔH/g = −22.6 kJ

C_9H_{12}: ΔH/g = −43.3 kJ

octane: ΔH/g = −47.9 kJ

Octane provides the largest amount of heat per gram upon combustion.

b, $\Delta H_f(C_9H_{17})$ = −46.1 kJ/mol

Contributors

Modified by Joshua Halpern (Howard University)

Answers

Exercise 8.8.1

–136.3 kJ/mol of C_2H_4

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8.9: Heats of Formation

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use appropriate mathematical expressions (**stoichiometry**, Hess's Law) and relevant experimental data (calorimetry, **bond energies, formation ΔH**/ΔG, standard molar entropy, definition of free energy) to calculate **ΔH,** ΔS, and ΔG for a chemical reaction.

Enthalpies of Formation

There are a wide variety of chemical reactions, and it might be useful to know the enthalpy of any reaction we choose. One way to do this would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data starting from the elemental forms of each atom at 25 °C and 1 atm pressure. These data are called the **Enthalpy of formation (ΔH_f).** Enthalpies of formation are the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The corresponding relationship is

- $$elements \rightarrow compound \qquad \Delta H_{rxn} = \Delta H_f \tag{8.9.1}$$

  For example,

$$C\left(s\right) + O_2\left(g\right) \rightarrow CO_2\left(g\right) \qquad \Delta H_{rxn} = \Delta H_f\left[CO_2\left(g\right)\right] \tag{8.9.2}$$

  The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed.

Note the Pattern

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Standard Enthalpies of Formation

The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

Our tables use the following standard conditions for molar enthalpies of formation: 1 atm for all gases and a concentration of 1.0 M for all species in solution, and a temperature of 25°C (298 K). In addition, each pure substance must be in its standard state, which is usually the most stable form of a pure substance at a pressure of 1 atm at a specified temperature. Enthalpies of formation measured under these conditions are called **standard enthalpies of formation (ΔH^{o}_{f})**, which is pronounced "delta H eff naught". **The standard enthalpy of formation of any element in its most stable form is zero by definition**. For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), O_2 is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H_2(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure 8.9.1).

Therefore, $O_2(g)$, $H_2(g)$, and graphite have ΔH°_f values of zero.



Figure 8.9.1 **Elemental Carbon** *Although graphite and diamond are both forms of elemental carbon, graphite is more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.*

Example 8.9.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

1. HCl(g)
2. $MgCO_3$(s)
3. $CH_3(CH_2)_{14}CO_2H$(s) (palmitic acid)

Given: compound

Asked for: balanced chemical equation for its formation from elements in standard states

Strategy:

Use Appendix A to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

Solution:

To calculate the standard enthalpy of formation of a compound, we must start with the elements in their standard states. The standard state of an element can be identified in the Reference Tables by a ΔH°_f value of 0 kJ/mol.

1. Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $H_2(g)$ and $Cl_2(g)$, respectively, the unbalanced chemical equation is $H_2(g) + Cl_2(g) \rightarrow HCl(g)$

   Fractional coefficients are required in this case because ΔH°_f values are reported for *1 mol* of the product, HCl. Multiplying both $H_2(g)$ and $Cl_2(g)$ by 1/2 balances the equation:

   $$\frac{1}{2}H_2\,(g) + \frac{1}{2}Cl_2\,(g) \rightarrow HCl\,(g)$$

2. The standard states of the elements in this compound are Mg(s), C(s, graphite), and $O_2(g)$. The unbalanced chemical equation is thus Mg(s) + C(s, graphite) + $O_2(g) \rightarrow MgCO_3(s)$

   This equation can be balanced by inspection to give

   $$Mg\,(g) + C\,(s, graphite)\,\frac{3}{2}O_2\,(g) \rightarrow MgCO_3\,(s)$$

3. Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows: C(s, graphite) + H_2(g) + O_2(g) → $CH_3(CH_2)_{14}CO_2H$(s)

   There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is

   16C(s, graphite) + 16H_2(g) + O_2(g) → $CH_3(CH_2)_{14}CO_2H$(s)

Exercise 8.9.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

1. NaCl(s)
2. H_2SO_4(l)
3. CH_3CO_2H(l) (acetic acid)

Answer available at the end of this section.

Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose ΔH_f^o values are known. The standard enthalpy of reaction (ΔH_{rxn})The enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard state. is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

$$aA + bB \rightarrow cC + dD \tag{8.9.3}$$

where A, B, C, and D are chemical substances and *a*, *b*, *c*, and *d* are their stoichiometric coefficients. The magnitude of ΔH^o is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

$$\Delta H^o_{rxn} = \underset{reactants}{\left[c\Delta H^o_f(C) + d\Delta H^o_f(D)\right]} - \underset{products}{\left[a\Delta H^o_f(A) + b\Delta H^o_f(B)\right]} \tag{8.9.4}$$

More generally, we can write

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f(products) - \sum n\Delta H^o_f(reactants) \tag{8.9.5}$$

where the symbol Σ means “sum of” and *m* and *n* are the stoichiometric coefficients of each of the products and the reactants, respectively. “Products minus reactants” summations such as Equation 8.9.6 arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, “products minus reactants” summations are very common in chemistry; we will encounter many others in subsequent chapters.

Note the Pattern

Products minus reactants” summations are typical of state functions.

To demonstrate the use of tabulated ΔH^o values, we will use them to calculate ΔH_{rxn} for the combustion of glucose, the reaction that provides energy for your brain:

$$C_6H_{12}O_6(s) + O_2(g) \rightarrow CO_2(g) + 6H_2O(l) \tag{8.9.6}$$

Using Equation 8.9.6, we write

$$\Delta H_f^o = \left\{6\Delta H_f^o\left[CO_2\left(g\right)\right] + 6\Delta H_f^o\left[H_2O\left(g\right)\right]\right\} - \left\{6\Delta H_f^o\left[C_6H_{12}O_6\left(s\right)\right] + 6\Delta H_f^o\left[O_2\left(g\right)\right]\right\} \tag{8.9.7}$$

From the Reference Tables, the relevant ΔH^o_f values are $\Delta H^o_f\,[CO_2(g)]$ = -393.5 kJ/mol, $\Delta H^o_f\,[H_2O(l)]$ = -285.8 kJ/mol, and $\Delta H^o_f\,[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol. Because $O_2(g)$ is a pure element in its standard state, $\Delta H^o_f\,[O_2(g)]$ = 0 kJ/mol. Inserting these values into Equation 9.4.7 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\begin{aligned}\Delta H^o_{comb} &= \left[6\left(-393.5\ kJ/mol\right) + 6\left(-285.8\ kJ/mol\right)\right] \\ &- \left[-1273.3 + 6\left(0\ kJ/mol\right)\right] = -2802.5\ kJ/mol\end{aligned} \tag{8.9.8}$$

As illustrated in Figure 8.9.3, we can use Equation 8.9.9 to calculate ΔH^o_f for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH^o_{comb} The alternative hypothetical pathway consists of four separate reactions that convert the reactants *to the elements* in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH^o_f values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned}\Delta H_1^o = \Delta H_f^o\left[glucose\left(s\right)\right] &= -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right) = +1273.3\ kJ \\ \Delta H_2^o = 6\Delta H_f^o\left[O_2\left(g\right)\right] &= 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right) = 0\ kJ\end{aligned} \tag{8.9.9}$$

(Recall that when we reverse a reaction, we must also reverse the sign of the accompanying enthalpy change.) The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

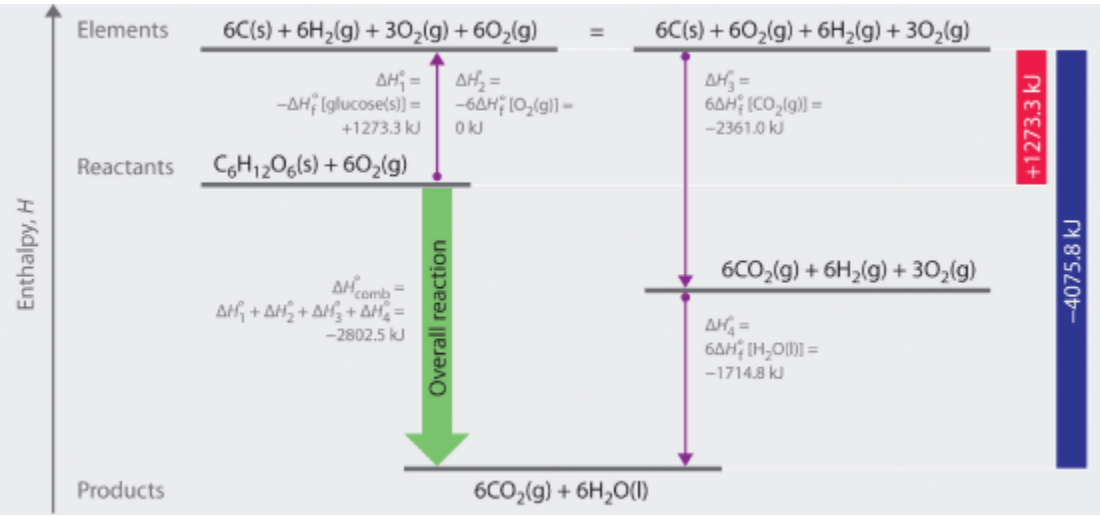


Figure 8.9.2 **A Thermochemical Cycle for the Combustion of Glucose** Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled ΔH^o_1 and ΔH^o_2). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled ΔH^o_3 and ΔH^o_4). Because enthalpy is a state function, ΔH^o_{comb} is equal to the sum of the enthalpy changes $\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$.

The reactions that convert the elements to final products (downward purple arrows in Figure 8.9.2) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes (from the Reference Tables) are

$$\begin{aligned}\Delta H_3^o = \Delta H_f^o\left[CO_2\left(g\right)\right] &= 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ \\ \Delta H_4^o = 6\Delta H_f^o\left[H_2O\left(l\right)\right] &= 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ\end{aligned} \tag{8.9.10}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore –4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (–4075.8 kJ):

$$\Delta H^o_{comb} = +1273.3\ kJ + (-4075.8\ kJ) = -2802.5\ kJ \tag{8.9.11}$$

This is the same result we obtained using the "products minus reactants" rule and ΔH^0_f values. The two results must be the same because Equation 8.9.11 is just a more compact way of describing the thermochemical cycle shown in Figure 8.9.2.

Example 8.9.2

Long-chain fatty acids such as palmitic acid [$CH_3(CH_2)_{14}CO_2H$] are one of the two major sources of energy in our diet (ΔH^0_f =–891.5 kJ/mol). Use the data in the Reference Table to calculate ΔH^0_{comb} for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel — glucose or palmitic acid?

Given: compound and ΔH^0_f values

Asked for: ΔH^0_{comb} per mole and per gram

Strategy:

A After writing the balanced chemical equation for the reaction, use Equation 8.9.6 and the values from the Reference Table to calculate ΔH^0_{comb} the energy released by the combustion of 1 mol of palmitic acid.

B Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated in Equation 8.9.9 for the combustion of glucose to determine which is the better fuel.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH^0_f As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_2\,(s) + 23O_2\,(g) \rightarrow 16CO_2\,(g) + 16H_2)\,(l) \tag{8.9.12}$$

Using Equation 9.4.5 ("products minus reactants") with ΔH^0_f values from the Reference Table (and omitting the physical states of the reactants and products to save space) gives

$$\Delta H^o_{comb} = \sum m\Delta H^o{}_f\,(products) - \sum n\Delta H^o{}_f\,(reactants)$$

$$= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\ )]$$

$$-\,[-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\ )]$$

$$= -9977.3\ kJ/mol$$

This is the energy released by the combustion of 1 mol of palmitic acid.

B The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{9977.3\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{256.42\ g}\right) = -38.910\ kJ/g$$

As calculated in Equation 8.9.9, ΔH^{o}_{f} of glucose is –2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H^{o}_{comb}\ per\ gram = \left(\frac{-2802.5\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{180.16\ g}\right) = -15.556\ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

Exercise 8.9.2

Use the data in Appendix A to calculate ΔH^{o}_{rxn} for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain H_2(g):

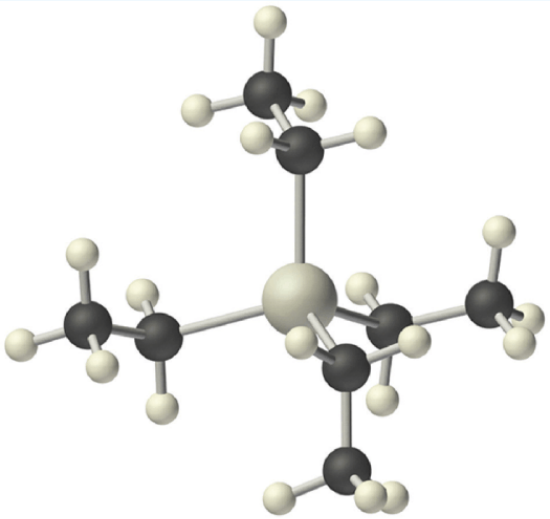
$$\underset{water-gas\ shift\ reaction}{CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g)}$$

Answer available at the end of this section.

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's ΔH^{o}_{f} which we cannot obtain otherwise. This procedure is illustrated in Example 3.

Example 8.9.3

Beginning in 1923, tetraethyllead [$(C_2H_5)_4Pb$] was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are CO_2(g), H_2O(l), and red PbO(s). What is the standard enthalpy of formation of tetraethyllead, given that ΔH^{o}_{f} is –19.29 kJ/g for the combustion of tetraethyllead and ΔH^{o}_{f} of red PbO(s) is –219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH^{o}_{comb} values

Asked for: ΔH^{o}_{f} of the reactants

Strategy:

A Write the balanced chemical equation for the combustion of tetraethyl lead. Then insert the appropriate quantities into Equation 9.4.4 to get the equation for ΔH^{o}_{f} of tetraethyl lead.

B Convert ΔH^{o}_{comb} per gram given in the problem to ΔH^{o}_{comb} per mole by multiplying ΔH^{o}_{comb} per gram by the molar mass of tetraethyllead.

C Use the Reference Table to obtain values of ΔH^{o}_{f} for the other reactants and products. Insert these values into the equation for ΔH^{o}_{f} of tetraethyl lead and solve the equation.

Solution:

A The balanced chemical equation for the combustion reaction is as follows:

$$\left(C_2H_5\right)_4 Pb\,(l) + 27O_2\,(g) \rightarrow 2PbO\,(s) + 16CO_2\,(g) + 20H_2O\,(l) \tag{8.9.13}$$

Using Equation 8.9.6 gives

$$\Delta H^{o}_{comb} = \left[2\Delta H^{o}_{f}\,(PbO) + 16\Delta H^{o}_{f}\,(CO_2) + 20\Delta H^{o}_{f}\,(H_2O)\right] - \left[2\Delta H^{o}_{f}\left(\left(C_2H_5\right)_4 Pb\right) + 27\Delta H^{o}_{f}\,(O_2)\right]$$

Solving for ΔH^{o}_{f} [$(C_2H_5)4Pb$] gives

$$\Delta H^{o}_{f}\left(\left(C_2H_5\right)_4 Pb\right) = \Delta H^{o}_{f}\,(PbO) + 8\Delta H^{o}_{f}\,(CO_2) + 10\Delta H^{o}_{f}\,(H_2O) - \frac{27}{2}\Delta H^{o}_{f}\,(O_2) - \frac{\Delta H^{o}_{comb}}{2}$$

The values of all terms other than ΔH^{o}_{f} [$(C_2H_5)4Pb$] are given in the Reference Table

B The magnitude of ΔH^{o}_{comb} is given in the problem in kilojoules per *gram* of tetraethyl lead. We must therefore multiply this value by the molar mass of tetraethyl lead (323.44 g/mol) to get ΔH^{o}_{comb} for 1 mol of tetraethyl lead:

$$\Delta H^{o}_{comb} = \left(\frac{-1929\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right) = -6329\ kJ/mol$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, ΔH^{o}_{rxn} is

$$\Delta H^{o}_{rxn} = 2\ \cancel{mol\ \left(C_2H5\right)_4 Pb}\left(\frac{-6929\ kJ}{1\ \cancel{mol\ \left(C_2H5\right)_4 Pb}}\right) = -12,480\ kJ$$

C Inserting the appropriate values into the equation for ΔH^{o}_{f} [$(C_2H_5)4Pb$] gives

$$\begin{aligned}\Delta H^{o}_{f}\left[\left(C_2H_4\right)_4 Pb\right] &= [1\ mol\ PbO\ \times 219.0\ kJ/mol] + [8\ mol\ CO_2 \times (-393.5\ kJ/mol)] \\ &\quad + [10\ mol\ H_2O \times (-285.8\ kJ/mol)] + [-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2] \\ &\quad [12,480.2\ kJ/mol\ \ \left(C_2H_5\right)_4 Pb] \\ &= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol\end{aligned}$$

Exercise 8.9.3

Ammonium sulfate [$(NH_4)_2SO_4$] is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(s)$

The value of ΔH^{o}_{rxn} is −2805 kJ/g H_2SO_4. Use the data in Appendix A to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer available at the end of this section.

Key Equations

relationship between ΔH^{o}_{rxn} and ΔH^{o}_{f}

Equation $8.9.6$: $\Delta H^{o}_{rxn} = \Sigma \Delta H^{o}_{f}(\text{products}) - \Delta H^{o}_{f}(\text{reactants})$

Summary

The **enthalpy of formation (ΔH_f)** is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH^{o}_{f}) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH^{o}_{rxn}) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the "products minus reactants" rule. The **enthalpy of solution (ΔH_{soln})** is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Key Takeaways

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 ^{o}C and 1 atm.
- The elemental form of each atom is that with the lowest enthalpy in the standard state.
- The standard state heat of formation for the elemental form of each atom is zero.

Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section $8.9.9$) before proceeding to the Conceptual Problems.

1. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.
2. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?
3. What is the difference between ΔH^{o}_{f} and ΔH_f?
4. How can ΔH^{o}_{f} of a compound be determined if the compound cannot be prepared by the reactions used to define its standard enthalpy of formation?
5. For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

   a. HBr

   b. CH_3OH

   c. $NaHCO_3$
6. Describe the distinction between ΔH_{soln} and ΔH_f.

7. The following table lists ΔH^{o}_{soln} values for some ionic compounds. If 1 mol of each solute is dissolved in 500 mL of water, rank the resulting solutions from warmest to coldest.

Compound	ΔH^{o}_{soln}(kJ/mol)
KOH	−57.61
$LiNO_3$	−2.51
$KMnO_4$	43.56
$NaC_2H_3O_2$	−17.32

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 8.9.9) before proceeding to the Numerical Problems.

1. Using "Appendix A, calculate ΔH^{o}_{rxn} for each chemical reaction.

   a. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

   b. $CaCO_3(s, \text{calcite}) \rightarrow CaO(s) + CO_2(g)$

   c. $AgNO_3(s) + NaCl(s) \rightarrow AgCl(s) + NaNO_3(s)$

2. Using "Appendix A, determine ΔH^{o}_{rxn} for each chemical reaction.

   a. $2Na(s) + Pb(NO_3)_2(s) \rightarrow 2NaNO_3(s) + Pb(s)$

   b. $Na_2CO_3(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + CO_2(g) + H_2O(l)$

   c. $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

3. Calculate ΔH^{o}_{rxn} for each chemical equation. If necessary, balance the chemical equations.

   a. $Fe(s) + CuCl_2(s) \rightarrow FeCl_2(s) + Cu(s)$

   b. $(NH_4)_2SO_4(s) + Ca(OH)_2(s) \rightarrow CaSO_4(s) + NH_3(g) + H_2O(l)$

   c. $Pb(s) + PbO_2(s) + H_2SO_4(l) \rightarrow PbSO_4(s) + H_2O(l)$

4. Calculate ΔH^{o}_{rxn} for each reaction. If necessary, balance the chemical equations.

   a. $4HBr(g) + O_2(g) \rightarrow 2H_2O(l) + 2Br_2(l)$

   b. $2KBr(s) + H_2SO_4(l) \rightarrow K_2SO_4(s) + 2HBr(g)$

   c. $4Zn(s) + 9HNO_3(l) \rightarrow 4Zn(NO_3)_2(s) + NH_3(g) + 3H_2O(l)$

5. Use the data in "Appendix A to calculate ΔH^{o}_{f} for the reaction $Sn(s, \text{white}) + 4HNO_3(l) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$.

6. Use the data in "Appendix A to calculate ΔH^{o}_{f} for the reaction $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(l)$.

7. How much heat is released or required in the reaction of 0.50 mol of HBr(g) with 1.0 mol of chlorine gas to produce bromine gas?

8. How much energy is released or consumed if 10.0 g of N_2O_5 is completely decomposed to produce gaseous nitrogen dioxide and oxygen?

9. In the mid-1700s, a method was devised for preparing chlorine gas from the following reaction:

   $NaCl(s) + H_2SO_4(l) + MnO_2(s) \rightarrow Na_2SO_4(s) + MnCl_2(s) + H_2O(l) + Cl_2(g)$

   Calculate ΔH^o_{rxn} for this reaction. Is the reaction exothermic or endothermic?

10. Would you expect heat to be evolved during each reaction?

    1. solid sodium oxide with gaseous sulfur dioxide to give solid sodium sulfite
    2. solid aluminum chloride reacting with water to give solid aluminum oxide and hydrogen chloride gas

11. How much heat is released in preparing an aqueous solution containing 6.3 g of calcium chloride, an aqueous solution containing 2.9 g of potassium carbonate, and then when the two solutions are mixed together to produce potassium chloride and calcium carbonate?

12.

Answers

1. a. –1203 kJ/mol O_2

   b. 179.2 kJ

   c. –59.3 kJ

2.
3.
4.

5. –174.1 kJ/mol

6.

7. –20.3 kJ

8.

9. –34.3 kJ/mol Cl_2; exothermic

10.

11. ΔH = –2.86 kJ $CaCl_2$: –4.6 kJ; K_2CO_3, –0.65 kJ; mixing, –0.28 kJ

Contributors

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Modified by Joshua Halpern

Answers

Exercise 8.9.1

1. $$Na\,(g) + \frac{1}{2}Cl_2\,(g) \rightarrow NaCl\,(s)$$
2. $$H_2\,(g) + \frac{1}{8}S_8\,(s) + 2O_2\,(g) \rightarrow H_2SO_4\,(l)$$

3. $2C(s) + O_2(g) + 2H_2(g) \rightarrow CH_3CO_2H(l)$

Exercise 8.9.2

–41.2 kJ/mol

Exercise 8.9.3

–1181 kJ/mol

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8.10: The Second Law of Thermodynamics

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use the 1st, **2nd,** and 3rd laws of thermodynamics to explain key relationships between heat, work, and physical or chemical processes.

The first law of thermodynamics governs changes in the state function we have called internal energy (U). Changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. We learned that energy must be conserved in any process.

What we have not learned, yet, however, is how to decide whether a particular process or reaction will occur spontaneously. Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure 8.10.1.

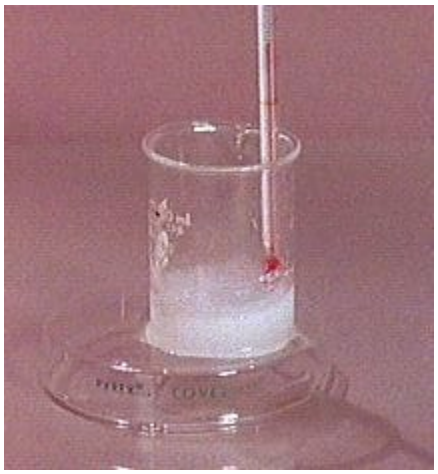


Figure 8.10.1: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called **entropy (S)**, a thermodynamic property of all substances that is proportional to their degree of "disorder". In Chapter 13, we introduced the concept of entropy in relation to solution formation. Here we further explore the nature of this state function and define it mathematically.

Entropy measures available *microstates;* more microstates = more entropy

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states: $\Delta S = S_f - S_i$.

We can illustrate the concepts of microstates and entropy using a deck of playing cards, as shown in Figure 8.10.2. In any new deck, the 52 cards are arranged by four suits, with each suit arranged in descending order. If the cards are shuffled, however, there are approximately 10^{68} different ways they might be arranged, which corresponds to 10^{68} different microscopic states. The entropy of an ordered new deck of cards is therefore low, whereas the entropy of a randomly shuffled deck is high. Card games assign a higher value to a hand that has a low degree of disorder. In games such as five-card poker, only 4 of the 2,598,960 different possible hands, or microstates, contain the highly ordered and valued arrangement of cards called a royal flush, almost 1.1 million hands contain one pair, and more than 1.3 million hands are completely disordered and therefore have no value. Because the last two arrangements are far more probable than the first, the value of a poker hand is inversely proportional to its entropy.

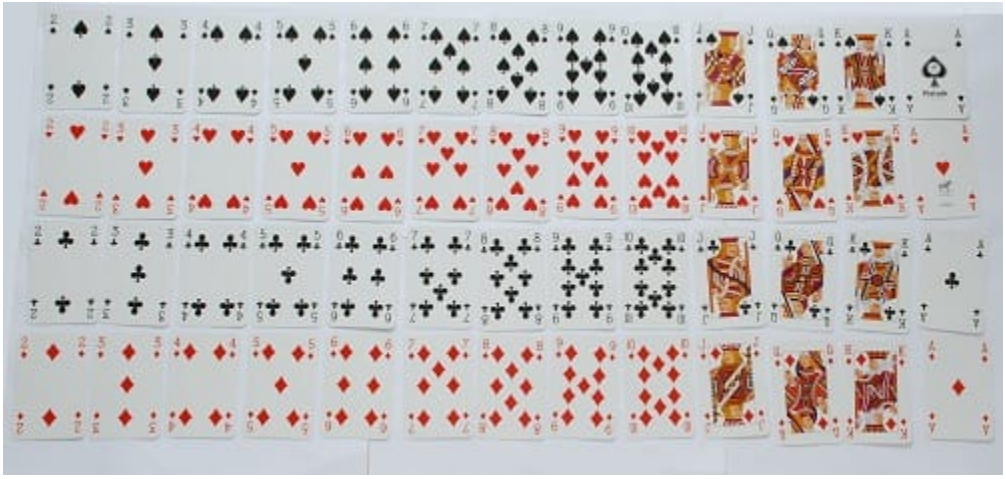


Figure 8.10.2: Illustrating Low- and High-Entropy States with a Deck of Playing Cards. An new, unshuffled deck has only a single arrangement, so there is only one microstate. In contrast, a randomly shuffled deck can have any one of approximately 10^{68} different arrangements, which correspond to 10^{68} different microstates. (CC BY-3.0 ; Trainler).

Instead of a deck of cards, let's now consider 1 L of an ideal gas at standard temperature and pressure (STP), which contains 2.69×10^{22} molecules (6.022×10^{23} molecules/22.4 L). If we allow the sample of gas to expand into a second 1 L container, the probability of finding all 2.69×10^{22} molecules in one container and none in the other at any given time is extremely small, approximately $\frac{2}{2.69 \times 10^{22}}$. The probability of such an occurrence is effectively zero. Although nothing prevents the molecules in the gas sample from occupying only one of the two bulbs, that particular arrangement is so improbable that it is never actually observed. The probability of arrangements with essentially equal numbers of molecules in each bulb is quite high, however, because there are many equivalent microstates in which the molecules are distributed equally. Hence a macroscopic sample of a gas occupies all of the space available to it, simply because this is the most probable arrangement.

Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Example 8.10.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.
b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

Exercise 8.10.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm or a sample of 2 mol of $NH_3(g)$ at 25°C and 1 atm

Answer a available at the end of this section.

Video Solution

The Second Law of Thermodynamics

For reasons we will not elaborate greatly on here, for a special type of process known as a *reversible process,* the amount of entropy gained or lost by the surroundings is related to the amount of heat lost or gained by the system. This is because the quantity of heat transferred from the system (q_{rev}) is directly proportional to the absolute temperature of the surroundings (T) according to the equation below.

$$\Delta S_{\textrm{surr}}=\dfrac{q_{\textrm{rev}}}{T}=\dfrac{\Delta H_{\textrm{sys}}}{T}$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K).

As an example, let's consider the reversible melting of a sample of ice right at its melting point of 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 8.10.6. The system is the ice, and the surroundings are a sample of low-density carbon foam that is thermally conductive and we can use to measure temperature. Because the carbon foam is initially warmer than the ice, heat will flow towards the ice as depicted by the arrow in the thermogram below going from red (warm carbon foam) to blue (cold

ice). From this process, we can write the entropy of fusion of ice as follows:

$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fus}}}{T}$$

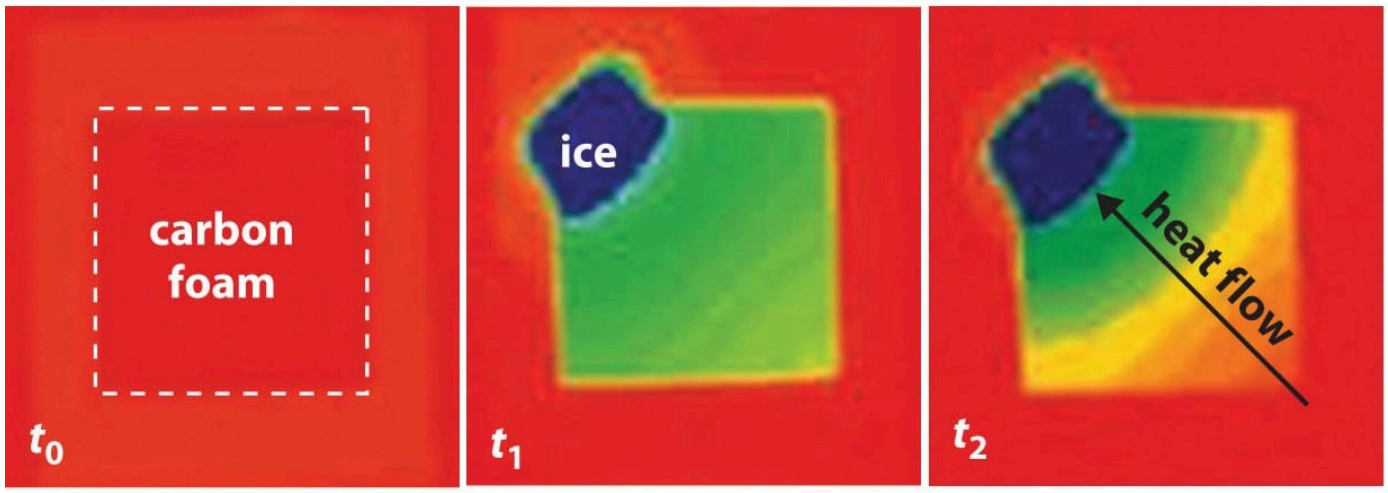


Figure 8.10.6: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change. However, the entropy change of the system is ΔS_{fus} = (6.01 kJ/mol)/(273 K) = 22.0 J/(mol•K) = ΔS_{sys}. On the other hand, the amount of heat lost by the surroundings is the same as the amount gained by the ice, so $\Delta S_{surr} = q_{rev}/T$ = –(6.01 kJ/mol)/(273 K) = –22.0 J/(mol•K). Once again, we see that the entropy of the universe does not change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 22.0 \text{ J/(mol•K)} - 22.0 \text{ J/(mol•K)} = 0$$

This reversible melting of ice is an example of a principle that is true of all reversible processes and constitutes part of the second law of thermodynamics: the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process.

The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an observable non-spontaneous process.

Processes can also be irreversible, but the second law still holds. As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{\text{univ}} = \Delta S_{\text{cold}} + \Delta S_{\text{hot}} = \frac{q}{T_{\text{cold}}} + \left(-\frac{q}{T_{\text{hot}}}\right) \tag{8.10.1}$$

The numerators on the right side of Equation 8.10.1 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which ΔS_{univ} is negative will not occur as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 8.10.7).



Figure 8.10.7: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

Example 8.10.2: Tin Pest

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon was argued to have plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers' uniforms were made of tin and may have disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with ΔH = −2.1 kJ/mol at 13.2°C.

a. What is ΔS for this process?
b. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation ??? to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution

a. We know from Equation ??? that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where q_{rev} = ΔH. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{(-2.1\ \text{kJ/mol})(1000\ \text{J/kJ})}{286.4\ \text{K}} = -7.3\ \ \text{J/(mol} \cdot \text{K)}$$

b. The fact that ΔS < 0 means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 8.10.1**:** *Time lapse tin pest reaction.*

Note: Whether failing buttons were indeed a contributing factor in the failure of the invasion remains disputed; critics of the theory point out that the tin used would have been quite impure and thus more tolerant of low temperatures. Laboratory tests provide evidence that the time required for unalloyed tin to develop significant tin pest damage at lowered temperatures is about 18 months, which is more than twice the length of Napoleon's Russian campaign. It is clear though that some of the regiments employed in the campaign had tin buttons and that the temperature reached sufficiently low values (at least -40 °C)

Exercise 8.10.2

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with ΔH = 0.401 kJ/mol at 1 atm.

a. What is ΔS for this process?
b. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer a available at the end of this section.

Summary

For a given system, the greater the number of microstates, the higher the entropy. During a spontaneous process, the entropy of the universe increases.

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{8.10.2}$$

A measure of the disorder of a system is its entropy (S), a state function whose value increases with an increase in the number of available microstates. A reversible process is one for which all intermediate states between extremes are equilibrium states; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

Answers

Exercise 8.10.1

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

a mixture of 3 mol of H_2(g) and 1 mol of N_2(g) at 25°C and 1 atm (more molecules of gas are present)

Exercise 8.10.2

1.09 J/(mol•K)

S_α

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8.11: Entropy Changes and the Third Law of Thermodynamics

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use the 1st, 2nd, **and 3rd** laws of thermodynamics to explain key relationships between heat, work, and physical or chemical processes.
- Use appropriate mathematical expressions (stoichiometry, Hess's Law) and relevant experimental data (calorimetry, bond energies, formation ΔH/ΔG, **standard molar entropy**, definition of free energy) to calculate ΔH, **ΔS,** and ΔG for a chemical reaction.

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 8.11.1). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum effects). Such a state of perfect order (or, conversely, zero disorder) corresponds to zero entropy. In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

Third Law of Thermodynamics

The entropy of any perfectly ordered, crystalline substance at absolute zero is *zero*.

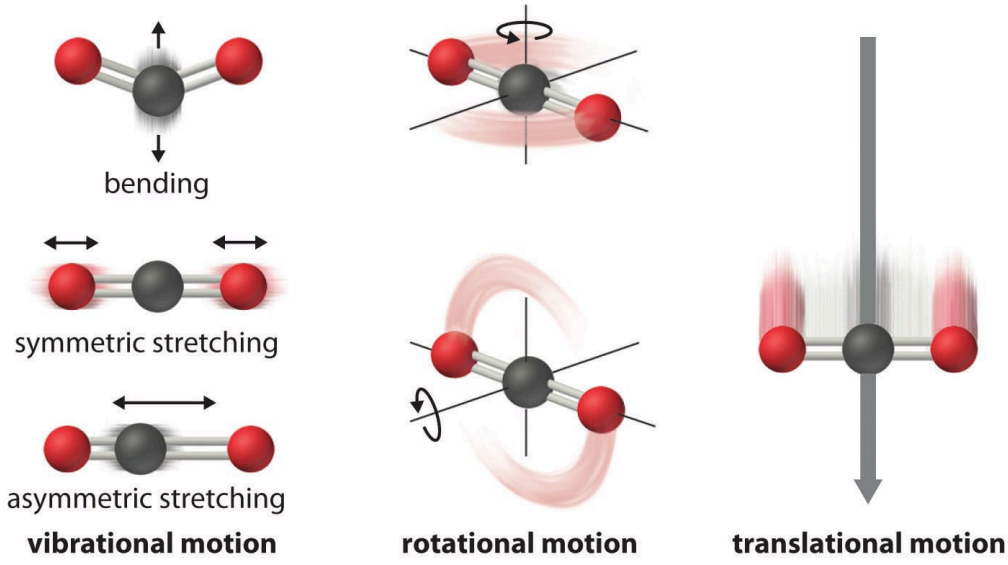


Figure 8.11.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature. In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The area under the curve

between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms.

Comparing Standard Molar Entropy Values

We can use the third law to calculate and tabulate values of the standard molar entropy (S°), which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of S° are J/(mol•K). That calculation is beyond the scope of this class. However, we can observe some general trends in standard molar entropy values.

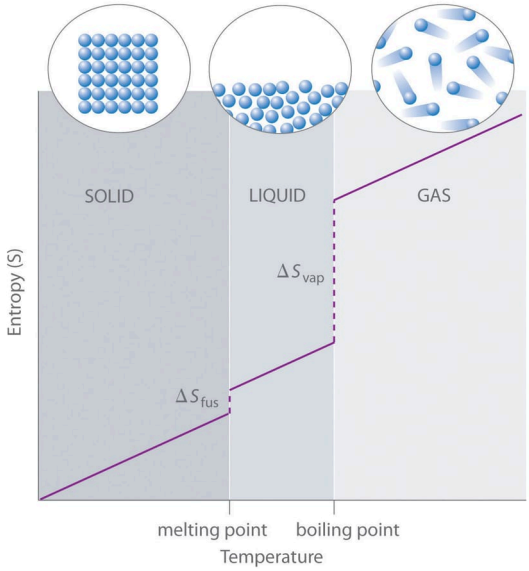


Figure 8.11.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}).

As shown in Table 8.11.1, for substances with approximately the same molar mass and number of atoms, S° values fall in the order S°(gas) > S°(liquid) > S°(solid). For instance, S° for liquid water is 70.0 J/(mol•K), whereas S° for water vapor is 188.8 J/(mol•K). Likewise, S° is 260.7 J/(mol•K) for gaseous I_2 and 116.1 J/(mol•K) for solid I2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases. The correlation between physical state and absolute entropy is illustrated in Figure 8.11.2, which is a generalized plot of the entropy of a substance versus temperature.

Table 8.11.1: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		Liquids		Solids	
Substance	*S° [J/(mol•K)]*	*Substance*	*S° [J/(mol•K)]*	*Substance*	*S° [J/(mol•K)]*
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1

CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

Note

Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.

A closer examination of Table 8.11.1 also reveals that substances with similar molecular structures tend to have similar S° values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond [S° = 2.4 J/(mol•K)]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S° [5.7 J/(mol•K)] due to more disorder in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S° values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S°, which reflects a more ordered structure.

Note

ΔS° for a reaction can be calculated from absolute entropy values using the same "products minus reactants" rule used to calculate ΔH°.

Calculating ΔS from Standard Molar Entropy Values

To calculate ΔS° for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 8.11.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

Example 8.11.1

Use the data in Table 8.11.1 to calculate ΔS° for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 8.11.1. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS° for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$$

We calculate ΔS° for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\Delta S^\circ_{\text{rxn}} = \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants}) \tag{8.11.1}$$

$$= [8S^\circ(\text{CO}_2) + 9S^\circ(\text{H}_2\text{O})] - [S^\circ(\text{C}_8\text{H}_{18}) + \frac{25}{2}S^\circ(\text{O}_2)] \tag{8.11.2}$$

$$= \{[8 \text{ mol } \text{CO}_2 \times 213.8 \text{ J/(mol} \cdot \text{K)}] + [9 \text{ mol } \text{H}_2\text{O} \times 188.8 \text{ J/(mol} \cdot \text{K)}]\} \tag{8.11.3}$$

$$- \left\{[1 \text{ mol } \text{C}_8\text{H}_{18} \times 329.3 \text{ J/(mol} \cdot \text{K)}] + \left[\frac{25}{2} \text{ mol } \text{O}_2 \times 205.2 \text{ J/(mol} \cdot \text{K)}\right]\right\} \tag{8.11.4}$$

$$= 515.3 \text{ J/K} \tag{8.11.5}$$

ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise 8.11.1

Use the data in Table 8.11.1 to calculate ΔS° for the reaction of H_2(g) with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer: −361.1 J/K

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8.12: Spontaneity is Related to Entropy

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Classify reactions as endothermic/exothermic (ΔH), **entropically favored/entropically disfavored (ΔS)**, or **spontaneous/nonspontaneous (ΔG)** given relevant thermodynamic data, balanced chemical equations, and/or a reaction coordinate diagram.

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. A **spontaneous process** is one that occurs naturally under certain conditions. A **nonspontaneous process**, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure 8.12.1).

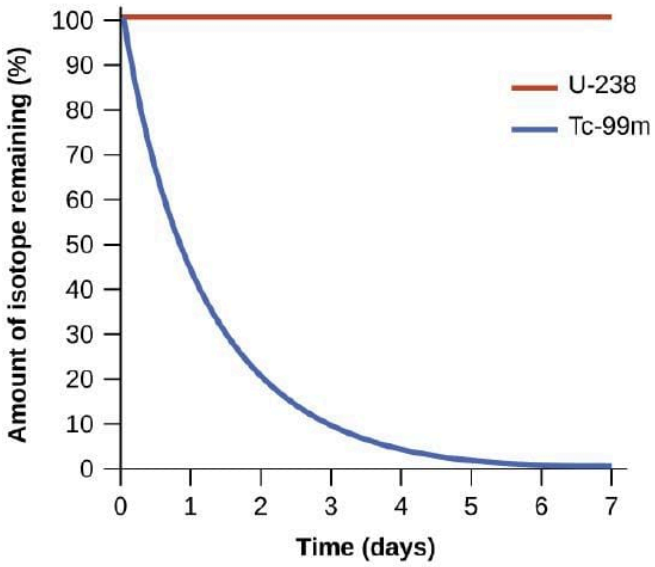


Figure 8.12.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (Figure 8.12.2).

$$C(s,\text{ diamond }) \longrightarrow C(s,\text{ graphite })$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic

calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow; so, for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

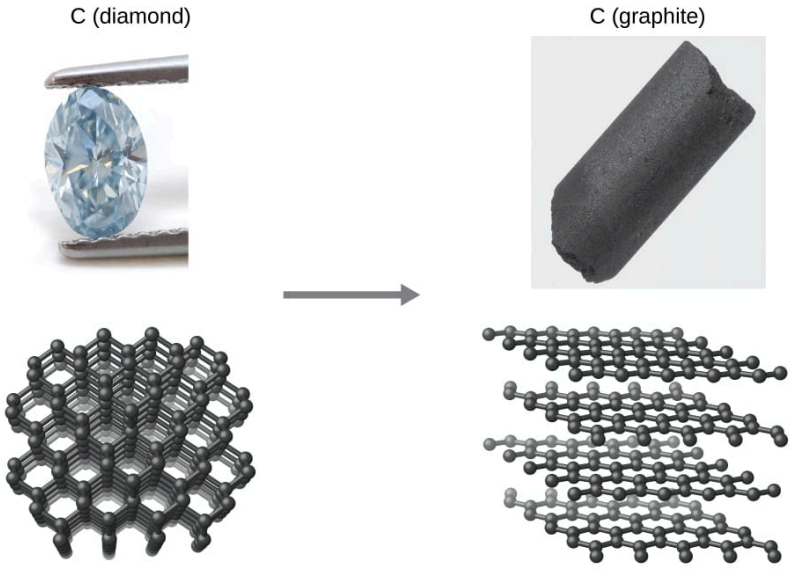


Figure 8.12.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Sponaneity Favors the Dispersal of Matter and Energy

Extending the discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas in one flask and the other flask is empty ($P = 0$) (Figure 8.12.3). When the valve is opened, the gas spontaneously expands to fill both flasks equally. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

\[w=-P \Delta V=0 \quad \quad (P=0 \text { in a vacuum })]

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The *first law of thermodynamics* confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w = 0 + 0 = 0$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

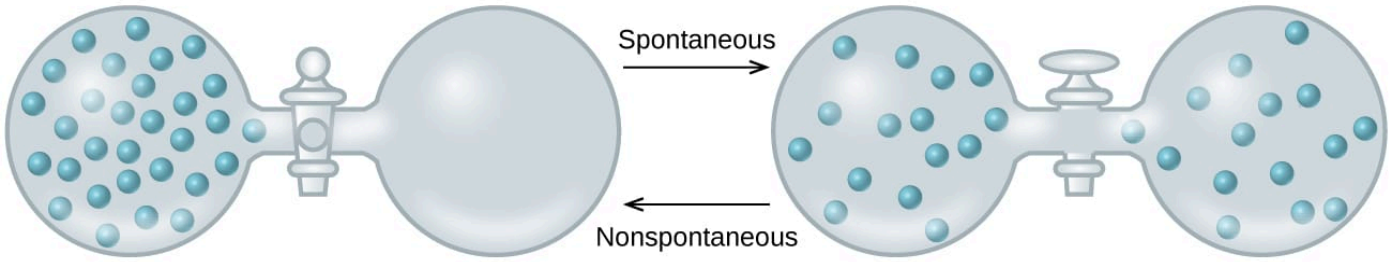


Figure 8.12.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 8.12.4). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure 8.12.4: When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 8.12.1: Redistribution of Matter during a Spontaneous Process

Describe how matter is redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution



(a) (b) (c)

Figure 8.12.5: (credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Paul A. Flowers)

a. Sublimation is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.
b. Condensation is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.
c. The process in question is diffusion. This process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Exercise 8.12.1

Describe how energy is redistributed when a spoon at room temperature is placed in a cup of hot coffee.

Answer available at the end of this section.

Answers

Exercise 8.12.1

Heat will spontaneously flow from the hotter object (coffee) to the colder object (spoon), resulting in a more uniform distribution of thermal energy as the spoon warms and the coffee cools.

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8.13: Entropy

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Classify reactions as endothermic/exothermic (ΔH), **entropically favored/entropically disfavored (ΔS)**, or spontaneous/nonspontaneous (ΔG) given relevant thermodynamic data, balanced chemical equations, and/or a reaction coordinate diagram.

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 8.13.4. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

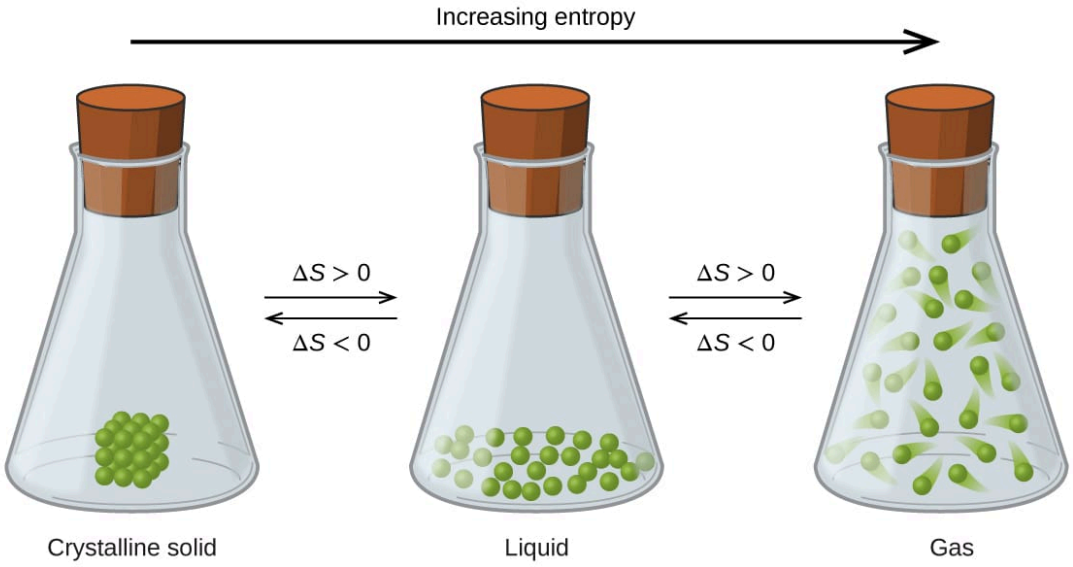


Figure 8.13.4: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the gaseous phase, in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance

increases with temperature (Figure 8.13.5).

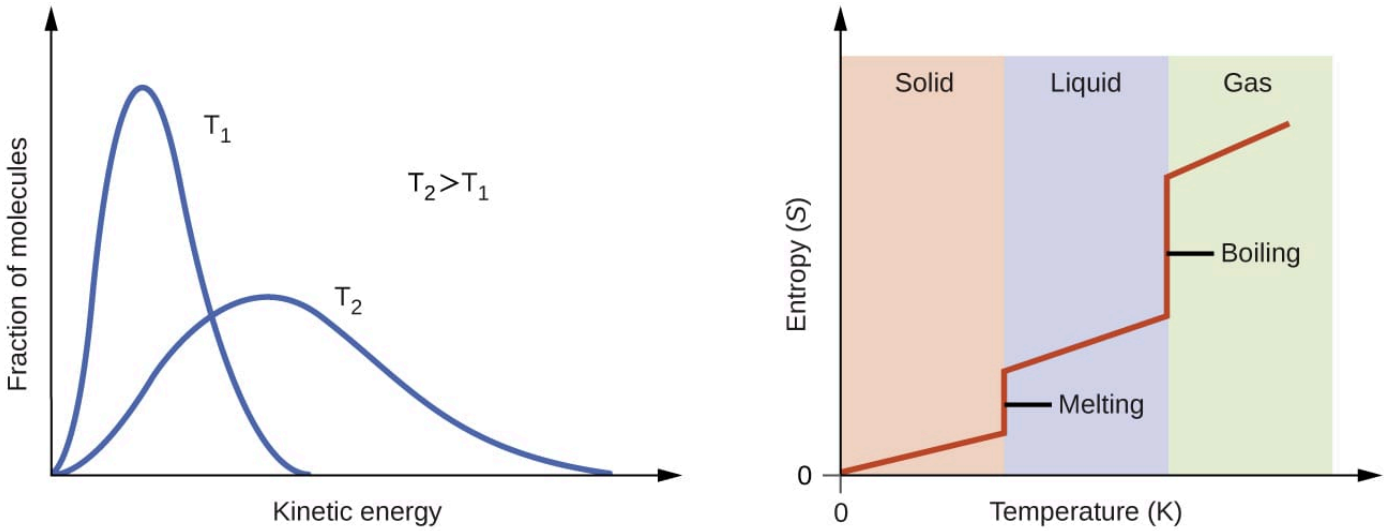


Figure 8.13.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

Link to Learning

Try this simulator with interactive visualization of the dependence of particle location and freedom of motion on physical state and temperature.

The entropy of a substance is influenced by the structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example 8.13.2.

Example 8.13.2: Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature one mole liquid water at 50 °C
b. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
c. \(C_6 H_6(l)+\frac{15}{2} O_2(g) \longrightarrow 6 CO_2(g)+3 H_2O(l))
d. $NH_3(s) \longrightarrow NH_3(l)$

Solution

a. positive, temperature increases

b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

Exercise 8.13.1

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

a. $NaNO_3(s) \longrightarrow Na^+(aq) + NO_3{}^-(aq)$
b. the freezing of liquid water
c. $CO_2(s) \longrightarrow CO_2(g)$
d. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

Answer available at the end of this section.

Answers

Exercise 8.13.1

(a) Positive; The solid dissolves to give an increase of mobile ions in solution.
(b) Negative; The liquid becomes a more ordered solid.
(c) Positive; The relatively ordered solid becomes a gas.
(d) Positive; There is a net increase in the amount of gaseous species.

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8.14: Free Energy is a Good Predictor of Spontaneity

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Classify reactions as endothermic/exothermic (ΔH), entropically favored/entropically disfavored (ΔS), **or spontaneous/nonspontaneous (ΔG)** given relevant thermodynamic data, balanced chemical equations, and/or a reaction coordinate diagram.
- Use appropriate mathematical expressions (stoichiometry, Hess's Law) and relevant experimental data (calorimetry, bond energies, formation ΔH/**ΔG**, standard molar entropy, **definition of free energy**) to calculate ΔH, ΔS, and **ΔG** for a chemical reaction.
- Predict how changing **temperature,** pressure, and/or volume conditions will affect the spontaneity of a physical process or chemical reaction.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for both a system and its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy (G), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{8.14.1}$$

Because it is a combination of state functions, G is also a state function.

J. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled "On the Equilibrium of Heterogeneous Substances" was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{8.14.2}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is

reversible or irreversible, and TΔS = q_{rev}. Using these expressions, we can reduce Equation 8.14.2 to $\Delta G = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, q = q_{rev} and ΔG = 0. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which ΔG ≠ 0? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T} \tag{8.14.3}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H \tag{8.14.4}$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{8.14.5}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \tag{8.14.6}$$

$$= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \tag{8.14.7}$$

Multiplying both sides of the inequality by –T reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \tag{8.14.8}$$

which is equal to ΔG (Equation 8.14.2). We can therefore see that for a spontaneous process, $\Delta G < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 8.14.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. For a system at constant temperature and pressure, we can summarize the following results:

- **If $\Delta G < 0$, the process occurs spontaneously.**
- **If $\Delta G = 0$, the system is at equilibrium.**
- **If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.**

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 8.14.5), we know that for 1 mol of water,

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b}}}$$

$$= \frac{40{,}657 \text{ J}}{373.15 \text{ K}}$$

$$= 108.96 \text{ J/K}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(383.15\ \text{K})(108.96\ \text{J/K})] \\ &= -1091\ \text{J}\end{aligned}$$

At 110°C, $\Delta G < 0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(363.15\ \text{K})(108.96\ \text{J/K})] \\ &= 1088\ \text{J}\end{aligned}$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ\text{C}} = 1090\ \text{J} = -\Delta G_{90^\circ\text{C}}$, as we would predict.

Relating Enthalpy and Entropy changes under Equilibrium Conditions

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 8.14.2), setting $\Delta G = 0$, and solving for T,

$$0\ \text{J} = 40{,}657\ \text{J} - T(108.96\ \text{J/K})$$
$$T = 373.15\ \text{K}$$

Thus $\Delta G = 0$ at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 8.14.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

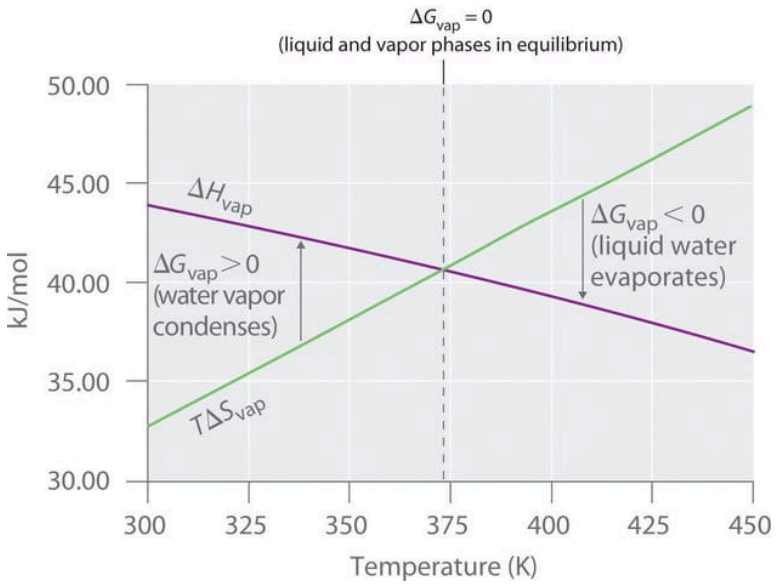


Figure 8.14.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH – TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy (ΔH > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid (ΔS > 0). At temperatures greater than 373 K, the TΔS term dominates, and ΔG < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 8.14.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{8.14.9}$$

This equation tells us that when energy is released during an exothermic process (ΔH < 0), such as during the combustion of a fuel, some of that energy can be used to do work (ΔG < 0), while some is used to increase the entropy of the universe (TΔS > 0). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 8.14.1, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 8.14.1: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach leaf cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10-20
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 8.14.10:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8.14.10}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG° means that the equilibrium constant is less than 1.

Example 8.14.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$\mathrm{H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O_2\,(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is –187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 8.14.10, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG° for the reaction, we need to know ΔH^o, ΔS^o, and T. We are given ΔH^o, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\ \text{mol}\ \mathrm{H_2O_2} \times 109.6\ \mathrm{J/(mol \cdot K)}] \\ &\quad - \{[1\ \text{mol}\ \mathrm{H_2} \times 130.7\ \mathrm{J/(mol \cdot K)}] + [1\ \text{mol}\ \mathrm{O_2} \times 205.2\ \mathrm{J/(mol \cdot K)}]\} \\ &= -226.3\ \mathrm{J/K}\ (\text{per mole of}\ \mathrm{H_2O_2})\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS^o is very negative for this reaction.

B Substituting the appropriate quantities into Equation 8.14.10,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\ \mathrm{kJ/mol} - (298.15\ \mathrm{K})[-226.3\ \mathrm{J/(mol \cdot K)} \times 1\ \mathrm{kJ}/1000\ \mathrm{J}] \\ &= -187.78\ \mathrm{kJ/mol} + 67.47\ \mathrm{kJ/mol} \\ &= -120.31\ \mathrm{kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS^o and ΔH^o for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH^o and $T\Delta S^o$ terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS^o term and for the energy needed to break bonds in the reactants.

Exercise 8.14.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).$$

Is the reaction spontaneous as written at 25°C?

Hint available at the end of this section.

Answer available at the end of this section.

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG_f°)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G_f^\circ = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \tag{8.14.11}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard

enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

$$\Delta G^o_{rxn} = \sum m\Delta G^o_f(products) - \sum n\Delta^o_f(reactants) \tag{8.14.12}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

The "Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG°_f values (Table T1) using the “products minus reactants” rule.

Example 8.14.2

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). Use the following data:

- ΔG°_f(isooctane) = –353.2 kJ/mol,
- $\Delta G^\circ_f(CO_2)$ = –394.4 kJ/mol, and
- $\Delta G^\circ_f(H_2O)$ = –237.1 kJ/mol. Is the reaction spontaneous as written?

Given: balanced chemical equation and values of ΔG°_f for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the “products minus reactants” rule to obtain ΔG°_{rxn}, remembering that ΔG°_f for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

$$\mathrm{C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \;\rightarrow 8\,CO_2\,(g) + 9\,H_2O\,(l)}$$

We are given ΔG°_f values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, ΔG°_f (O_2) is zero. Using the “products minus reactants” rule,

$$\begin{aligned}\Delta G^\circ &= [8\Delta G^\circ_f(\mathrm{CO_2}) + 9\Delta G^\circ_f(\mathrm{H_2O})] - \left[1\Delta G^\circ_f(\mathrm{C_8H_{18}}) + \frac{25}{2}\Delta G^\circ_f(\mathrm{O_2})\right] \\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\ &\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\ &= -4935.9\text{ kJ (per mol of } \mathrm{C_8H_{18}})\end{aligned}$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Exercise 8.14.2

Calculate ΔG° for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer available at the end of this section.

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 8.14.3

Calculate (a) ΔG° and (b) $\Delta G_{300^\circ C}$ for the reaction $N_2(g)+3H_2(g) \diamondsuit 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S^\circ(N_2)$ = 191.6 J/(mol•K),
- $S^\circ(H_2)$ = 130.7 J/(mol•K),
- $S^\circ(NH_3)$ = 192.8 J/(mol•K), and
- ΔH°_f (NH_3) = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG° and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 8.14.10 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 8.14.2 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 8.14.10, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ_{rxn} &= 2S^\circ(NH_3) - [S^\circ(N_2) + 3S^\circ(H_2)] \\ &= [2\text{ mol } NH_3 \times 192.8\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol } N_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol } H_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\} \\ &= -198.1\text{ J/K (per mole of } N_2) \end{aligned} \tag{8.14.13}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of ΔH°_f (NH_3) is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_f(\text{NH}_3) - [\Delta H^\circ_f(\text{N}_2) + 3\Delta H^\circ_f(\text{H}_2)] \\ &= [2 \times (-45.9\ \text{kJ/mol})] - [(1 \times 0\ \text{kJ/mol}) + (3 \times 0\ \text{kJ/mol})] \\ &= -91.8\ \text{kJ(per mole of N}_2\text{)}\end{aligned}$$

B Inserting the appropriate values into Equation 8.14.10

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ - T\Delta S^\circ = (-91.8\ \text{kJ}) - (298\ \text{K})(-198.1\ \text{J/K})(1\ \text{kJ}/1000\ \text{J}) = -32.7\ \text{kJ (per mole of N}_2\text{)}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 8.14.2:

$$\begin{aligned}\Delta G_{300^\circ\text{C}} &= \Delta H_{300^\circ\text{C}} - (573\ \text{K})(\Delta S_{300^\circ\text{C}}) \\ &= \Delta H^\circ - (573\ \text{K})\Delta S^\circ \\ &= (-91.8\ \text{kJ}) - (573\ \text{K})(-198.1\ \text{J/K})(1\ \text{kJ}/1000\ \text{J}) \\ &= 21.7\ \text{kJ (per mole of N}_2\text{)}\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the –TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

Exercise 8.14.3

Calculate

a. ΔG° and
b. $\Delta G_{750°C}$

for the following reaction

$$2\,\text{NO}\,(\text{g}) + \text{O}_2\,(\text{g}) \rightleftharpoons 2\,\text{NO}_2\,(\text{g})$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- ΔH°_f(NO_2) = 33.2 kJ/mol, and
- ΔH°_f (NO) = 91.3 kJ/mol.

Answer a available at the end of this section.

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting ΔG° = 0 in Equation 8.14.10, as illustrated in Example 8.14.4.

Example 8.14.4

As you saw in Example 8.14.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 9.5.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG° equal to zero in Equation 8.14.10 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 8.14.3, we calculated that ΔH° is –91.8 kJ/mol of N_2 and ΔS° is –198.1 J/K per mole of N_2, corresponding to ΔG° = –32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG° equal to zero and rearranging Equation 8.14.10 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{-198.1\ \text{J/K}} = 463\ \text{K}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise 8.14.4

As you found in the exercise in Example 8.14.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer available at the end of this section.

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change:

$$\Delta G = \Delta H - T\Delta S$$

- Standard free-energy change:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse

direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG° for a reaction.

Answers

Exercise 8.14.1

At 25°C, the standard enthalpy change (ΔH^o) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are

- S°(N_2H_4) = 121.2 J/(mol•K),
- S°(N_2) = 191.6 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Exercise 8.14.1

149.5 kJ/mol

no, not spontaneous

Video Solution

Exercise 8.14.2

92.8 kJ; no

Video Solution

Exercise 8.14.3

–72.5 kJ/mol of O_2

33.8 kJ/mol of O_2

Exercise 8.14.4

792.6 K

Video Solution

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8.15: Temperature Dependence of Free Energy

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Predict how changing **temperature**, pressure, and/or volume conditions will affect the spontaneity of a physical process or chemical reaction.

Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

Note

The numerical value of ΔG^{o} is always dependent on the temperature. In this section we are determining whether or not the **sign** of ΔG^{o} is dependent on the temperature.

To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

The extent of a process, as reflected in the arithmetic sign of its standard free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (Kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both $\Delta H°$ and $\Delta S°$ are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, $\Delta G°$ will be negative if the magnitude of the $T\Delta S°$ term is greater than $\Delta H°$. If the $T\Delta S°$ term is less than $\Delta H°$, the free energy change will be positive. Such a process is *product-favored at equilibrium at high temperatures and reactant-favored at equilibrium at low temperatures*.
2. **Both $\Delta H°$ and $\Delta S°$ are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, $\Delta G°$ will be negative if the magnitude of the $T\Delta S°$ term is less than $\Delta H°$. If the $T\Delta S°$ term's magnitude is greater than $\Delta H°$, the free energy change will be positive. Such a process is *product-favored at equilibrium at low temperatures* and *reactant-favored at equilibrium at high temperatures*.
3. **$\Delta H°$ is positive and $\Delta S°$ is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, $\Delta G°$ will be positive regardless of the temperature. Such a process is *reactant-favored at equilibrium at all temperatures*.
4. **$\Delta H°$ is negative and $\Delta S°$ is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, $\Delta G°$ will be negative regardless of the temperature. Such a process is *product-favored at equilibrium at all temperatures*.

These four scenarios are summarized in Table $8.15.1$

Table 8.15.1

Sign of ΔH^o	Sign of ΔS^o	Sign of ΔG^o	Temperature Dependence of ΔG^o
-	+	-	The sign of ΔG^o does not depend on the temperature.The reaction is product-favored at equilibrium at all temperatures.
+	-	+	The sign of ΔG^o does not depend on the temperature.The reaction is reactant-favored at equilibrium at all temperatures.
-	-	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Example 8.15.3: Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,\mathrm{C}(s)+\mathrm{O}_2(g) \longrightarrow 2\,\mathrm{CO}(g)$$

Does the sign of ΔG° of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H^{\circ} < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S^{\circ} > 0$). The reaction is therefore product-favored at equilibrium ($\Delta G^{\circ} < 0$) at all temperatures.

Exercise 8.15.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,\mathrm{Fe}(s)+3\,\mathrm{O}_2(g) \longrightarrow 2\,\mathrm{Fe}_2\mathrm{O}_3(s)$$

Does the sign of ΔG^o of this process depend upon temperature?

Answer available at the end of this section.

When considering the conclusions drawn regarding the temperature dependence of the sign of $\Delta G°$, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is reactant-favored at equilibrium at one temperature but product-favored at equilibrium at another temperature will necessarily undergo a change in “extent” (as reflected by its $\Delta G°$) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which $\Delta G°$ is plotted on the *y* axis versus *T* on the *x* axis:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$y = b + mx$$

Such a plot is shown in Figure 8.15.2. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependence for the sign of $\Delta G°$ as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative $\Delta G°$) to the other at a temperature that is characteristic of the process in question. This

temperature is represented by the *x*-intercept of the line, that is, the value of *T* for which ΔG° is zero:

$$\Delta G^{\circ} = 0 = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$$

Thus, saying a process is product-favored at equilibrium at "high" or "low" temperatures means the temperature is above or below, respectively, that temperature at which Δ*G*° for the process is zero.

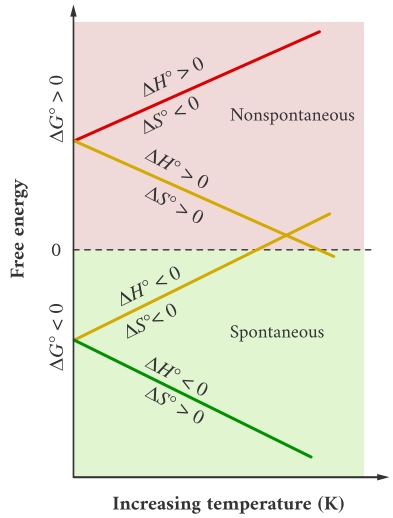


Figure 8.15.2: These plots show the variation in ΔG° with temperature for the four possible combinations of arithmetic sign for ΔH° and ΔS°. Note that in this graph of ΔG°, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

Example 8.15.4: Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its solid and liquid phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Tables T1 or T2 to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

When this process is at equilibrium, Δ*G* = 0, so the following is true:

$$0 = \Delta H^{\circ} - T\Delta S^{\circ} \qquad \text{or} \qquad T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$$

Using the standard thermodynamic data from Tables T1 or T2,

$$\begin{aligned}\Delta H^{\circ} &= \Delta H_{\mathrm{f}}^{\circ}(\mathrm{H_2O}(g)) - \Delta H_{\mathrm{f}}^{\circ}(\mathrm{H_2O}(l)) \\ &= -241.82\ \mathrm{kJ/mol} - (-285.83\ \mathrm{kJ/mol}) = 44.01\ \mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^{\circ} &= \Delta S_{298}^{\circ}(\mathrm{H_2O}(g)) - \Delta S_{298}^{\circ}(\mathrm{H_2O}(l)) \\ &= 188.8\ \mathrm{J/K \cdot mol} - 70.0\ \mathrm{J/K \cdot mol} = 118.8\ \mathrm{J/K \cdot mol}\end{aligned}$$

$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{44.01 \times 10^3\ \mathrm{J/mol}}{118.8\ \mathrm{J/K \cdot mol}} = 370.5\ \mathrm{K} = 97.3\ ^{\circ}\mathrm{C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Tables T1 or T2.). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

Exercise 8.15.4

Use the information in Tables T1 or T2 to estimate the boiling point of CS_2.

Answer available at the end of this section.

Answers

Exercise 8.15.3

$\Delta H°$ and $\Delta S°$ are both negative; the reaction is product-favored at equilibrium at low temperatures.

Exercise 8.15.4

313 K (accepted value 319 K).

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8.16: Free Energy

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for both a system and its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy (G), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{8.16.1}$$

Because it is a combination of state functions, G is also a state function.

J. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled “On the Equilibrium of Heterogeneous Substances” was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{8.16.2}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 8.16.2 to $\Delta G = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T} \tag{8.16.3}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H \tag{8.16.4}$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{8.16.5}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \tag{8.16.6}$$

$$= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \tag{8.16.7}$$

Multiplying both sides of the inequality by –T reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \tag{8.16.8}$$

which is equal to ΔG (Equation 8.16.2). We can therefore see that for a spontaneous process, $\Delta G < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 8.16.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 8.16.5), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{40{,}657\ \text{J}}{373.15\ \text{K}} \\ &= 108.96\ \text{J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(383.15\ \text{K})(108.96\ \text{J/K})] \\ &= -1091\ \text{J}\end{aligned}$$

At 110°C, $\Delta G < 0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(363.15\ \text{K})(108.96\ \text{J/K})] \\ &= 1088\ \text{J}\end{aligned}$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ\text{C}} = 1090\ \text{J} = -\Delta G_{90^\circ\text{C}}$, as we would predict.

Relating Enthalpy and Entropy changes under Equilibrium Conditions

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 8.16.2), setting $\Delta G = 0$, and solving for T,

0 J=40,657 J−T(108.96 J/K)
T=373.15 K

Thus $\Delta G = 0$ at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 8.16.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

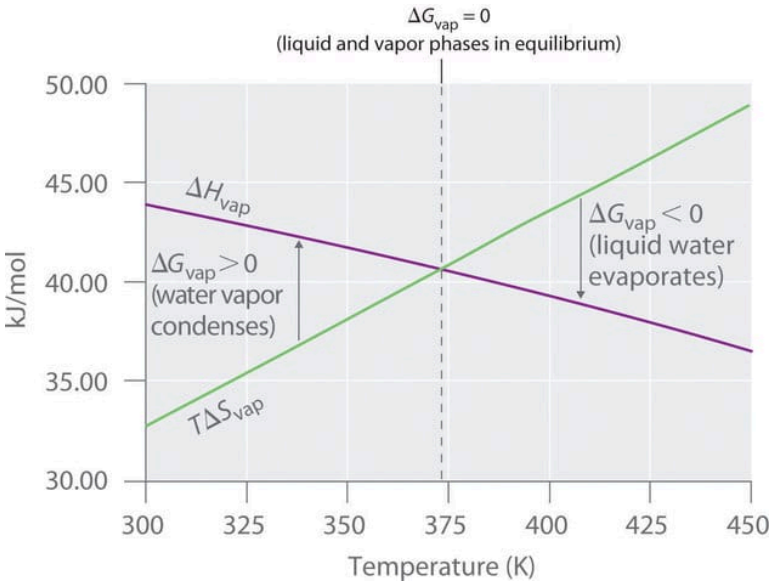


Figure 8.16.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy ($\Delta H > 0$), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid ($\Delta S > 0$). At temperatures greater than 373 K, the $T\Delta S$ term dominates, and $\Delta G < 0$, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 8.16.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{8.16.9}$$

This equation tells us that when energy is released during an exothermic process ($\Delta H < 0$), such as during the combustion of a fuel, some of that energy can be used to do work ($\Delta G < 0$), while some is used to increase the entropy of the universe ($T\Delta S > 0$). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 8.16.1, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 8.16.1: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach leaf cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10-20
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during

a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 8.16.10:

$$\Delta G° = \Delta H° - T\Delta S° \tag{8.16.10}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG° means that the equilibrium constant is less than 1.

Example 8.16.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$\mathrm{H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O_2\,(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is –187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 8.16.10, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG° for the reaction, we need to know ΔH^o, ΔS^o, and T. We are given ΔH^o, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the “products minus reactants” rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\ \mathrm{mol\ H_2O_2} \times 109.6\ \mathrm{J/(mol \cdot K)}] \\ &\quad - \{[1\ \mathrm{mol\ H_2} \times 130.7\ \mathrm{J/(mol \cdot K)}] + [1\ \mathrm{mol\ O_2} \times 205.2\ \mathrm{J/(mol \cdot K)}]\} \\ &= -226.3\ \mathrm{J/K\ (per\ mole\ of\ H_2O_2)}\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS^o is very negative for this reaction.

B Substituting the appropriate quantities into Equation 8.16.10,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\ \text{kJ/mol} - (298.15\ \text{K})[-226.3\ \text{J/(mol}\cdot\text{K)} \times 1\ \text{kJ/1000 J}] \\ &= -187.78\ \text{kJ/mol} + 67.47\ \text{kJ/mol} \\ &= -120.31\ \text{kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS^o and ΔH^o for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH^o and $T\Delta S^o$ terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS^o term and for the energy needed to break bonds in the reactants.

Exercise 8.16.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).$$

Is the reaction spontaneous as written at 25°C?

Hint available at the end of this section.

Answer available at the end of this section.

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG_f°)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G_f^\circ = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \tag{8.16.11}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

$$\Delta G_{rxn}^o = \sum m\Delta G_f^o(products) - \sum n\Delta_f^o(reactants) \tag{8.16.12}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

The "Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG°_f values (Table T1) using the “products minus reactants” rule.

Example 8.16.2

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). Use the following data:

- $\Delta G°_f$(isooctane) = –353.2 kJ/mol,
- $\Delta G°_f(CO_2)$ = –394.4 kJ/mol, and

- $\Delta G°_f(H_2O)$ = –237.1 kJ/mol. Is the reaction spontaneous as written?

Given: balanced chemical equation and values of $\Delta G°_f$ for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the "products minus reactants" rule to obtain $\Delta G°_{rxn}$, remembering that $\Delta G°_f$ for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

$$\mathrm{C_8H_{18}\,(l)} + \tfrac{25}{2}\,\mathrm{O_2\,(g)} \rightarrow 8\,\mathrm{CO_2\,(g)} + 9\,\mathrm{H_2O\,(l)}$$

We are given $\Delta G°_f$ values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, $\Delta G°_f\,(O_2)$ is zero. Using the "products minus reactants" rule,

$$\begin{aligned}\Delta G° &= [8\Delta G°_f(\mathrm{CO_2}) + 9\Delta G°_f(\mathrm{H_2O})] - \left[1\Delta G°_f(\mathrm{C_8H_{18}}) + \frac{25}{2}\Delta G°_f(\mathrm{O_2})\right]\\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})]\\ &\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right]\\ &= -4935.9\text{ kJ (per mol of }\mathrm{C_8H_{18}})\end{aligned}$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the $\Delta G°_f$ of the stable products: water and carbon dioxide.

Exercise 8.16.2

Calculate ΔG° for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- $\Delta G°_f$(benzene) = 124.5 kJ/mol
- $\Delta G°_f$ (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer available at the end of this section.

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 8.16.3

Calculate (a) ΔG° and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)⟶2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- S°(N_2) = 191.6 J/(mol•K),
- S°(H_2) = 130.7 J/(mol•K),
- S°(NH_3) = 192.8 J/(mol•K), and
- ΔH°_f (NH_3) = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG° and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 8.16.10 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 8.16.2 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 8.16.10, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)] \\ &= [2\text{ mol NH}_3 \times 192.8\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol N}_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol H}_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\} \\ &= -198.1\text{ J/K (per mole of N}_2\text{)}\end{aligned} \tag{8.16.13}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of ΔH°_f (NH_3) is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_f(\text{NH}_3) - [\Delta H^\circ_f(\text{N}_2) + 3\Delta H^\circ_f(\text{H}_2)] \\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})] \\ &= -91.8\text{ kJ(per mole of N}_2\text{)}\end{aligned}$$

B Inserting the appropriate values into Equation 8.16.10

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ - T\Delta S^\circ = (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) = -32.7\text{ kJ (per mole of N}_2\text{)}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 8.16.2:

$$\begin{aligned}\Delta G_{300^\circ\text{C}} &= \Delta H_{300^\circ\text{C}} - (573\text{ K})(\Delta S_{300^\circ\text{C}}) \\ &= \Delta H^\circ - (573\text{ K})\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) \\ &= 21.7\text{ kJ (per mole of N}_2\text{)}\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more

rapidly also changes the thermodynamics by causing the –TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

Exercise 8.16.3

Calculate

a. ΔG° and
b. $\Delta G_{750^\circ C}$

for the following reaction

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- ΔH°_f(NO_2) = 33.2 kJ/mol, and
- ΔH°_f (NO) = 91.3 kJ/mol.

Answer a available at the end of this section.

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting ΔG° = 0 in Equation 8.16.10, as illustrated in Example 8.16.4.

Example 8.16.4

As you saw in Example 8.16.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 9.5.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG° equal to zero in Equation 8.16.10 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 8.16.3, we calculated that ΔH° is –91.8 kJ/mol of N_2 and ΔS° is –198.1 J/K per mole of N_2, corresponding to ΔG° = –32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG° equal to zero and rearranging Equation 8.16.10 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{-198.1\text{ J/K}} = 463\text{ K}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise 8.16.4

As you found in the exercise in Example 8.16.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer available at the end of this section.

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change:

$$\Delta G = \Delta H - T\Delta S$$

- Standard free-energy change:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG° for a reaction.

Answers

Exercise 8.16.1

At 25°C, the standard enthalpy change (ΔH^o) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are

- S°(N_2H_4) = 121.2 J/(mol•K),
- S°(N_2) = 191.6 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Exercise 8.16.1

149.5 kJ/mol

no, not spontaneous

Video Solution

Exercise 8.16.2

92.8 kJ; no

Video Solution

Exercise 8.16.3

–72.5 kJ/mol of O_2

33.8 kJ/mol of O_2

Exercise $8.16.4$

792.6 K

Video Solution

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9: PROCESSES START OUT UNDER KINETIC CONTROL

9.1: Overview and Objectives

9.2: Chemical Reaction Rates

9.3: Rate Laws

9.4: Integrated Rate Laws

9.5: Factors Affecting Reaction Rates

9.6: Catalysis

9.7: Collision Theory

9.8: Reaction Mechanisms

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9.1: Overview and Objectives

> "Chemical reactions work similarly to a demolition derby, where atoms and molecules move and occasionally collide. For a reaction to happen, these collisions must be effective, meaning they need to be hard enough and properly aligned." (Hank Green, Crash Course)

Although we can't see the "demolition derby" movements and collisions with the naked eye, this general underlying principle helps us to explain why reactions proceed at the rates they do and to predict the composition of a mixture at any point when it is under *kinetic control*; that is, before the reaction has proceeded so far as for amounts of reactants and products to become constant. In this chapter, we'll look at how this plays out in terms of macroscopic results (amounts of reactants and products), as well as to develop a fuller picture of this "demolition derby" at the atomic and molecular level.

Chapter Objectives

- Use experimental rate and concentration data to determine the rate and/or rate law of a chemical reaction and/or the amount of a reactant or product present at a given point in the reaction.
- Draw reaction coordinate diagrams for chemical reactions, labeling the reactants, products, transition state, and ΔH on these diagrams.
- Qualitatively (reaction coordinate diagram, mechanisms) and quantitatively (Arrhenius equation) describe the effect of a catalyst or temperature on reaction kinetics.

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9.2: Chemical Reaction Rates

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use experimental rate and concentration data to **determine the rate a**nd/or rate law **of a chemical reaction** and/or the amount of a reactant or product present at a given point in the reaction.

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. For example, the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution changes slowly over time as it decomposes according to the equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned} H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[H_2O_2]}{\Delta t} \end{aligned}$$

This mathematical representation of the change in species concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[\mathrm{H_2O_2}]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[\mathrm{H_2O_2}]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t2; and Δ[H2O2] represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[\mathrm{H_2O_2}]$ is a negative quantity. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by –1. Figure $9.2.1$ provides an example of data collected during the decomposition of $\mathrm{H_2O_2}$.

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
0.00	1.000			
		−0.500	6.00	0.0833
6.00	0.500			
		−0.250	6.00	0.0417
12.00	0.250			
		−0.125	6.00	0.0208
18.00	0.125			
		−0.062	6.00	0.010
24.00	0.0625			

Figure 9.2.1: The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta\left[H_2O_2\right]}{\Delta t} = \frac{-(0.500mol/L - 1.000mol/L)}{(6.00h - 0.00h)} = 0.0833molL^{-1}h^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta\left[H_2O_2\right]}{\Delta t} = \frac{-(0.0625mol/L - 0.125mol/L)}{(24.00h - 18.00h)} = 0.010molL^{-1}h^{-1}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an **average rate** for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its **instantaneous rate**. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its **initial rate**. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. In a plot of the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure 9.2.2). These tangent line slopes may be evaluated using calculus, but the procedure for doing so is beyond the scope of this chapter.

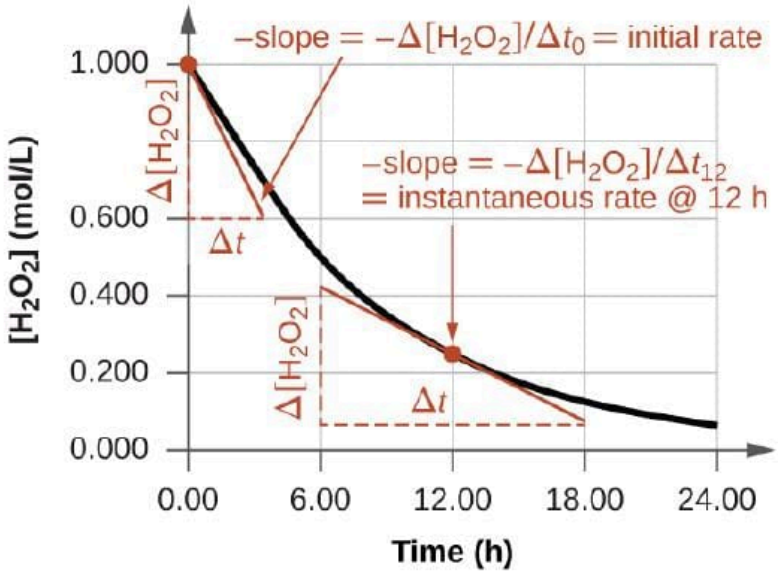


Figure 9.2.2: This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at *t* = 0 h ("initial rate") and at *t* = 12 h ("instantaneous rate" at 12 h).

Chemistry in Everyday Life: Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 9.2.3). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$C_6H_{12}O_6 + O_2 \overset{\text{catalyst}}{\longrightarrow} C_6H_{10}O_6 + H_2O_2$$

$$2H_2O_2 + 2I^- \overset{\text{catalyst}}{\longrightarrow} I_2 + 2H_2O + O_2$$

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

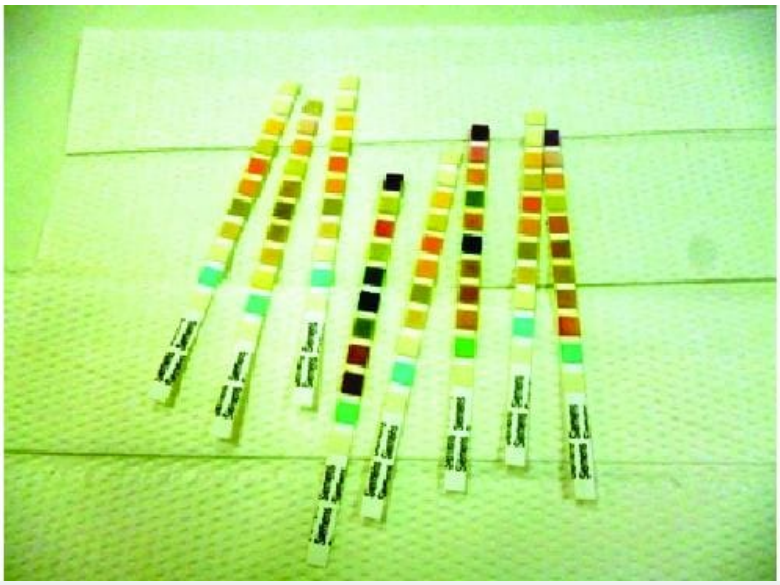


Figure 9.2.3: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

Relative Rates of Reaction

The rate of a reaction may be expressed as the change in concentration of any reactant or product. For any given reaction, these rate expressions are all related simply to one another according to the reaction stoichiometry. The rate of the general reaction

$$A \longrightarrow B \tag{9.2.1}$$

can be expressed in terms of the decrease in the concentration of A or the increase in the concentration of B. These two rate expressions are related by the stoichiometry of the reaction:

$$\text{rate } = -\left(\frac{1}{a}\right)\left(\frac{\Delta A}{\Delta t}\right) = \left(\frac{1}{b}\right)\left(\frac{\Delta B}{\Delta t}\right)$$

Consider the reaction represented by the following equation:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta mol\ NH_3}{\Delta t} \times \frac{1mol\ N_2}{2mol\ NH_3} = \frac{\Delta mol\ N_2}{\Delta t}$$

This may be represented in an abbreviated format by omitting the units of the stoichiometric factor:

$$-\frac{1}{2}\frac{\Delta mol\ NH_3}{\Delta t} = \frac{\Delta mol\ N_2}{\Delta t}$$

Note that a negative sign has been included as a factor to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). For homogeneous reactions, both the reactants and products are present in the same solution and thus occupy the same volume, so the molar amounts may be replaced with molar concentrations:

$$-\frac{1}{2}\frac{\Delta\left[NH_3\right]}{\Delta t} = \frac{\Delta\left[N_2\right]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 are produced for each mole of N_2 produced.

$$\frac{1}{3}\frac{\Delta\left[H_2\right]}{\Delta t} = \frac{\Delta\left[N_2\right]}{\Delta t}$$

Figure 9.2.4: illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. Slopes of the tangent lines at t = 500 s show that the instantaneous rates derived from all three species involved in the reaction are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6} M/s}{9.70 \times 10^{-7} M/s} \approx 3$$

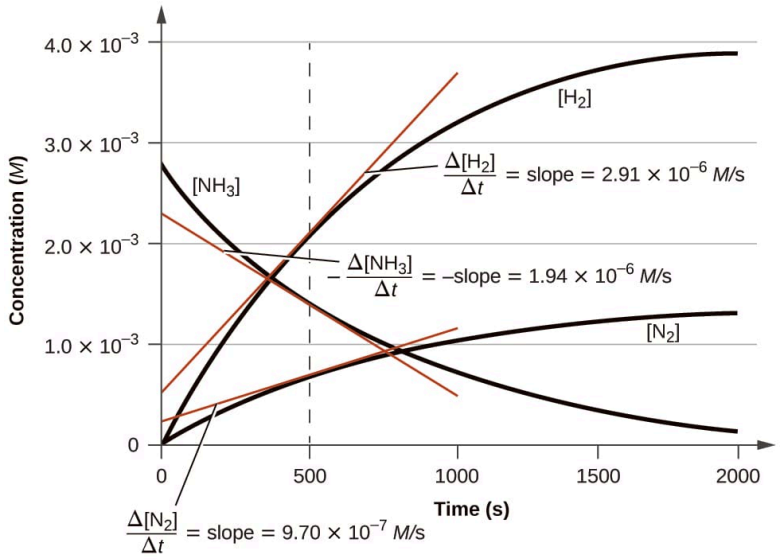


Figure 9.2.4: Changes in concentrations of the reactant and products for the reaction $2\,\mathrm{NH_3} \longrightarrow \mathrm{N_2} + 3\,\mathrm{H_2}$. The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at t = 500 s.

Example 9.2.1: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \tag{9.2.2}$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4}\frac{\Delta\left[NH_3\right]}{\Delta t} = -\frac{1}{5}\frac{\Delta\left[O_2\right]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta\left[H_2O\right]}{\Delta t}$$

Exercise 9.2.1

The rate of formation of Br_2 is 6.0 10^{-6} mol/L/s in a reaction described by the following net ionic equation:

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer available at the end of this section.

Example 9.2.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 9.2.2: shows the rate of the decomposition of H_2O_2 over time:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be 3.20×10^{-2} mol/L/h, that is:

$$-\frac{1}{2}\frac{\Delta\left[\mathrm{H_2O_2}\right]}{\Delta t} = \frac{1}{2}\frac{\Delta\left[\mathrm{H_2O}\right]}{\Delta t} = \frac{\Delta\left[\mathrm{O_2}\right]}{\Delta t} \tag{9.2.3}$$

What is the instantaneous rate of production of $\mathrm{H_2O}$ and $\mathrm{O_2}$?

Solution

The reaction stoichiometry shows that

$$-\frac{1}{2}\frac{\Delta\left[\mathrm{H_2O_2}\right]}{\Delta t} = \frac{1}{2}\frac{\Delta\left[\mathrm{H_2O}\right]}{\Delta t} = \frac{\Delta\left[\mathrm{O_2}\right]}{\Delta t} \tag{9.2.4}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2} molL^{-1}h^{-1} = \frac{\Delta\left[O_2\right]}{\Delta t}$$

and

$$\frac{\Delta\left[O_2\right]}{\Delta t} = 1.60 \times 10^{-2} molL^{-1}h^{-1}$$

Exercise 9.2.2

If the rate of decomposition of ammonia, NH_3, at 1150 K is 2.10×10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

Answer available at the end of this section.

Answers

Exercise 9.2.1

$$-\frac{1}{5}\frac{\Delta\left[Br^-\right]}{\Delta t} = -\frac{\Delta\left[BrO_3^-\right]}{\Delta t} = -\frac{1}{6}\frac{\Delta\left[H^+\right]}{\Delta t} = \frac{1}{3}\frac{\Delta\left[Br_2\right]}{\Delta t} = \frac{1}{3}\frac{\Delta\left[H_2O\right]}{\Delta t}$$

Exercise 9.2.2

1.05×10^{-6} mol/L/s, N_2 and 3.15×10^{-6} mol/L/s, H_2.

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9.3: Rate Laws

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use experimental rate and concentration data to determine the rate and/or **rate law of a chemical reaction** and/or the amount of a reactant or product present at a given point in the reaction.

As described in the previous module, the rate of a reaction is often affected by the concentrations of reactants. Rate laws (sometimes called *differential rate laws*) or rate equations are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. As an example, consider the reaction described by the chemical equation

$$aA + bB \longrightarrow \text{ products}$$

where a and b are stoichiometric coefficients. The rate law for this reaction is written as:

$$\text{rate } = k[A]^m[B]^n$$

in which [*A*] and [*B*] represent the molar concentrations of reactants, and *k* is the **rate constant**, which is specific for a particular reaction at a particular temperature. The exponents *m* and *n* are the **reaction orders** and are typically positive integers, though they can be fractions, negative, or zero. The rate constant *k* and the reaction orders *m* and *n* must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant *k* is independent of the reactant concentrations, but it does vary with temperature.

The reaction orders in a rate law describe the mathematical dependence of the rate on reactant concentrations. Referring to the generic rate law above, the reaction is *m* order with respect to *A* and *n* order with respect to *B*. For example, if *m* = 1 and *n* = 2, the reaction is first order in *A* and second order in *B*. The overall reaction order is simply the sum of orders for each reactant. For the example rate law here, the reaction is third order overall (1 + 2 = 3). A few specific examples are shown below to further illustrate this concept.

The rate law:

$$\text{rate } = k\left[H_2O_2\right]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate } = k\left[\mathrm{C_4H_6}\right]^2$$

describes a reaction that is second order in $\mathrm{C_4H_6}$ and second order overall. The rate law:

$$\text{rate } = k\left[\mathrm{H^+}\right]\left[\mathrm{OH^-}\right]$$

describes a reaction that is first order in $\mathrm{H^+}$, first order in $\mathrm{OH^-}$, and second order overall.

Example 9.3.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\mathrm{NO_2\,(g) + CO\,(g) \longrightarrow NO\,(g) + CO_2\,(g)}$$

is second order in $\mathrm{NO_2}$ and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k\left[\text{NO}_2\right]^m\left[\text{CO}\right]^n$$

The reaction is second order in NO_2; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k\left[\text{NO}_2\right]^2\left[\text{CO}\right]^0 = k\left[\text{NO}_2\right]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why the CO concentration term may be omitted from the rate law: the rate of reaction is solely dependent on the concentration of NO_2. A later chapter section on reaction mechanisms will explain how a reactant's concentration can have no effect on a reaction rate despite being involved in the reaction.

Exercise 9.3.1A

The rate law for the reaction:

$$\text{H}_2\left(\text{g}\right) + 2\,\text{NO}\left(\text{g}\right) \longrightarrow \text{N}_2\text{O}\left(\text{g}\right) + \text{H}_2\text{O}\left(\text{g}\right)$$

has been determined to be rate = $k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer available at the end of this section.

Exercise 9.3.1B

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($\text{CH}_3\text{CH}_2\text{OCOCH}_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\text{CH}_3\text{OH} + \text{CH}_3\text{CH}_2\text{OCOCH}_3 \longrightarrow \text{CH}_3\text{OCOCH}_3 + \text{CH}_3\text{CH}_2\text{OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate} = k\left[\text{CH}_3\text{OH}\right]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer available at the end of this section.

A common experimental approach to the determination of rate laws is the **method of initial rates**. This method involves measuring reaction rates for multiple experimental trials carried out using different initial reactant concentrations. Comparing the measured rates for these trials permits determination of the reaction orders and, subsequently, the rate constant, which together are used to formulate a rate law. This approach is illustrated in the next two example exercises.

Example 9.3.2: Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure 9.3.1). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

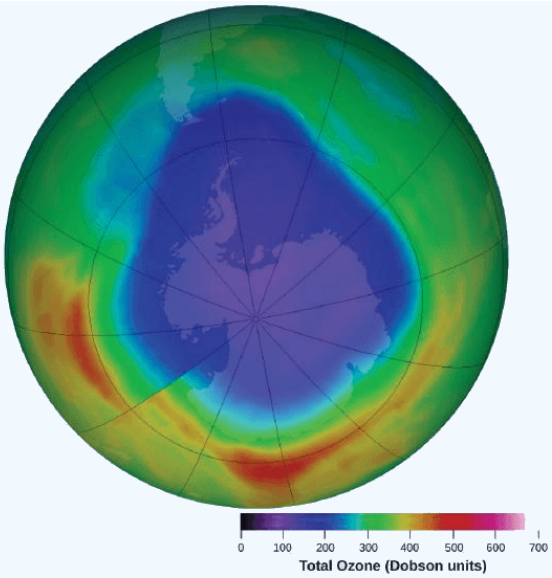


Figure 9.3.1: A contour map showing stratospheric ozone concentration and the “ozone hole” that occurs over Antarctica during its spring months. (credit: modification of work by NASA)

$$\mathrm{NO\,(g)} + \mathrm{O_3\,(g)} \longrightarrow \mathrm{NO_2\,(g)} + \mathrm{O_2\,(g)}$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O_3] (mol/L)	$\frac{\Delta[\mathrm{NO_2}]}{\Delta t}(\mathrm{molL^{-1}s^{-1}})$
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate } = k[NO]^m\,[O_3]^n$$

Determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

Step 1:

Determine the value of m *from the data in which [NO] varies and [O_3] is constant.* In the last three experiments, [NO] varies while [O_3] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.

Step 2:

Determine the value of n *from data in which [O_3] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O_3] varies. The reaction rate changes in direct proportion to the change in [O_3]. When [O_3] doubles from trial 1 to 2, the rate doubles; when [O_3] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O_3], and *n* is equal to 1.The rate law is thus:

$$\text{rate } = k[NO]^1\,[O_3]^1 = k[NO]\,[O_3]$$

Step 3:

Determine the value of k *from one set of concentrations and the corresponding rate*. The data from trial 1 are used below:

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}]\,[\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}}{\left(1.00 \times 10^{-6}\ \text{mol L}^{-1}\right)\left(3.00 \times 10^{-6}\ \text{mol L}^{-1}\right)} \\ &= 2.20 \times 10^{7}\ \text{L mol}^{-1}\text{s}^{-1} \end{aligned}$$

Exercise 9.3.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO}\,(\text{g}) \longrightarrow \text{CH}_4\,(\text{g}) + \text{CO}\,(\text{g})$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	[CH_3CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ (mol $L^{-1}s^{-1}$)
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer available at the end of this section.

Example 9.3.3: Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Trial	[NO] (mol/L)	[Cl_2] (mol/L)	$-\frac{\Delta[\text{CO}]}{\Delta t}$ (mol $L^{-1}s^{-1}$)
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate } = k[NO]^m\,[Cl_2]^n$$

As in Example 9.3.2, approach this problem in a stepwise fashion, determining the values of *m* and *n* from the experimental data and then using these values to determine the value of *k*. In this example, however, an explicit algebraic approach (vs. the implicit approach of the previous example) will be used to determine the values of *m* and *n*:

Step 1

Determine the value of m from the data in which $[\mathrm{NO}]$ varies and $[\mathrm{Cl_2}]$ is constant. Write the ratios with the subscripts x and y to indicate data from two different trials:

$$\frac{\text{rate }_x}{\text{rate }_y} = \frac{k[NO]_x^m\,[Cl_2]_x^n}{k[NO]_y^m\,[Cl_2]_y^n}$$

Using the third trial and the first trial, in which $[\mathrm{Cl_2}]$ does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

Canceling equivalent terms in the numerator and denominator leaves:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

Use logarithms to determine the value of the exponent *m*:

$$\ln(2.25) = m\ln(1.5)$$
$$\frac{\ln(2.25)}{\ln(1.5)} = m$$
$$2 = m$$

Confirm the result

$$1.5^2 = 2.25$$

Step 2

Determine the value of n from data in which $[\mathrm{Cl_2}]$ varies and $[\mathrm{NO}]$ is constant.

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

Cancelation gives:

$$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n}$$

which simplifies to:

$$1.5 = (1.5)^n$$

Thus n must be 1, and the form of the rate law is:

$$\text{rate } = k[NO]^m\,[Cl_2]^n = k[NO]^2\,[Cl_2]$$

Step 3.

Determine the numerical value of the constant with appropriate units. The units for the rate of a reaction are mol/L/s. The units for are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3. The units for *k* should be mol^{-} L/s so that the rate is in terms of mol/L/s.

To determine the value of *k* once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for *k*:

$$0.00300 \text{ mol } L^{-1}s^{-1} = k\left(0.10 \text{ mol } L^{-1}\right)^2\left(0.10 \text{ mol } L^{-1}\right)^1$$
$$k = 3.0 \text{ mol}^{-2}L^2s^{-1}$$

Exercise 9.3.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$OCl^-(aq) + I^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq)$$

Trial	[OCl^-] (mol/L)	[I^-] (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant *k* with appropriate units for this reaction.

Answer available at the end of this section.

Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case.

Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$$\begin{aligned}
NO_2 + CO &\longrightarrow NO + CO_2 & \text{rate} &= k\left[NO_2\right]^2\\
CH_3\ CHO &\longrightarrow CH_4 + CO & \text{rate} &= k\left[CH_3CHO\right]^2\\
2\,N_2\ O_5 &\longrightarrow NO_2 + O_2 & \text{rate} &= k\left[N_2O_5\right]\\
2\,NO_2 + F_2 &\longrightarrow 2\,NO_2\ F & \text{rate} &= k\left[NO_2\right]\left[F_2\right]\\
2\,NO_2\ Cl &\longrightarrow 2\,NO_2 + Cl_2 & \text{rate} &= k\left[NO_2Cl\right]
\end{aligned}$$

Note

It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

The units for a rate constant will vary as appropriate to accommodate the overall order of the reaction. The unit of the rate constant for the second-order reaction described in Example 9.3.2 was determined to be k was derived to be $L\ mol^{-1}s^{-1}$. For the third-order reaction, k was derived to be $L^2mol^{-2}s^{-1}$. Dimensional analysis requires the rate constant unit for a reaction whose overall order is x to be $L^{x-1}\ mol^{1-x}s^{-1}$. Table 9.3.1 summarizes the rate constant units for common reaction orders.

Table 9.3.1: Rate Constant Units for Common Reaction Orders

Overall Reaction Order (x)	Rate Constant Unit (L^{x-1} mol^{1-x} s^{-1})
0 (zero)	mol L^{-1} s^{-1}
1 (first)	s^{-1}
2 (second)	L mol^{-1} s^{-1}
3 (third)	L^2 mol^{-2} s^{-1}

Note that the units in this table were derived using specific units for concentration (mol/L) and time (s), though any valid units for these two properties may be used.

Answers

Exercise 9.3.1*A*

order in NO = 2; order in H_2 = 1; overall order = 3

Exercise 9.3.1*B*

order in CH_3OH = 1; order in $CH_3CH_2OCOCH_3$ = 0; overall order = 1

Exercise 9.3.2

$\text{rate} = k[CH_3CHO]^2$ with k = 6.7310^{-6} L/mol/s

Exercise 9.3.3

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$

Substituting the concentration data from trial 1 and solving for k yields:

$$\text{rate} = k[OCl^-]^2[I^-]^1$$

$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4 mol^{-2}L^2s^{-1}$$

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9.4: Integrated Rate Laws

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use experimental rate and concentration data to determine the rate and/or rate law **of a chemical reaction and/or the amount of a reactant or product present at a given point in the reaction**.

The rate laws discussed thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called **integrated rate laws**. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

First-Order Reactions

Integration of the rate law for a simple first-order reaction (rate = $k[A]$) results in an equation describing how the reactant concentration varies with time:

$$[A]_t = [A]_0 e^{-kt}$$

where $[A]t$ is the concentration of A at any time t, $[A]_0$ is the initial concentration of A, and k is the first-order rate constant.

For mathematical convenience, this equation may be rearranged to other formats, including direct and indirect proportionalities:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

or

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

and a format showing a linear dependence of concentration in time:

$$\ln [A]_t = \ln [A]_0 - kt$$

Example 9.4.1: The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, $\mathrm{C_4H_8}$ at 500 °C is 9.2 10^{-3} s^{-1}:

$$\mathrm{C_4H_8} \longrightarrow 2\,\mathrm{C_2H_4}$$

How long will it take for 80.0% of a sample of $\mathrm{C_4H_8}$ to decompose?

Solution

Since the relative change in reactant concentration is provided, a convenient format for the integrated rate law is:

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

The initial concentration of C_4H_8, $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let *x* be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of *x* or 0.200*x*. Rearranging the rate law to isolate *t* and substituting the provided quantities yields:

$$\begin{aligned} t &= \ln\frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln 5 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.7 \times 10^{2}\ \text{s} \end{aligned}$$

Exercise 9.4.1

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

The decay is first-order with a rate constant of 0.138 d^{-1}. How many days will it take for 90% of the iodine–131 in a 0.500 *M* solution of this substance to decay to Xe-131?

Answer available at the end of this section.

In the next example exercise, a linear format for the integrated rate law will be convenient:

$$\begin{aligned} \ln[A]_t &= (-k)(t) + \ln[A]_0 \\ y &= mx + b \end{aligned}$$

A plot of $\ln[A]_t$ versus *t* for a first-order reaction is a straight line with a slope of –*k* and a *y*-intercept of $\ln[A]_0$. If a set of rate data are plotted in this fashion but do *not* result in a straight line, the reaction is not first order in *A*.

Example 9.4.2: Graphical Determination of Reaction Order and Rate Constant

Show that the data in Figure 9.4.1 can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the decomposition of H_2O_2 from these data.

Solution

The data from Figure 9.4.1 are tabulated below, and a plot of $\ln[H_2O_2]$ is shown in Figure 9.4.1.

Time (h)	$[H_2O_2]$ (*M*)	$\ln[H_2O_2]$
0.00	1.000	0.000
6.00	0.500	–0.693
12.00	0.250	–1.386
18.00	0.125	–2.079

Time (h)	$[H_2O_2]$ (*M*)	$\ln[H_2O_2]$
24.00	0.0625	−2.772

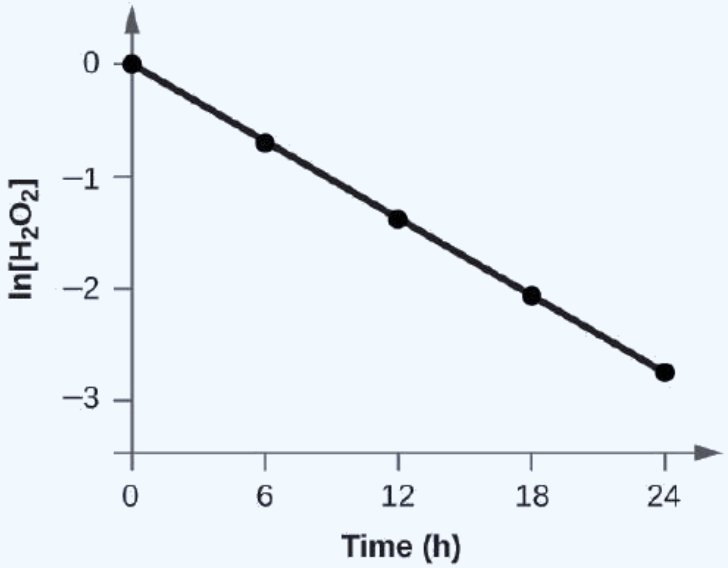


Figure 9.4.1: A linear relationship between $\ln[H_2O_2]$ and time suggests the decomposition of hydrogen peroxide is a first-order reaction.

The plot of $\ln[H_2O_2]$ versus time is linear, indicating that the reaction may be described by a first-order rate law.

According to the linear format of the first-order integrated rate law, the rate constant is given by the negative of this plot's slope.

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln [H_2O_2]}{\Delta t}$$

The slope of this line may be derived from two values of $\ln[H_2O_2]$ at different values of *t* (one near each end of the line is preferable). For example, the value of $\ln[H_2O_2]$ when *t* is 0.00 h is 0.000; the value when *t* = 24.00 h is −2.772

$$\begin{aligned} \text{slope} &= \frac{-2.772 - 0.000}{24.00 - 0.00h} \\ &= \frac{-2.772}{24.00h} \\ &= -0.116h^{-1} \\ k = -\text{ slope} &= -\left(-0.116h^{-1}\right) = 0.116h^{-1} \end{aligned}$$

Exercise 9.4.2

Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

Time (s)	[*A*]
4.0	0.220
8.0	0.144
12.0	0.110
16.0	0.088
20.0	0.074

Answer available at the end of this section.

Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions can be fairly complicated. To illustrate the point with minimal complexity, only the simplest second-order reactions will be described here, namely, those whose rates depend on the concentration of just one reactant. For these types of reactions, the differential rate law is written as:

$$\text{rate } = k[A]^2$$

For these second-order reactions, the integrated rate law is:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

where the terms in the equation have their usual meanings as defined earlier.

Example 9.4.3: The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) to yield C_8H_{12} gas is described by the equation:

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

This "dimerization" reaction is second order with a rate constant equal to 5.76 10^{-2} L mol^{-1} min^{-1} under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration after 10.0 min?

Solution

For a second-order reaction, the integrated rate law is written

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

We know three variables in this equation: $[A]_0$ = 0.200 mol/L, k = 5.76 10^{-2} L/mol/min, and t = 10.0 min. Therefore, we can solve for [*A*], the fourth variable:

$$\begin{aligned}\frac{1}{[A]_t} &= \left(5.76 \times 10^{-2} L mol^{-1} min^{-1}\right)(10 min) + \frac{1}{0.200 mol^{-1}} \\ &= \left(5.76 \times 10^{-1} L mol^{-1}\right) + 5.00 L mol^{-1} \\ &= 5.58 L mol^{-1} \\ [A]_t &= 1.79 \times 10^{-1} mol L^{-1}\end{aligned}$$

Therefore 0.179 mol/L of butadiene remain at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

Exercise 9.4.3

If the initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer available at the end of this section.

The integrated rate law for second-order reactions has the form of the equation of a straight line:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$

A plot of $\frac{1}{[A]_t}$ versus t for a second-order reaction is a straight line with a slope of k and a y-intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

Example 9.4.4: Graphical Determination of Reaction Order and Rate Constant

The data below are for the same reaction described in Example 9.4.3. Prepare and compare two appropriate data plots to identify the reaction as being either first or second order. After identifying the reaction order, estimate a value for the rate constant.

Solution

Time (s)	$[C_4H_6]$ (M)
0	1.00×10^{-2}
1600	5.04×10^{-3}
3200	3.37×10^{-3}
4800	2.53×10^{-3}
6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, prepare a plot of $\ln[C_4H_6]_t$ versus t and compare it to a plot of $\frac{1}{[C_4H_6]_t}$ versus t. The values needed for these plots follow.

Time (s)	$\frac{1}{[C_4H_6]}(M^{-1})$	$\ln[C_4H_6]$
0	100	−4.605
1600	198	−5.289
3200	296	−5.692
4800	395	−5.978
6200	481	−6.175

The plots are shown in Figure 9.4.2, which clearly shows the plot of $\ln [C_4H_6]_t$ versus t is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]_t}$ versus t is linear, indicating that the reaction is second order.

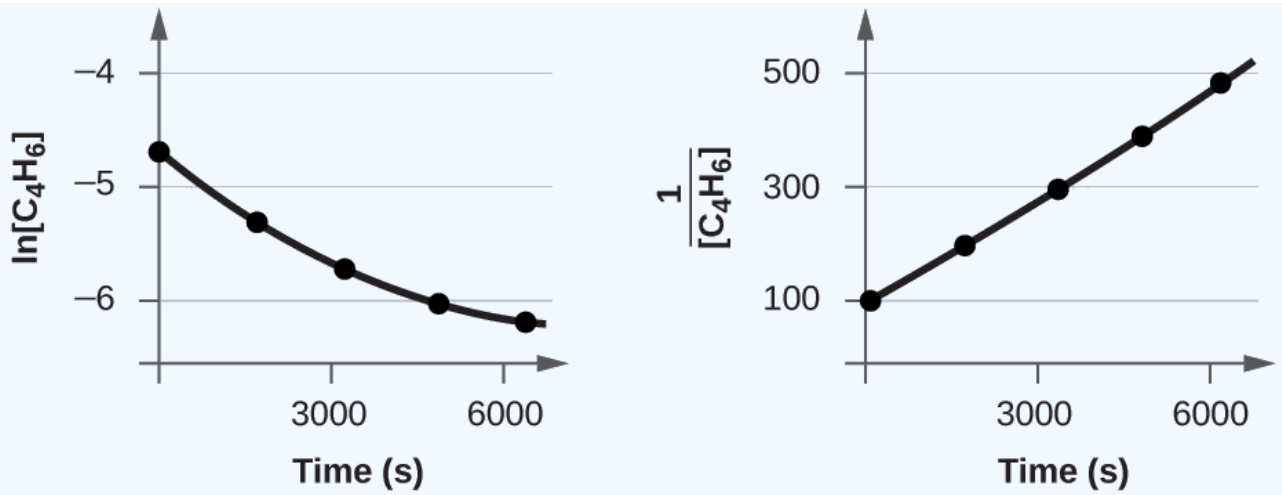


Figure 9.4.2: These two graphs show first- and second-order plots for the dimerization of C_4H_6. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

According to the second-order integrated rate law, the rate constant is equal to the slope of the versus *t* plot. Using the data for *t* = 0 s and *t* = 6200 s, the rate constant is estimated as follows:

$$k = \text{ slope } = \frac{(481M^{-1} - 100M^{-1})}{(6200s - 0s)} = 0.0614M^{-1}s^{-1}$$

Exercise 9.4.4

Do the following data fit a second-order rate law?

Time (s)	[*A*] (*M*)
5	0.952
10	0.625
15	0.465
20	0.370
25	0.308
35	0.230

Answer available at the end of this section.

Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{rate } = k$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactant(s). This may seem counterintuitive, since the reaction rate certainly can't be finite when the reactant concentration is zero. For purposes of this introductory text, it will suffice to note that zero-order kinetics are observed for some reactions only under certain specific conditions. These same reactions exhibit different kinetic behaviors when the specific conditions aren't met, and for this reason the more prudent term *pseudo-zero-order* is sometimes used.

The integrated rate law for a zero-order reaction is a linear function:

$$[A]_t = -kt + [A]_0$$
$$y = mx + b$$

A plot of [*A*] versus *t* for a zero-order reaction is a straight line with a slope of –*k* and a *y*-intercept of $[A]_0$. Figure 9.4.3: shows a plot of $[NH_3]$ versus *t* for the thermal decomposition of ammonia at the surface of two different heated solids. The decomposition reaction exhibits first-order behavior at a quartz (SiO_2) surface, as suggested by the exponentially decaying plot of concentration versus time. On a tungsten surface, however, the plot is linear, indicating zero-order kinetics.

Example 9.4.5: Graphical Determination of Zero-Order Rate Constant

Use the data plot in Figure 9.4.3 to graphically estimate the zero-order rate constant for ammonia decomposition at a tungsten surface.

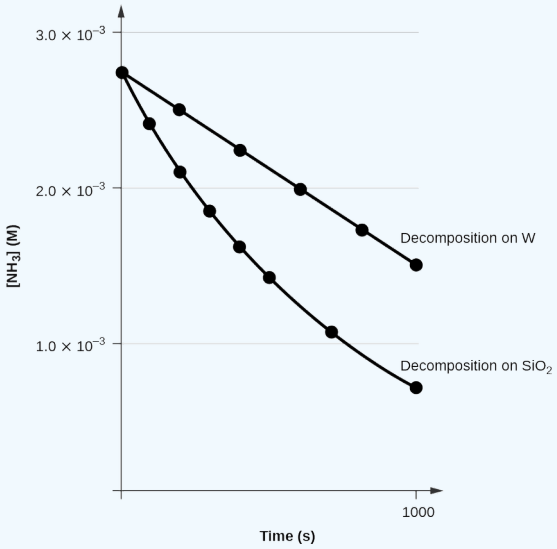


Figure 9.4.3: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

Solution

The integrated rate law for zero-order kinetics describes a linear plot of reactant concentration, $[A]_t$, versus time, *t*, with a slope equal to the negative of the rate constant, –*k*. Following the mathematical approach of previous examples, the slope of the linear data plot (for decomposition on W) is estimated from the graph. Using the ammonia concentrations at *t* = 0 and *t* = 1000 s:

$$k = -\text{ slope } = -\frac{(0.0015 molL^{-1} - 0.0028 molL^{-1})}{(1000s - 0s)} = 1.3 \times 10^{-6} molL^{-1}s^{-1}$$

Exercise 9.4.5

The zero-order plot in Figure 9.4.3 shows an initial ammonia concentration of 0.0028 mol L^{-1} decreasing linearly with time for 1000 s. Assuming no change in this zero-order behavior, at what time (min) will the concentration reach 0.0001 mol L^{-1}?

Answer available at the end of this section.

The Half-Life of a Reaction

The half-life of a reaction ($t_{1/2}$) is the time required for one-half of a given amount of reactant to be consumed. In each succeeding

half-life, half of the remaining concentration of the reactant is consumed. Using the decomposition of hydrogen peroxide (Figure 9.4.1) as an example, we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 *M* to 0.500 *M*. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 *M* to 0.250 *M*; during the third half-life, it decreases from 0.250 *M* to 0.125 *M*. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

First-Order Reactions

An equation relating the half-life of a first-order reaction to its rate constant may be derived from the integrated rate law as follows:

$$\ln \frac{[A]_0}{[A]_t} = kt$$

$$t = \ln \frac{[A]_0}{[A]_t} \times \frac{1}{k}$$

Invoking the definition of half-life, symbolized requires that the concentration of *A* at this point is one-half its initial concentration: $t = t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$

Substituting these terms into the rearranged integrated rate law and simplifying yields the equation for half-life:

$$t_{1/2} = \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k}$$

$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

$$t_{1/2} = \frac{0.693}{k}$$

This equation describes an expected inverse relation between the half-life of the reaction and its rate constant, *k*. Faster reactions exhibit larger rate constants and correspondingly shorter half-lives. Slower reactions exhibit smaller rate constants and longer half-lives.

Example 9.4.6: Calculation of a First-order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C, using the data given in Figure 9.4.4.

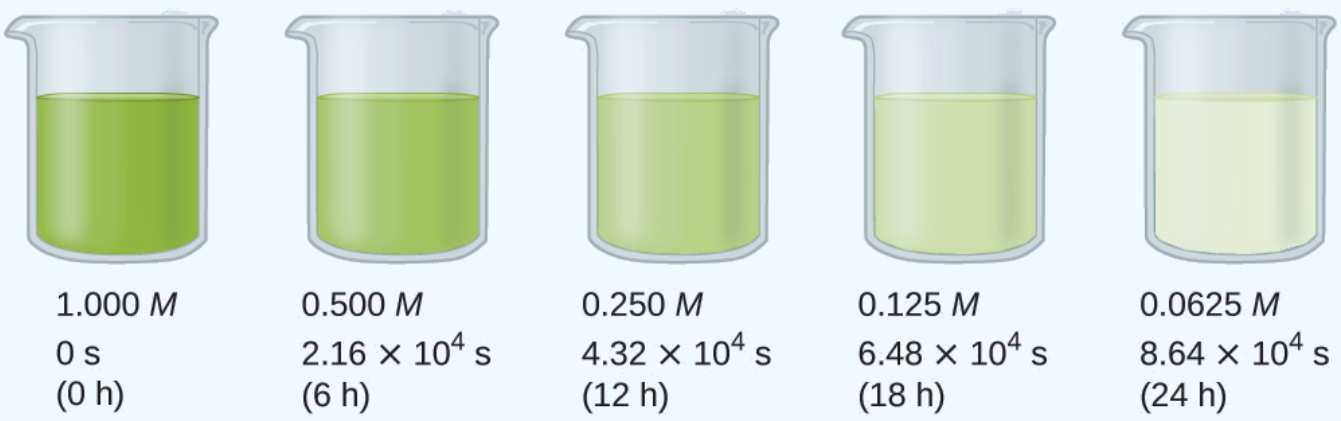


Figure 9.4.4: The decomposition of H_2O_2 at 40 °C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.

Solution

Inspecting the concentration/time data in Figure 9.4.4 shows the half-life for the decomposition of H_2O_2 is 2.16 × 10^4 s:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4 s} = 3.21 \times 10^{-5} s^{-1}$$

Exercise 9.4.1

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

Answer available at the end of this section.

Second-Order Reactions

Following the same approach as used for first-order reactions, an equation relating the half-life of a second-order reaction to its rate constant and initial concentration may be derived from its integrated rate law:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

Restrict t to $t_{1/2}$

$$t = t_{1/2}$$

define $[A]_t$ as one-half $[A]_0$

$$[A]_t = \frac{1}{2}[A]_0$$

and then substitute into the integrated rate law and simplify:

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

For a second-order reaction, $t_{1/2}$ is inversely proportional to the concentration of the reactant, and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

Zero-Order Reactions

As for other reaction orders, an equation for zero-order half-life may be derived from the integrated rate law:

$$[A] = -kt + [A]_0$$

Restricting the time and concentrations to those defined by half-life: and Substituting these terms into the zero-order integrated rate law yields:

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

As for all reaction orders, the half-life for a zero-order reaction is inversely proportional to its rate constant. However, the half-life of a zero-order reaction increases as the initial concentration increases.

Equations for both differential and integrated rate laws and the corresponding half-lives for zero-, first-, and second-order reactions are summarized in Table 9.4.1.

Table 9.4.1: Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	M s^{-1}	s^{-1}	M^{-1} s^{-1}
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	ln$[A]$ vs. t	vs. t
relationship between slope of linear plot and rate constant	k = –slope	k = –slope	k = slope
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Example 9.4.7: Half-Life for Zero-Order and Second-Order Reactions

What is the half-life for the butadiene dimerization reaction described in Example 9.4.3?

Solution

The reaction in question is second order, is initiated with a 0.200 mol L^{-1} reactant solution, and exhibits a rate constant of 0.0576 L mol^{-1} min^{-1}. Substituting these quantities into the second-order half-life equation:

$$t_{1/2} = \frac{1}{[(0.0576 L mol^{-1} min^{-1})\,(0.200 mol L^{-1})]} = 86.8 \text{ min}$$

Exercise 9.4.7

What is the half-life (min) for the thermal decomposition of ammonia on tungsten (see Figure 9.4.3)?

Answer available at the end of this section.

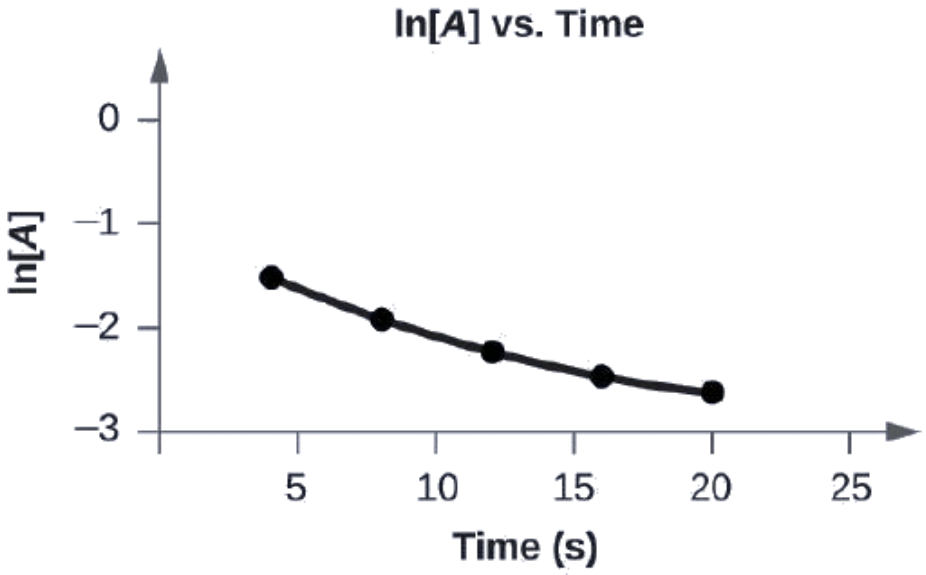
Answers

Exercise 9.4.1

16.7 days

Exercise 9.4.2

The plot of ln$[A]_t$ vs. t is not linear, indicating the reaction is not first order:

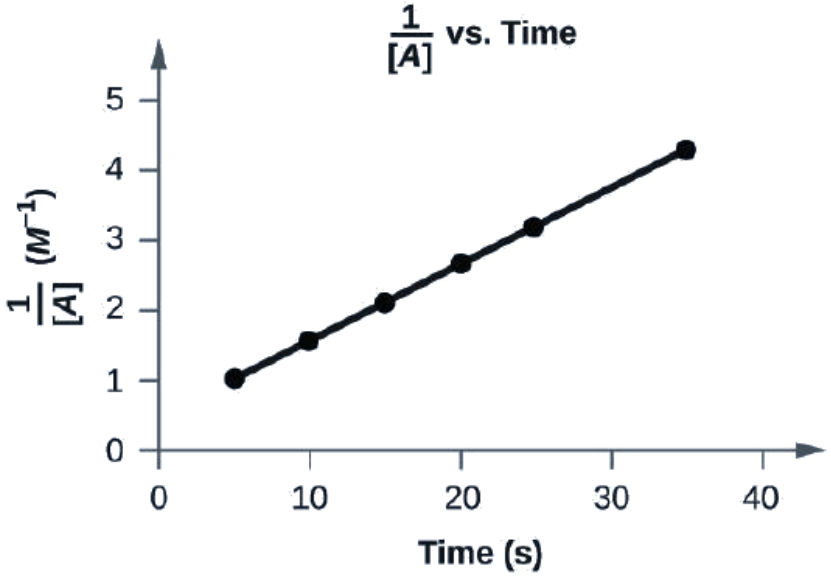


Exercise 9.4.3

0.0195 mol/L

Exercise 9.4.4

Yes. The plot of $\frac{1}{[A]_t}$ vs. t is linear:



Exercise 9.4.5

35 min

Exercise 9.4.1

5.02 d.

Exercise 9.4.7

87 min

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9.5: Factors Affecting Reaction Rates

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- **Qualitatively** (reaction coordinate diagram, mechanisms) and quantitatively (Arrhenius equation) describe the effect of a catalyst or temperature on reaction kinetics.

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Five factors typically affecting the rates of chemical reactions will be explored in this section: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The Physical States of the Reactants

A chemical reaction between two or more substances requires intimate contact between the reactants. When reactants are in different physical states, or phases (solid, liquid, gaseous, dissolved), the reaction takes place only at the interface between the phases. Consider the heterogeneous reaction between a solid phase and either a liquid or gaseous phase. Compared with the reaction rate for large solid particles, the rate for smaller particles will be greater because the surface area in contact with the other reactant phase is greater. For example, large pieces of iron react more slowly with acids than they do with finely divided iron powder (Figure 9.5.1). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.

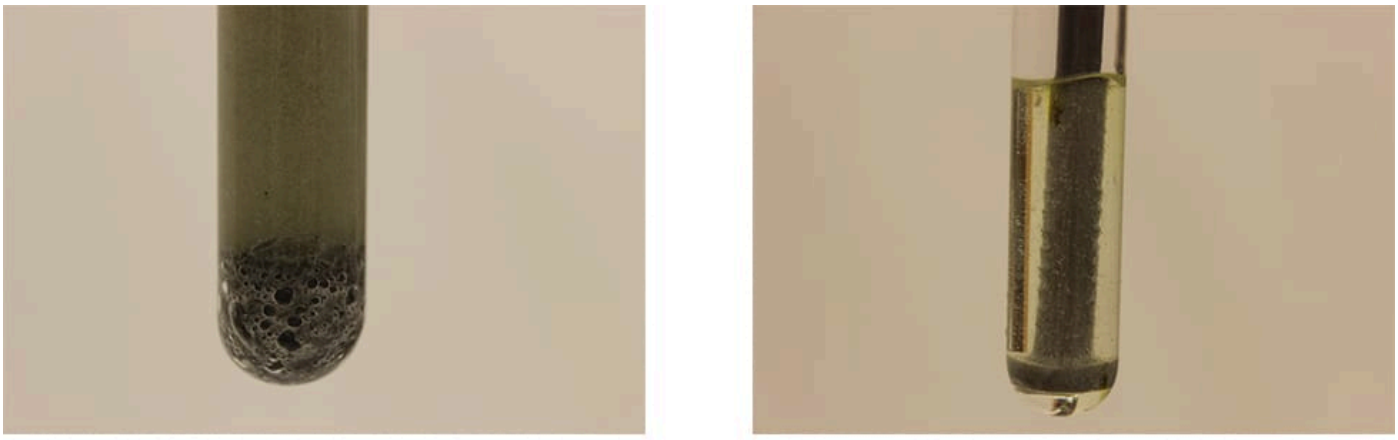


Figure 9.5.1: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: $2Fe(s) + 6HCl(aq)\ 2FeCl_3(aq) + 3H_2(g)$. (b) An iron nail reacts more slowly because the surface area exposed to the acid is much less.

Link to Learning

Watch this video to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. Gas burners, hot plates, and ovens are often used in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. For many chemical processes, reaction rates are approximately doubled when the temperature is raised by 10 °C.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure 9.5.2). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathrm{SO_2\,(g) + H_2O\,(g) \longrightarrow H_2SO_3\,(aq)}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathrm{CaCO_3\,(s) + H_2SO_3\,(aq) \longrightarrow CaSO_3\,(aq) + CO_2\,(g) + H_2O\,(l)}$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

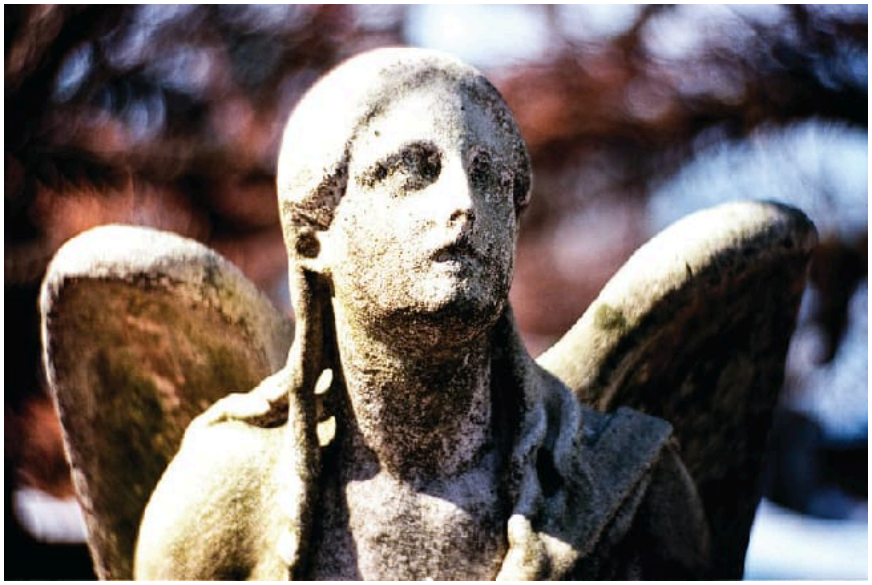


Figure 9.5.2: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)

Link to Learning

Phosphorus burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this video to see an example.

The Presence of a Catalyst

Relatively dilute aqueous solutions of hydrogen peroxide, $\mathrm{H_2O_2}$, are commonly used as topical antiseptics. Hydrogen peroxide decomposes to yield water and oxygen gas according to the equation:

$$2\,\mathrm{H_2O_2\,(aq)} \longrightarrow 2\,\mathrm{H_2O\,(l)} + \mathrm{O_2\,(g)}$$

Under typical conditions, this decomposition occurs very slowly. When dilute $\mathrm{H_2O_2\,(aq)}$ is poured onto an open wound, however, the reaction occurs rapidly and the solution foams because of the vigorous production of oxygen gas. This dramatic difference is caused by the presence of substances within the wound's exposed tissues that accelerate the decomposition process. Substances that function to increase the rate of a reaction are called **catalysts**, a topic treated in greater detail later in this chapter.

Link to Learning

Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

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9.6: Catalysis

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Draw reaction coordinate diagrams for chemical reactions, labeling the reactants, products, transition state, and ΔH on these diagrams.
- **Qualitatively** (reaction coordinate diagram, mechanisms) and quantitatively (Arrhenius equation) describe the effect of a catalyst or temperature on reaction kinetics.

Among the factors affecting chemical reaction rates discussed earlier in this chapter was the presence of a *catalyst*, a substance that can increase the reaction rate without being consumed in the reaction. The concepts introduced in the previous section on reaction mechanisms provide the basis for understanding how catalysts are able to accomplish this very important function.

Figure 9.6.1 shows reaction diagrams for a chemical process in the absence and presence of a catalyst. Inspection of the diagrams reveals several traits of these reactions. Consistent with the fact that the two diagrams represent the same overall reaction, both curves begin and end at the same energies (in this case, because products are more energetic than reactants, the reaction is endothermic). The reaction mechanisms, however, are clearly different. The uncatalyzed reaction proceeds via a one-step mechanism (one transition state observed), whereas the catalyzed reaction follows a two-step mechanism (two transition states observed) with *a notably lesser activation energy*. This difference illustrates the means by which a catalyst functions to accelerate reactions, namely, by providing an alternative reaction mechanism with a lower activation energy. Although the catalyzed reaction mechanism for a reaction needn't necessarily involve a different number of steps than the uncatalyzed mechanism, it must provide a reaction path whose rate determining step is faster (lower E_a).

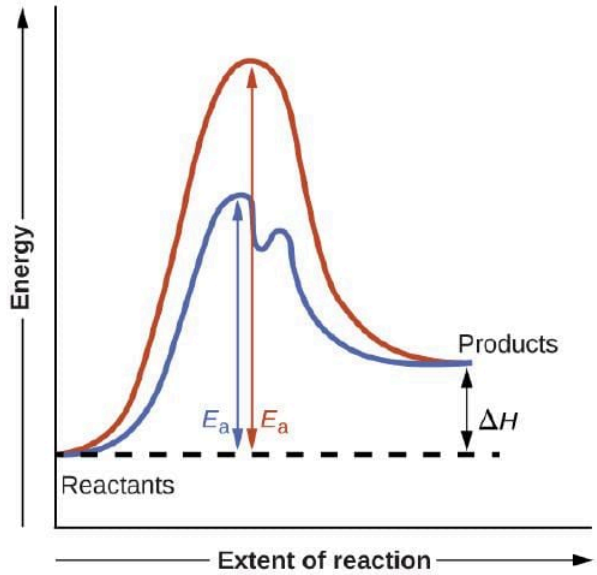
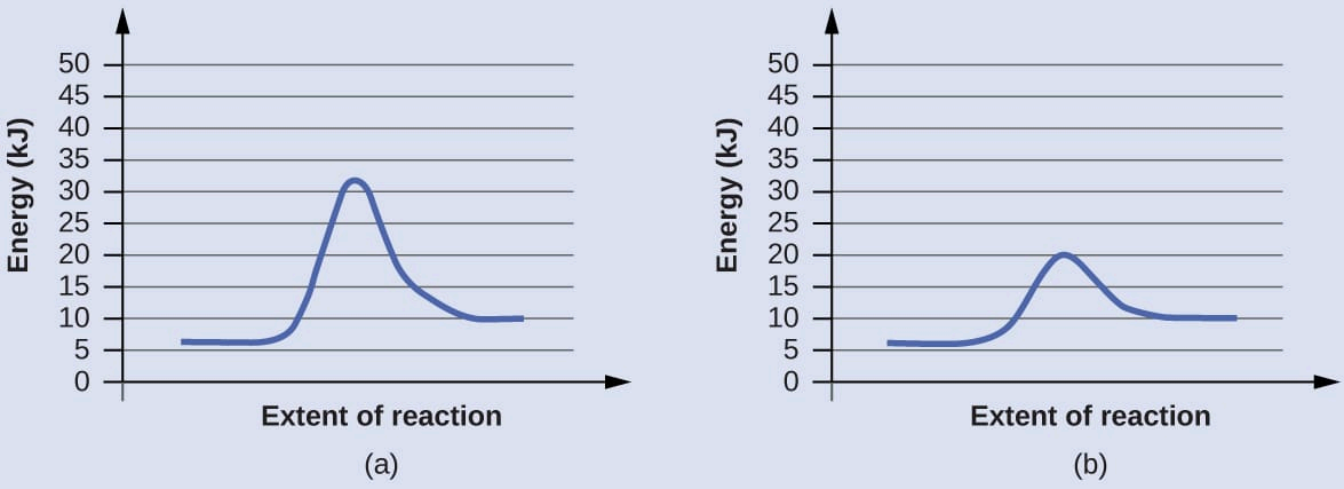


Figure 9.6.1: Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example 9.6.1: Reaction Diagrams for Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Estimate the activation energy for each process, and identify which one involves a catalyst.



Solution

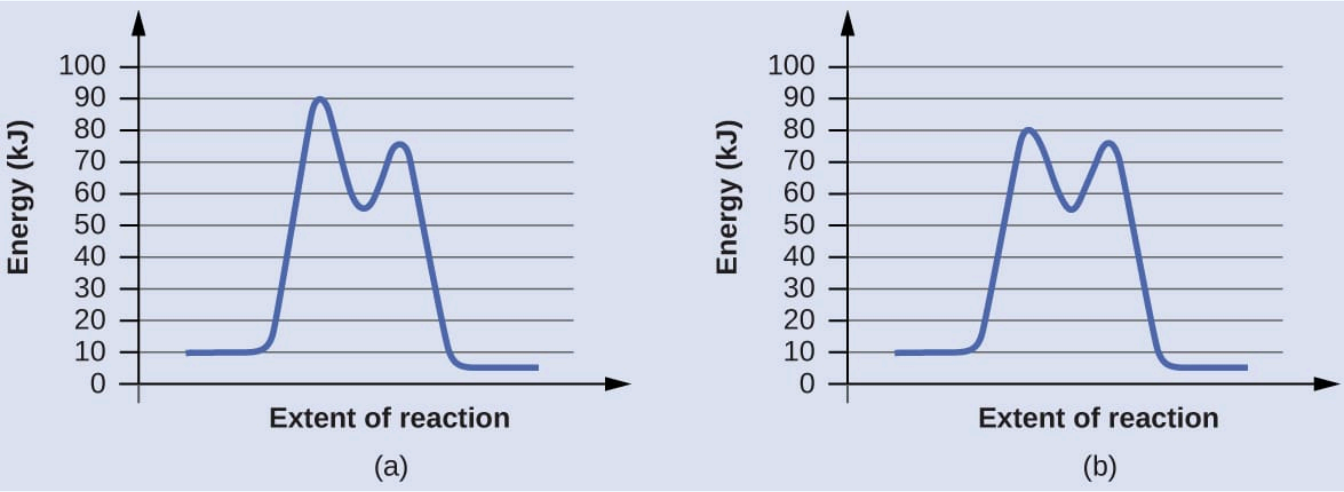
Activation energies are calculated by subtracting the reactant energy from the transition state energy.

$$\text{diagram}(a): E_a = 32kJ - 6kJ = 26kJ$$
$$\text{diagram}(b): E_a = 20kJ - 6kJ = 14kJ$$

The catalyzed reaction is the one with lesser activation energy, in this case represented by diagram b.

Exercise 9.6.1

Reaction diagrams for a chemical process with and without a catalyst are shown below. Both reactions involve a two-step mechanism with a rate-determining first step. Compute activation energies for the first step of each mechanism, and identify which corresponds to the catalyzed reaction. How do the second steps of these two mechanisms compare?



Answer available at the end of this section.

Homogeneous Catalysts

A homogeneous catalyst is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and

form product.

As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

$$3O_2(g) \xrightarrow{h\nu} 2O_3(g)$$

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following two-step mechanism:

$$O_3 \longrightarrow O_2 + O$$
$$O + O_3 \longrightarrow 2O_2$$

A number of substances can catalyze the decomposition of ozone. For example, the nitric oxide–catalyzed decomposition of ozone is believed to occur via the following three-step mechanism:

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$
$$O_3(g) \longrightarrow O_2(g) + O(g)$$
$$NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g)$$

As required, the overall reaction is the same for both the two-step uncatalyzed mechanism and the three-step NO-catalyzed mechanism:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that NO is a reactant in the first step of the mechanism and a product in the last step. This is another characteristic trait of a catalyst: Though it participates in the chemical reaction, it is not consumed by the reaction.

Portrait of a Chemist: Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 9.6.2), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[1] Molina's initial discovery of stratospheric depletion of ozone by chlorine atoms was done at the University of California Irvine, he later moved to the NASA/Jet Propulsion Laboratory, MIT and the University of California, San Diego. At the time of his death in 2020 Molina, a Mexican citizen had established a new center for the study of energy and the environment in Mexico City.

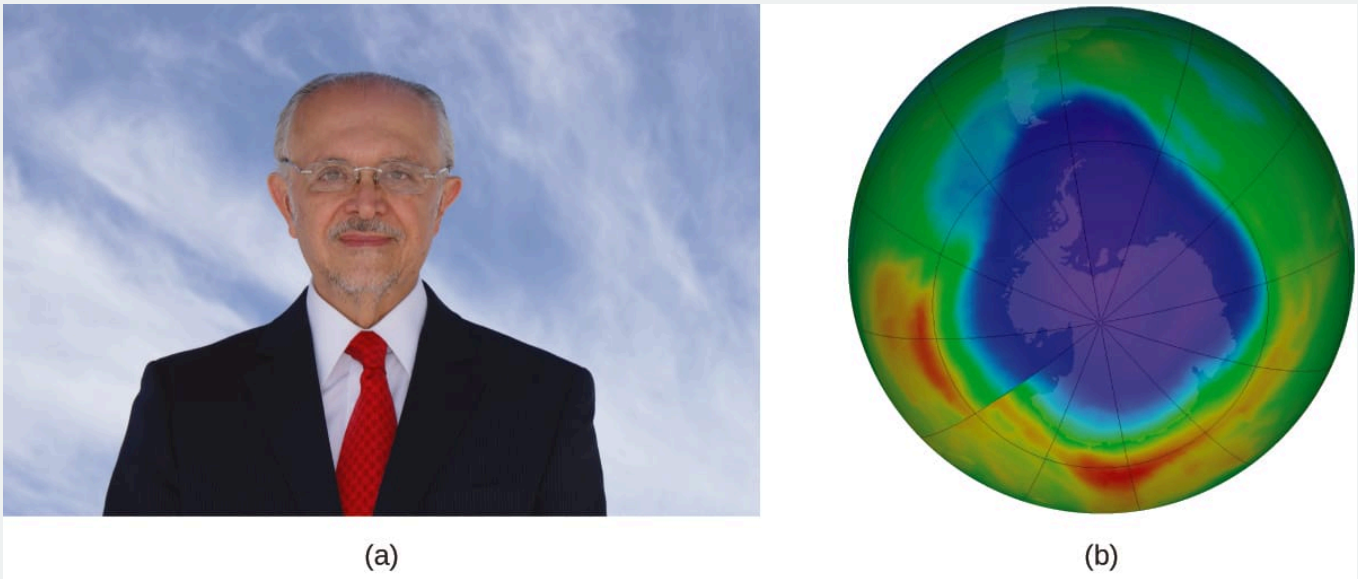


Figure 9.6.2: (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his (b) early research on stratospheric depletion of ozone and later the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

$$CH_3Cl + OH \longrightarrow Cl + \text{ other products} \tag{9.6.1}$$

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$

overall Reaction: $O_3 + O \longrightarrow 2O_2$ \nonumber \]

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 12.21, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (Figure $9.6.4$).

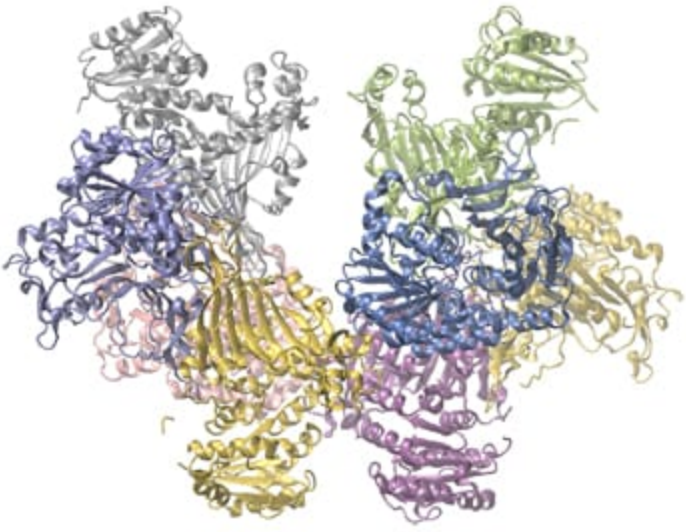


Figure 12.21 Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

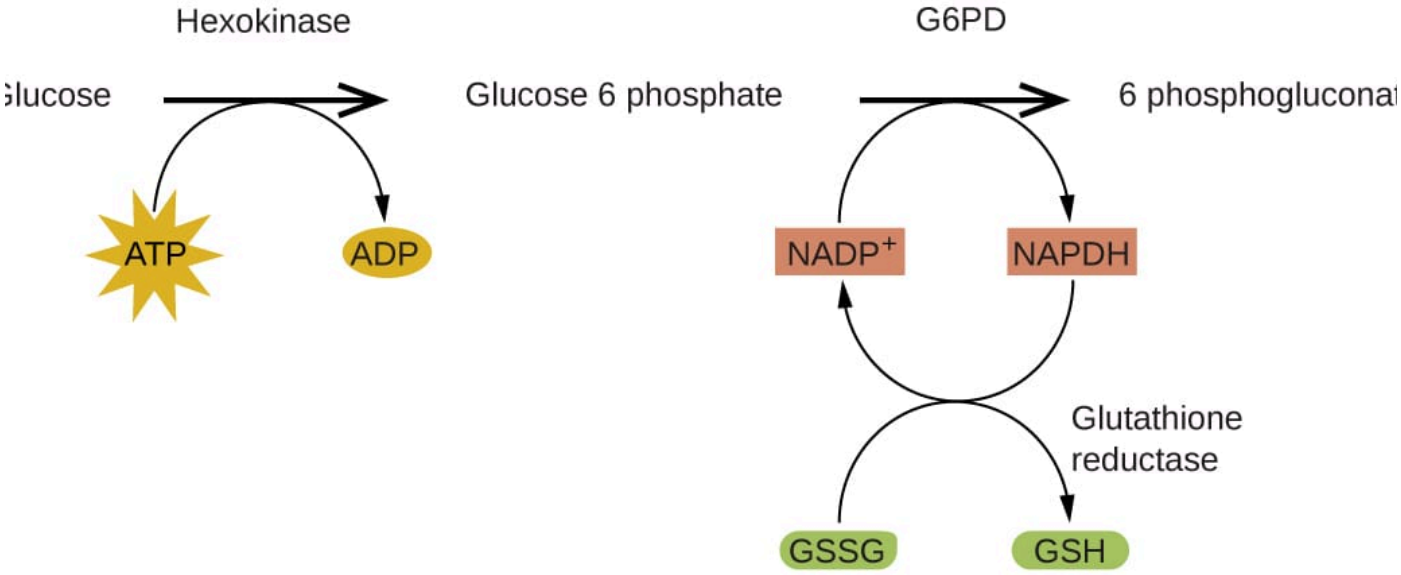


Figure 9.6.4: In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

Heterogeneous Catalysts

A heterogeneous catalyst is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis typically involves the following processes:

1. Adsorption of the reactant(s) onto the surface of the catalyst
2. Activation of the adsorbed reactant(s)

3. Reaction of the adsorbed reactant(s)

Figure 9.6.5: illustrates the steps of a mechanism for the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

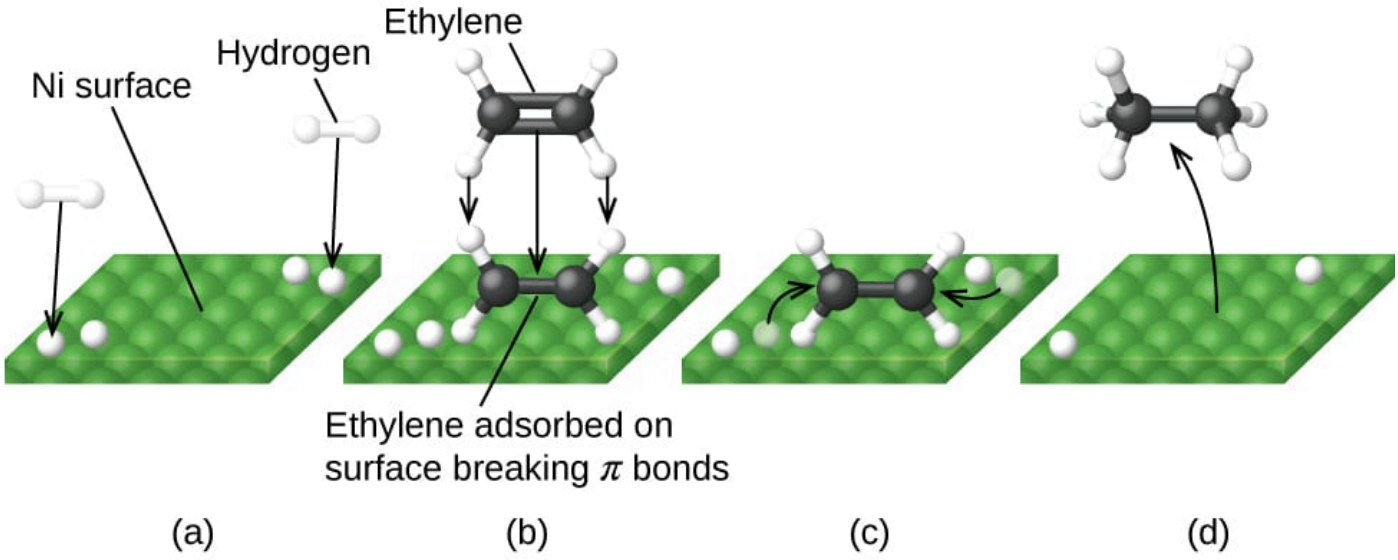


Figure 9.6.5: Mechanism for the Ni-catalyzed reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the C–C π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules desorb from the Ni surface.

Many important chemical products are prepared via industrial processes that use heterogeneous catalysts, including ammonia, nitric acid, sulfuric acid, and methanol. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 9.6.6).

Chemistry in Everyday Life: Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 9.6.6).

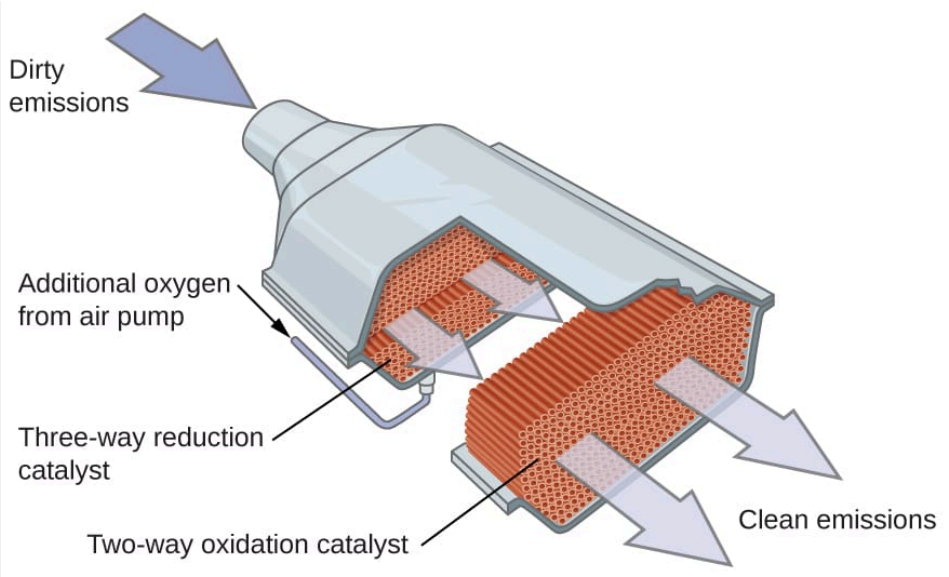


Figure 9.6.6: A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2NO_2(g) \longrightarrow N_2(g) + 2O_2(g)$$
$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$
$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

Link to Learning

The LibreTexts provides a thorough explanation of how catalytic converters work.

How Sciences Interconnect: Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in Table 9.6.1.

Table 9.6.1: Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds

Class	Function
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure 9.6.7).

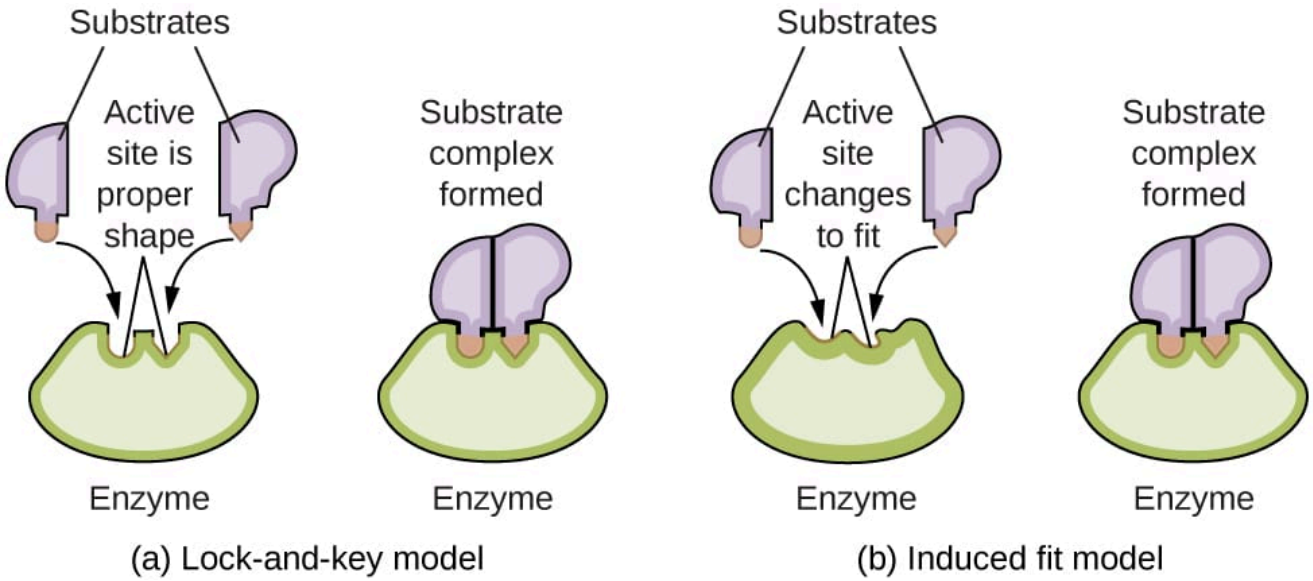


Figure 9.6.7: (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Link to Learning

The Royal Society of Chemistry provides an excellent introduction to enzymes for students and teachers.

Footnotes

- 1"The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, http://www.nobelprize.org/nobel_priz...aureates/1995/.

Answers

Exercise 9.6.1

For the first step, E_a = 80 kJ for (a) and 70 kJ for (b), so diagram (b) depicts the catalyzed reaction. Activation energies for the second steps of both mechanisms are the same, 20 kJ.

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9.7: Collision Theory

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Qualitatively (reaction coordinate diagram, mechanisms) and **quantitatively** (Arrhenius equation) describe the effect of a catalyst or temperature on reaction kinetics.

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

Collision theory is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:
$$\text{reaction rate} \propto \frac{\#\text{ collisions}}{\text{time}}$$
2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2\,\mathrm{CO}\,(\mathrm{g}) + \mathrm{O_2}\,(\mathrm{g}) \longrightarrow 2\,\mathrm{CO_2}\,(\mathrm{g})$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient amounts, the reaction will occur at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$\mathrm{CO}\,(\mathrm{g}) + \mathrm{O_2}\,(\mathrm{g}) \longrightarrow \mathrm{CO_2}\,(\mathrm{g}) + \mathrm{O}\,(\mathrm{g})$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure $9.7.1$. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms (\ce{O=C=O}\). This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

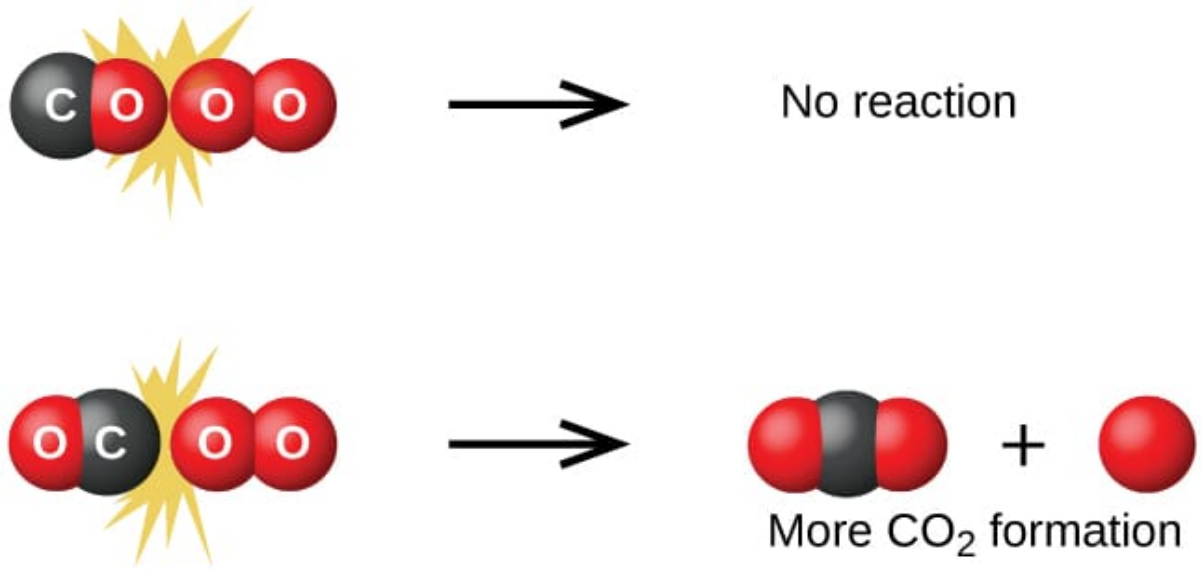


Figure 9.7.1: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an **activated complex** or a **transition state**. These species are very short lived and usually undetectable by most analytical instruments. In some cases, sophisticated spectral measurements have been used to observe transition states.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the **activation energy** (E_a). How this energy compares to the kinetic energy provided by colliding reactant molecules is a primary factor affecting the rate of a chemical reaction. If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly since only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, a large fraction of molecules will be adequately energetic and the reaction will proceed rapidly.

Figure 9.7.2 shows how the energy of a chemical system changes as it undergoes a reaction converting reactants to products according to the equation

$$\mathrm{A^+B} \longrightarrow \mathrm{C^+D}$$

These reaction diagrams are widely used in chemical kinetics to illustrate various properties of the reaction of interest. Viewing the diagram from left to right, the system initially comprises reactants only, $\mathrm{A} + \mathrm{B}$. Reactant molecules with sufficient energy can collide to form a high-energy activated complex or transition state. The unstable transition state can then subsequently decay to yield stable products, *C* + *D*. The diagram depicts the reaction's activation energy, E_a, as the energy difference between the reactants and the transition state. Using a specific energy, the *enthalpy* (see chapter on thermochemistry), the enthalpy change of the reaction, ΔH, is estimated as the energy difference between the reactants and products. In this case, the reaction is exothermic ($\Delta H < 0$) since it yields a decrease in system enthalpy.

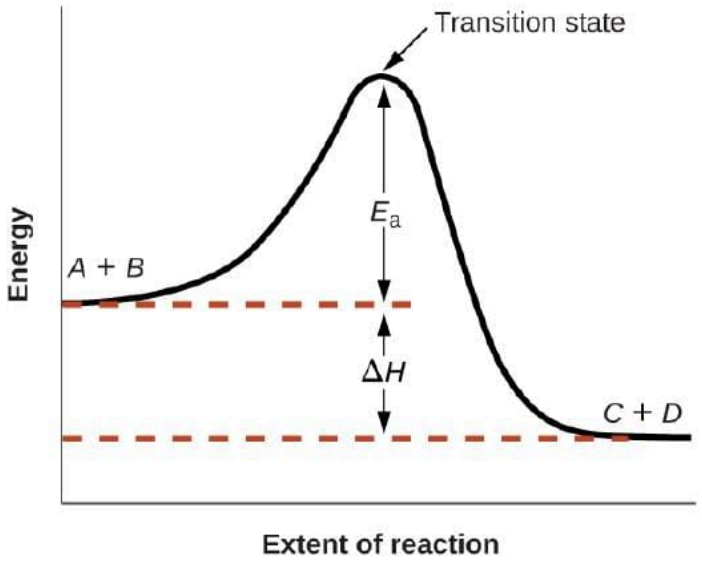


Figure 9.7.2: Reaction diagram for the exothermic reaction

The **Arrhenius equation** relates the activation energy and the rate constant, *k*, for many chemical reactions:

$$k = Ae^{-E_a/RT}$$

In this equation, R is the ideal gas constant, which has a value 8.314 J/mol/K, T is temperature on the Kelvin scale, E_a is the activation energy in joules per mole, *e* is the constant 2.7183, and *A* is a constant called the **frequency factor**, which is related to the frequency of collisions and the orientation of the reacting molecules.

Postulates of collision theory are nicely accommodated by the Arrhenius equation. The frequency factor, *A*, reflects how well the reaction conditions favor properly oriented collisions between reactant molecules. An increased probability of effectively oriented collisions results in larger values for *A* and faster reaction rates.

The exponential term, $e^{-Ea/RT}$, describes the effect of activation energy on reaction rate. According to kinetic molecular theory (see chapter on gases), the temperature of matter is a measure of the average kinetic energy of its constituent atoms or molecules. The distribution of energies among the molecules composing a sample of matter at any given temperature is described by the plot shown in Figure 9.7.3*a*. Two shaded areas under the curve represent the numbers of molecules possessing adequate energy (*RT*) to overcome the activation barriers (E_a). A lower activation energy results in a greater fraction of adequately energized molecules and a faster reaction.

The exponential term also describes the effect of temperature on reaction rate. A higher temperature represents a correspondingly greater fraction of molecules possessing sufficient energy (*RT*) to overcome the activation barrier (E_a), as shown in Figure 9.7.3*b*. This yields a greater value for the rate constant and a correspondingly faster reaction rate.

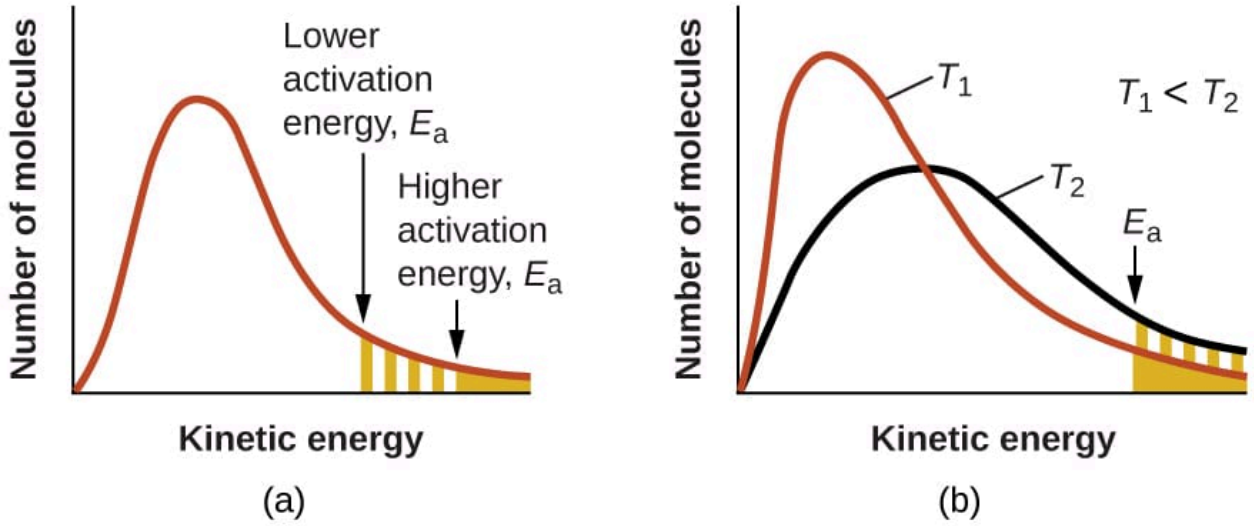


Figure 9.7.3: Molecular energy distributions showing numbers of molecules with energies exceeding (a) two different activation energies at a given temperature, and (b) a given activation energy at two different temperatures.

A convenient approach for determining E_a for a reaction involves the measurement of *k* at two or more different temperatures and using an alternate version of the Arrhenius equation that takes the form of a linear equation

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

$$y = mx + b$$

A plot of $\ln k$ versus $\frac{1}{T}$ is linear with a slope equal to $\frac{-E_a}{R}$ and a y-intercept equal to $\ln A$.

Example 9.7.1: Determination of E_a

The variation of the rate constant with temperature for the decomposition of $\mathrm{HI(g)}$ to $\mathrm{H_2(g)}$ and $\mathrm{I_2(g)}$ is given here. What is the activation energy for the reaction?

$$2\,\mathrm{HI(g)} \longrightarrow \mathrm{H_2(g) + I_2(g)}$$

T (K)	*k* (L/mol/s)
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

Solution

Use the provided data to derive values of $\frac{1}{T}$ and $\ln k$:

$\frac{1}{T}$	$\ln k$
1.80×10^{-3}	−14.860
1.74×10^{-3}	−13.617

$\frac{1}{T}$	$\ln k$
1.55×10^{-3}	−9.362
1.43×10^{-3}	−6.759
1.28×10^{-3}	−3.231

Figure 9.7.4 is a graph of $\ln k$ versus $\frac{1}{T}$. In practice, the equation of the line (slope and *y*-intercept) that best fits these plotted data points would be derived using a statistical process called regression. This is helpful for most experimental data because a perfect fit of each data point with the line is rarely encountered. For the data here, the fit is nearly perfect and the slope may be estimated using any two of the provided data pairs. Using the first and last data points permits estimation of the slope.

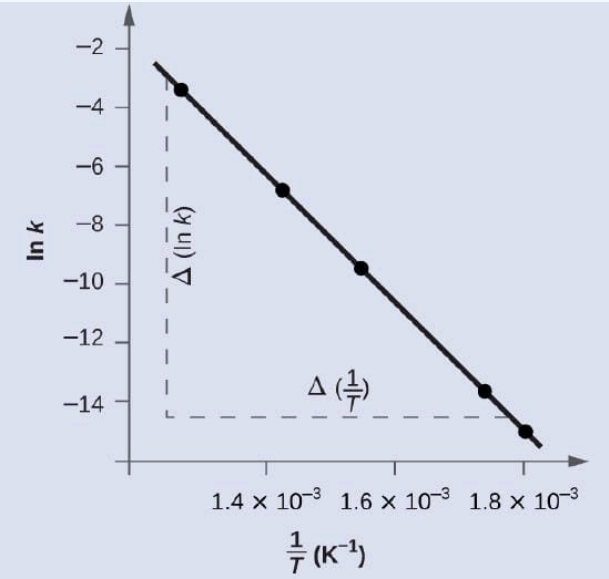


Figure 9.7.4: This graph shows the linear relationship between $\ln k$ versus $\frac{1}{T}$ for the reaction $2HI \longrightarrow H_2 + I_2$ according to the Arrhenius equation.

$$\begin{aligned}
\text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\
&= \frac{(-14.860) - (-3.231)}{\left(1.80 \times 10^{-3} K^{-1}\right) - \left(1.28 \times 10^{-3} K^{-1}\right)} \\
&= \frac{-11.629}{0.52 \times 10^{-3} K^{-1}} = -2.2 \times 10^{4} K \\
&= -\frac{E_a}{R} \\
E_a &= -\ \text{slope}\ \times R = -\left(-2.2 \times 10^{4} K \times 8.314 J mol^{-1} K^{-1}\right) \\
&\quad 1.8 \times 10^{5} J mol^{-1} \text{ or } 180 k J mol^{-1}
\end{aligned}$$

Alternative approach: A more expedient approach involves deriving activation energy from measurements of the rate constant at just two temperatures. In this approach, the Arrhenius equation is rearranged to a convenient two-point form:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Rearranging this equation to isolate activation energy yields:

$$E_a = -R\left(\frac{\ln k_2 - \ln k_1}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)}\right)$$

Any two data pairs may be substituted into this equation—for example, the first and last entries from the above data table:

$$E_a = -8.314 J mol^{-1} K^{-1}\left(\frac{-3.231 - (-14.860)}{1.28 \times 10^{-3} K^{-1} - 1.80 \times 10^{-3} K^{-1}}\right)$$

and the result is E_a = 1.8 10^5 J mol^{-1} or 180 kJ mol^{-1}

This approach yields the same result as the more rigorous graphical approach used above, as expected. In practice, the graphical approach typically provides more reliable results when working with actual experimental data.

Exercise 9.7.1

The rate constant for the rate of decomposition of $\mathrm{N_2O_5}$ to NO and $\mathrm{O_2}$ in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$2\,\mathrm{N_2O_5\,(g)} \longrightarrow 4\,\mathrm{NO\,(g)} + 3\,\mathrm{O_2\,(g)}$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer available at the end of this section.

Answers

Exercise 9.7.1

1.1 10^5 J mol^{-1} or 110 kJ mol^{-1}

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9.8: Reaction Mechanisms

Learning Objectives

By the end of this section, you will have background that will help you to be able to:

- Qualitatively (reaction coordinate diagram, **mechanisms**) and quantitatively (Arrhenius equation) describe the effect of a catalyst or temperature on reaction kinetics.

Chemical reactions very often occur in a step-wise fashion, involving two or more distinct reactions taking place in sequence. A balanced equation indicates what is reacting and what is produced, but it reveals no details about how the reaction actually takes place. The reaction mechanism (or reaction path) provides details regarding the precise, step-by-step process by which a reaction occurs.

The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$O_3(g) \longrightarrow O_2(g) + O$$
$$O + O_3(g) \longrightarrow 2O_2(g)$$

Each of the steps in a reaction mechanism is an **elementary reaction**. These elementary reactions occur precisely as represented in the step equations, and they must sum to yield the balanced chemical equation representing the overall reaction:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called intermediates.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction *does not involve the direct collision and reaction of two ozone molecules*. Instead, one O_3 decomposes to yield O_2 and an oxygen atom, and a second O_3 molecule subsequently reacts with the oxygen atom to yield two additional O_2 molecules.

Unlike balanced equations representing an overall reaction, the equations for elementary reactions are explicit representations of the chemical change taking place. The reactant(s) in an elementary reaction's equation undergo only the bond-breaking and/or making events depicted to yield the product(s). For this reason, *the rate law for an elementary reaction may be derived directly from the balanced chemical equation describing the reaction*. This is not the case for typical chemical reactions, for which rate laws may be reliably determined only via experimentation.

Unimolecular Elementary Reactions

The molecularity of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a unimolecular reaction involves the reaction of a *single* reactant species to produce one or more molecules of product:

$$A \longrightarrow \text{ products}$$

The rate law for a unimolecular reaction is first order:

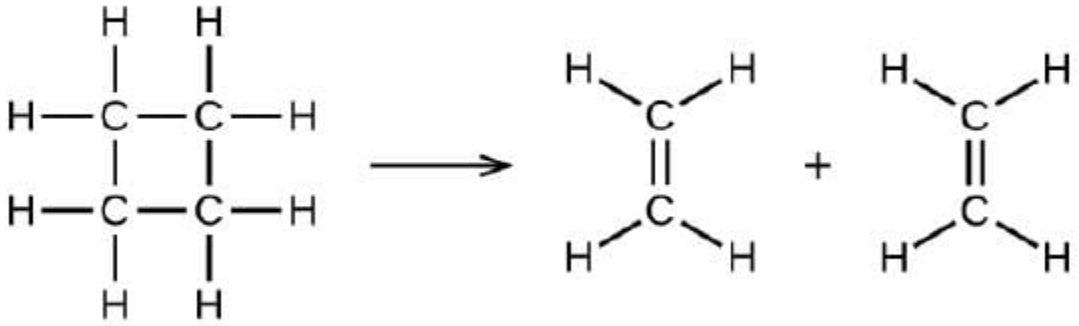
$$\text{rate } = k[A]$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$O_3 \longrightarrow O_2 + O$$

illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism as described above.

However, some unimolecular reactions may be the only step of a single-step reaction mechanism. (In other words, an "overall" reaction may also be an elementary reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, is represented by the following chemical equation:



This equation represents the overall reaction observed, and it might also represent a legitimate unimolecular elementary reaction. The rate law predicted from this equation, assuming it is an elementary reaction, turns out to be the same as the rate law derived experimentally for the overall reaction, namely, one showing first-order behavior:

$$\text{rate } = -\frac{\Delta\left[C_4H_8\right]}{\Delta t} = k\left[C_4H_8\right]$$

This agreement between observed and predicted rate laws is interpreted to mean that the proposed unimolecular, single-step process is a reasonable mechanism for the butadiene reaction.

Bimolecular Elementary Reactions

A bimolecular reaction involves two reactant species, for example:

$$A + B \longrightarrow \text{ products}$$

and

$$2A \longrightarrow \text{ products}$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in *A* and first order in *B* (second-order overall):

$$\text{rate } = k[A][B]$$

For the second type, in which two identical molecules collide and react, the rate law is second order in *A*:

$$\text{rate } = k[A][A] = k[A]^2$$

Some chemical reactions occur by mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

(see Figure 9.8.1)



Figure 9.8.1: The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is the second step of the two-step ozone decomposition mechanism discussed earlier in this section:

$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$

Termolecular Elementary Reactions

An elementary termolecular reaction involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:

$$2NO + O_2 \longrightarrow 2NO_2$$
$$\text{rate } = k[NO]^2\,[O_2]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$2NO + Cl_2 \longrightarrow 2NOCl$$
$$\text{rate } = k[NO]^2\,[Cl_2]$$

Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the rate-limiting step (or rate-determining step) of the reaction Figure 9.8.2.



Figure 9.8.2: A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanisms. In every case, the rate law must be determined from experimental data and the reaction mechanism subsequently deduced from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate } = k\,[NO_2]\,[CO]$$

The reaction is first order with respect to NO_2 and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO_2:

$$\text{rate } = k\,[NO_2]^2$$

This rate law is not consistent with the single-step mechanism, but is consistent with the following two-step mechanism:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)\ \text{(slow)}$$
$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)\ \text{(fast)}$$

The rate-determining (slower) step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving a rapidly reversible reaction the rate law for the overall reaction may be more difficult to derive.

As discussed in several chapters of this text, a reversible reaction is at *equilibrium* when the rates of the forward and reverse processes are equal. Consider the reversible elementary reaction in which NO dimerizes to yield an intermediate species N_2O_2.

$$NO + NO \rightleftharpoons N_2O_2$$

When this reaction is at equilibrium:

$$\text{rate}_{\text{ forward}} = \text{rate}_{\text{ reverse}}$$
$$k_1[NO]^2 = k_{-1}\,[N_2O_2]$$

This expression may be rearranged to express the concentration of the intermediate in terms of the reactant NO:

$$\left(\frac{k_1[NO]^2}{k_{-1}}\right) = [N_2O_2]$$

Since intermediate species concentrations are not used in formulating rate laws for overall reactions, this approach is sometimes necessary, as illustrated in the following example exercise.

Example 9.8.1: Deriving a Rate Law from a Reaction Mechanism

The two-step mechanism below has been proposed for a reaction between nitrogen monoxide and molecular chlorine:

$$\text{Step 1:}\quad \mathrm{NO\,(g) + Cl_2\,(g) \rightleftharpoons NOCl_2\,(g)} \qquad \text{(fast)}$$
$$\text{Step 2:}\quad \mathrm{NOCl_2\,(g) + NO\,(g) \rightleftharpoons 2\,NOCl\,(g)} \qquad \text{(slow)}$$

Use this mechanism to derive the equation and predicted rate law for the overall reaction.

Solution

The equation for the overall reaction is obtained by adding the two elementary reactions:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

To derive a rate law from this mechanism, first write rates laws for each of the two steps.

$$\text{rate}_1 = k_1[NO]\,[Cl_2] \text{ for the forward reaction of step 1}$$
$$\text{rate}_{-1} = k_{-1}\,[NOCl_2] \text{ for the reverse reaction of step 1}$$
$$\text{rate}_2 = k_2\,[NOCl_2]\,[NO] \text{ for step 2}$$

Step 2 is the rate-determining step, and so the rate law for the overall reaction should be the same as for this step. However, the step 2 rate law, as written, contains an intermediate species concentration, [$NOCl_2$]. To remedy this, use the first step's rate laws to derive an expression for the intermediate concentration in terms of the reactant concentrations.

Assuming step 1 is at equilibrium:

$$\text{rate}_1 = \text{rate}_{-1}$$
$$k_1[NO]\,[Cl_2] = k_{-1}\,[NOCl_2]$$
$$[NOCl_2] = \left(\frac{k_1}{k_{-1}}\right)[NO]\,[Cl_2]$$

Substituting this expression into the rate law for step 2 yields:

$$\text{rate}_2 = \text{rate}_{\text{overall}} = \left(\frac{k_2 k_1}{k_{-1}}\right)[NO]^2\,[Cl_2]$$

Exercise 9.8.1

The first step of a proposed multistep mechanism is:

\[\ce{F2(g) <=> 2 F(g) \tag{fast} \]

Derive the equation relating atomic fluorine concentration to molecular fluorine concentration.

Answer available at the end of this section.

Answers

Exercise 9.8.1

$$[\text{F}] = \left(\frac{k_1\,[F_2]}{k_{-1}}\right)^{1/2}$$

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10: PROCESSES END UP AT EQUILIBRIUM

10.1: Overview and Objectives
10.2: The Concept of Chemical Equilibrium
10.3: The Equilibrium Constant
10.4: Solving Equilibrium Problems
10.5: Non-equilibrium Conditions
10.6: Factors That Affect Equilibrium
10.7: Spontaneity and Equilibrium
10.8: Comparing Thermodynamics and Kinetics

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10.1: Overview and Objectives

> "If we maintain that for a given chemical process two opposing forces are in effect, one which strives to form new substances and one which strives to restore the original compounds from the new, it is enlightening that, when in the chemical process these forces become equally large, the system is in equilibrium. That the same equilibrium state occurs under the same conditions, whether one goes one way or the other in the process, lies in the nature of the matter" (C.M. Guldberg and P. Waage)

Guldberg and Waage's lecture on chemical equilibrium, which is the source of this quote, was among the first to formulate the *law of mass action,* which is the underpinning of chemical equilibrium. Instead of affirming that all chemical reactions would eventually proceed in one direction or the other to their end, which was the prevailing view of the time, they suggested that all chemical systems have two competing affinities: one to make products from reactants, and one to regenerate reactants from products. These two forces would eventually become equal and opposite, so that the amounts of reactants and products remained constant. In this chapter, we will examine these concepts of equilibrium and apply them to describing the composition of chemical systems.

Chapter Objectives

- Compare and contrast product-favored equilibria to reactant-favored equilibria in terms of equilibrium composition, ΔG, and K.
- Determine the equilibrium constant and/or the equilibrium composition of a mixture from a balanced chemical equation and initial amounts.
- Evaluate the direction of reaction (left to right, right to left, or at equilibrium) based on the reaction quotient.
- Predict how stresses in concentration, temperature, and pressure affect a mixture's equilibrium composition.

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10.2: The Concept of Chemical Equilibrium

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Compare and contrast product-favored equilibria to reactant-favored equilibria in terms of equilibrium composition, ΔG, and *K*.

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2). NO_2 is responsible for the brown color we associate with smog. When a sealed tube containing solid N_2O_4 (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of NO_2 appears (Figure 15.1.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

$$N_2O_4(g) colorless \rightleftharpoons 2NO_{2(g)}\ red-brown \tag{15.1.1}$$

The double arrow indicates that both the forward and reverse reactions are occurring simultaneously; it is read “is in equilibrium with.”



Figure 15.1.1 The **$N_2O_4(g)$ ⇌ $2NO_2(g)$ System at Different Temperatures** (left) At dry ice temperature (−78.4°C), the system contains essentially pure solid N_2O_4, which is colorless. (center) As the system is warmed above the melting point of N_2O_4 (−9.3°C), the N_2O_4 melts and then evaporates, and some of the vapor dissociates to red-brown NO_2. (right) Eventually the sample reaches room temperature, and a mixture of gaseous N_2O_4 and NO_2 is present. The composition of the mixture and hence the color do not change further with time: the system has reached equilibrium at the new temperature.

Figure 15.1.2shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO_2 were zero, then it increases as the concentration of N_2O_4 decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N_2O_4 but an initial NO_2 concentration twice the initial concentration of N_2O_4 in part (a) in Figure 15.1.2, in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition, as shown in part (b) in Figure 15.1.2. Thus equilibrium can be approached from *either direction* in a chemical reaction.

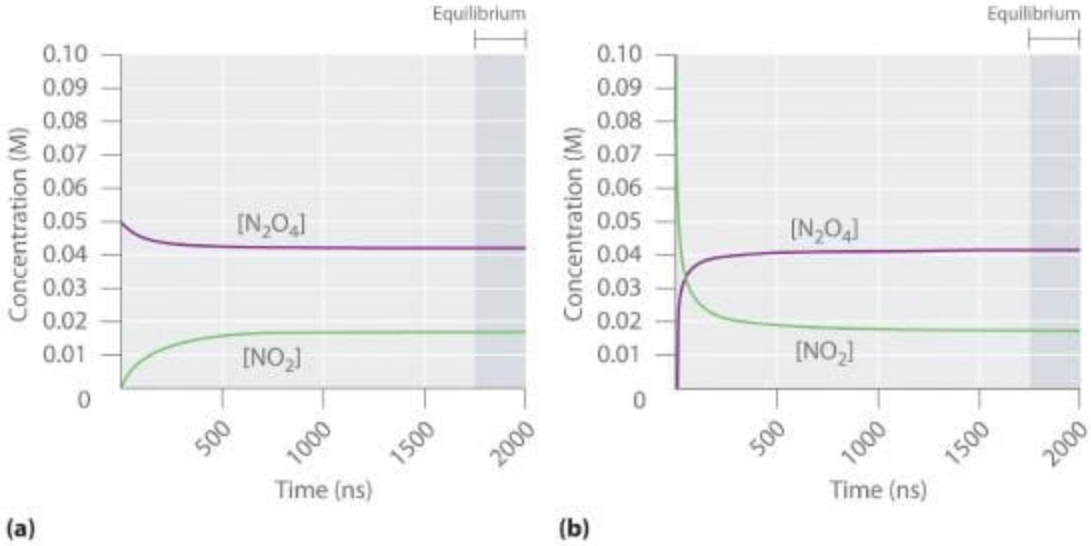


Figure 15.1.2 The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: $[N_2O_4]$ = 0.0422 M and $[NO_2]$ = 0.0156 M at equilibrium.

Figure 15.1.3 shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high (2.0×10^6 M/s), but it decreases rapidly as the concentration of NO_2 decreases. (The reaction rate of the dimerization reaction is expected to decrease rapidly because the reaction is second order in NO_2: rate = $k_r[NO_2]^2$, where k_r is the rate constant for the reverse reaction shown in Equation 15.1.1.) As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equation 15.1.1). Eventually, the forward and reverse reaction rates become identical, $k_F = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at *different* rates, then the system is *not* at equilibrium.

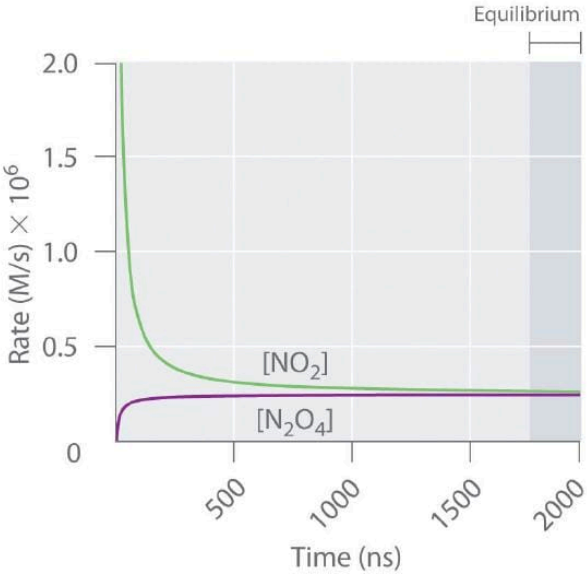


Figure 15.1.2

The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at t = 0 is also zero. As the

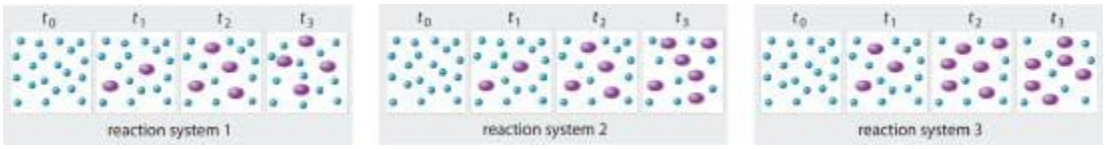
dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.

Note the Pattern

At equilibrium, the forward reaction rate is equal to the reverse reaction rate.

Example 15.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation $2\mathrm{A} \rightleftharpoons \mathrm{B}$, where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

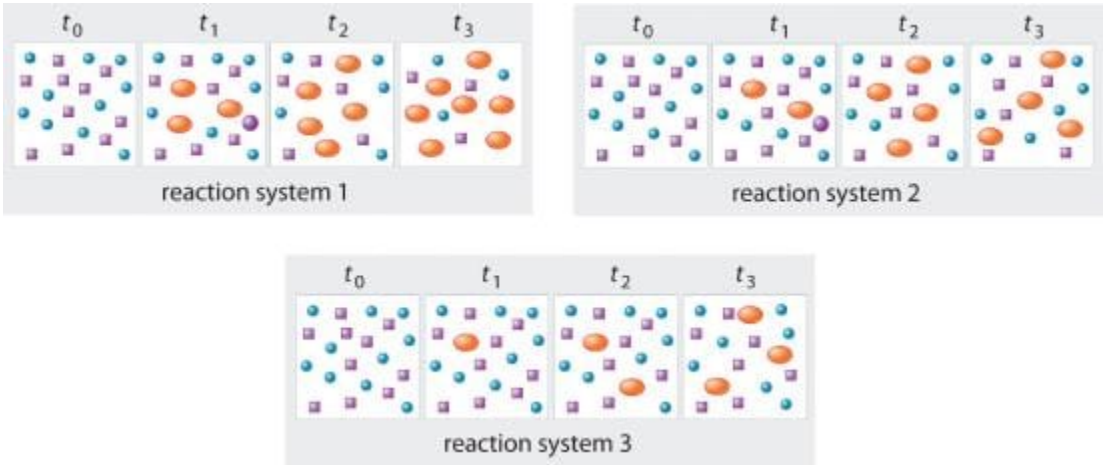
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



Answer: system 2

Summary

Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

Key Takeaway

- At equilibrium, the forward and reverse reactions of a system proceed at equal rates.

Conceptual Problems

1. What is meant when a reaction is described as “having reached equilibrium”? What does this statement mean regarding the forward and reverse reaction rates? What does this statement mean regarding the concentrations or amounts of the reactants and the products?

2. Is it correct to say that the reaction has “stopped” when it has reached equilibrium? Explain your answer and support it with a specific example.

3. Why is chemical equilibrium described as a dynamic process? Describe this process in the context of a saturated solution of NaCl in water. What is occurring on a microscopic level? What is happening on a macroscopic level?

4. Which of these systems exists in a state of chemical equilibrium?

    1. oxygen and hemoglobin in the human circulatory system
    2. iodine crystals in an open beaker
    3. the combustion of wood
    4. the amount of ^{14}C in a decomposing organism

Answer

1.
2.

3. Both forward and reverse reactions occur but at the same rate. Na^+ and Cl^- ions continuously leave the surface of an NaCl crystal to enter solution, while at the same time Na^+ and Cl^- ions in solution precipitate on the surface of the crystal.

4.

- Anonymous

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10.3: The Equilibrium Constant

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Compare and contrast product-favored equilibria to reactant-favored equilibria in terms of equilibrium composition, ΔG, and *K*.
- Determine the equilibrium constant and/or the equilibrium composition of a mixture from a balanced chemical equation and initial amounts.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the system described in Equation 15.2.1, the decomposition of N_2O_4 to NO_2. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_4] \tag{15.2.1}$$

and

$$\text{reverse rate} = k_r[NO_2]^2 \tag{15.2.2}$$

At equilibrium, the forward rate equals the reverse rate:

$$k_f[N_2O_4] = k_r[NO_2]^2 \tag{15.2.3}$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \tag{15.2.4}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (*K*)The ratio of the rate constants for the forward reaction and the reverse reaction; that is, K =k_f/k_r It is also the equilibrium constant calculated from solution concentrations: K =$[C]^c[D]^d/[A]^a[B]^b$ for the general reaction aA + bB ⇌cC +dD in which each component is in solution. which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{15.2.5}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: *under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions*.

Note the Pattern

The equilibrium constant is equal to the rate constant for the *forward* reaction divided by the rate constant for the *reverse* reaction.

Table 15.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 15.1.1. At equilibrium the magnitude of the quantity $[NO_2]^2/[N_2O_4]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of NO_2 and N_2O_4 are, at equilibrium the quantity $[NO_2]^2/[N_2O_4]$ will *always* be 6.53 ± 0.03 × 10^{-3} at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions. That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of

the reactants and products vary depending on their initial concentrations.

Table 15.2.1 Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for *any* reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{15.2.6}$$

where A and B are reactants, C and D are products, and *a*, *b*, *c*, and *d* are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass actionFor the general balanced chemical equation aA+bB = cC+ dD the equilibrium constant expression is K =$[C]^c[D]^d/[A]^a[B]^b$ and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.2.7}$$

where *K* is the equilibrium constant for the reaction. Equation 15.7 is called the equilibrium equationFor the general balanced chemical equation aA+bB = cC+ dD the equilibrium constant expression is K =$[C]^c[D]^d/[A]^a[B]^b$, and the right side of Equation 15.2.7 is called the equilibrium constant expression. The relationship shown in Equation 15.2.7 is true for *any* pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of *K* shown in Table 15.2.2 , for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of *K* greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of *K* less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 15.2.2 Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (*K*)
$S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$	300	4.4×10^{53}
$2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H2O_{(g)}$	500	2.4×10^{47}
***Equilibrium constants vary with temperature. The *K* values shown are for systems at the indicated temperatures.**		

Reaction	Temperature (K)	Equilibrium Constant (*K*)
$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$	300	1.6×10^{33}
$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$	300	4.1×10^{18}
$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$	300	4.2×10^{13}
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	300	2.7×10^{8}
$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$	100	1.92
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	300	2.9×10^{-1}
$I_{2(g)} \rightleftharpoons 2I_{(g)}$	800	4.6×10^{-7}
$Br_{2(g)} \rightleftharpoons 2Br_{(g)}$	1000	4.0×10^{-7}
$Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$	1000	1.8×10^{-9}
$F_{2(g)} \rightleftharpoons 2F_{(g)}$	500	7.4×10^{-13}
***Equilibrium constants vary with temperature. The *K* values shown are for systems at the indicated temperatures.**		

You will also notice in Table 15.2.2 that equilibrium constants have no units, even though Equation 15.2.7 suggests that the units of concentration might not always cancel because the exponents may vary. In fact, equilibrium constants are calculated using "effective concentrations," or *activities*, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M. As shown in Equation 15.2.8, the units of concentration cancel, which makes *K* unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{15.2.8}$$

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)} \tag{15.10}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{10.3.1}$$

with *K* varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 15.2.1summarizes the relationship between the magnitude of *K* and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants ⇌ products Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equation 15.2.8 and Equation 15.2.7), when $k_f >> k_r$, *K* is a large number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f << k_r$, *K* is a very small number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

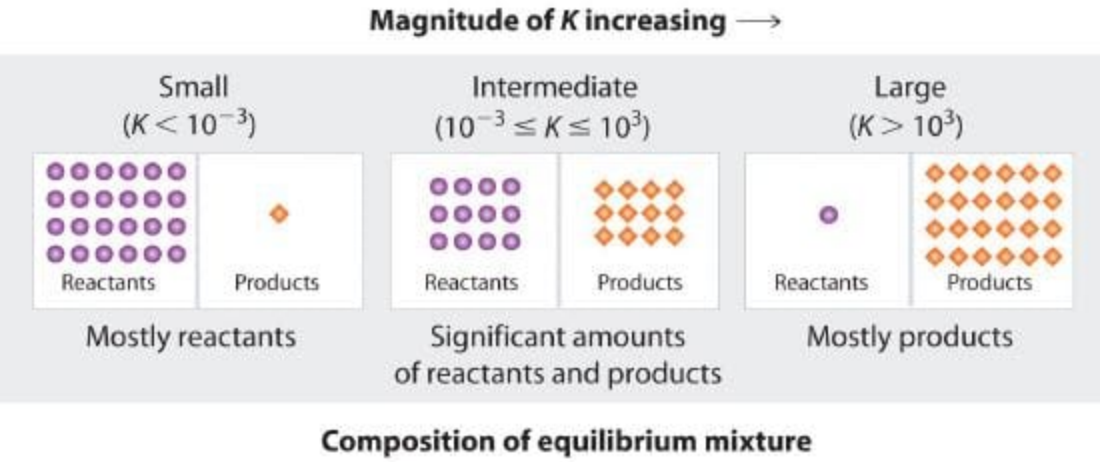


Figure 15.2.1 The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium **Constant**The larger the *K*, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

Note the Pattern

> **A large value of the equilibrium constant *K* means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.**

Example 15.2.1

Write the equilibrium constant expression for each reaction.

1. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
2. $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$
3. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 15.2.7. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

1. The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H_2 has a coefficient of 3. The equilibrium constant expression is as follows:
$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$
2. The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of 1/2 Thus the equilibrium constant expression is as follows:
$$\frac{[CO_2]}{[CO][O_2]^{1/2}}$$
3. This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$\frac{[CO]^2[O_2]}{[CO_2]^2}$$

Exercise

Write the equilibrium constant expression for each reaction.

1. $N_2O_{(g)} \rightleftharpoons N_{2(g)} + \frac{1}{2}O_{2(g)}$
2. $2C_8H_{18(g)} + 25O_{2(g)} \rightleftharpoons 16CO_{2(g)} + 18H_2O_{(g)}$
3. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Answer

1. $K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$
2. $K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$
3. $K = \frac{[HI]^2}{[H_2][I_2]}$

Example 15.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of *K*

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

1. Only system 4 has $K >> 10^3$, so at equilibrium it will consist of essentially only products.
2. System 2 has $K << 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
3. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Values of the equilibrium constant at various temperatures were reported as $K_{25°C} = 3.3 \times 10^8$, $K_{177°C} = 2.6 \times 10^3$, and $K_{327°C} = 4.1$.

1. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
2. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you

design a commercial reactor to operate to maximize the yield of ammonia?

Answer

1. 327°C, where *K* is smallest
2. 25°C

Equilibrium Constant Expressions for Reverse Reactions

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 15.7 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{15.2.10}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{15.2.11}$$

This expression is the inverse of the expression for the original equilibrium constant, so *K*′ = 1/*K*. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction N_2O_4 ⇄ $2NO_2$ is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{15.2.12}$$

but for the opposite reaction, $2NO_2$ ⇄ N_2O_4 the equilibrium constant *K*′ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{15.2.13}$$

Consider another example, the formation of water: $2H_2(g) + O_2(g)$ ⇄ $2H_2O(g)$ Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

Note the Pattern

The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{10.3.2}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{10.3.3}$$

with the equilibrium constant *K*″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{15.2.14}$$

The values for *K*′ (Equation 15.2.13) and *K*″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{15.2.15}$$

In general, if all the coefficients in a balanced chemical equation are subsequently multiplied by *n*, then the new equilibrium constant is the original equilibrium constant raised to the *n*th power.

Example 15.2.3

At 745 K, *K* is 0.118 for the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

What is the equilibrium constant for each related reaction at 745 K?

1. $2NH_{3(g)} \rightleftharpoons N2(g) + 3H_{2(g)}$
2. $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$

Given: balanced equilibrium equation, *K* at a given temperature, and equations of related reactions

Asked for: values of *K* for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate *K* for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $N_2(g)$ with $H_2(g)$ to produce $NH_3(g)$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

1. This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

2. In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

Exercise

At 527°C, the equilibrium constant for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

\[SO_{3(g)} \rightleftharpoons SO_{2(g)}+\frac{1}{2}O_{2(g) \notag \]

Answer: 3.6×10^{-3}

Equilibrium Constant Expressions for Systems that Contain Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_pAn equilibrium constant expressed as the ratio of the partial pressures of the

products and reactants, each raised to its coefficient in the chemical equation. is used to denote equilibrium constants calculated from partial pressures. For the general reaction aA + bB ⇌ cC + dD in which all the components are gases, we can write the equilibrium constant expression as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \tag{15.2.16}$$

Thus K_p for the decomposition of N_2O_4 (Equation 15.1.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{15.2.17}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an “effective pressure,” the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity.The “effective pressure” is called the *fugacity*, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{15.2.18}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of gaseous products and gaseous reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in kelvins. According to Equation 15.19, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction, $K_p = K(RT)^1 = KRT$.

Example 15.2.4

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 15.19 to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745$ K. Thus, from Equation 15.2.15, we have the following:

$$K_p = K(RT)^{-2} = \frac{K}{(RT)^2} = \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} = 3.16 \times 10^{-5}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise

Calculate K_p for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer: $K_p = 1.2 \times 10^3$

Homogeneous and Heterogeneous Equilibria

When the products and reactants of an equilibrium reaction form any single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids. Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)} \tag{15.2.19}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CO]^2}{[CO_2][C]} \tag{15.2.20}$$

Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:

$$[C] = \frac{2.26\ \cancel{g}/\cancel{cm^3}}{12.01\ \cancel{g}/mol} \times 1000\ \cancel{cm^3}/L = 188\ mol/L = 188\ M \tag{15.2.21}$$

We can rearrange Equation 15.2.17 so that the constant terms are on one side:

$$K[C] = K(188) = \frac{[CO]^2}{[CO_2]} \tag{15.2.22}$$

Incorporating the constant value of [C] into the equilibrium equation for the reaction in Equation 15.2.16,

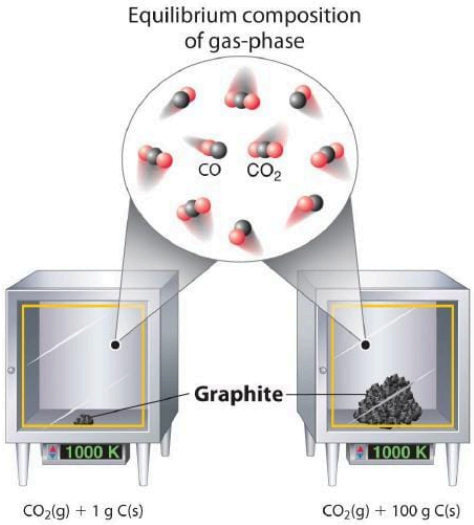
$$K' = \frac{[CO]^2}{[CO_2]} \tag{15.2.23}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{15.2.24}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 15.2.16 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 15.2.2, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.



$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Figure 15.2.2 Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 15.2.5

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

1. $PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)}$
2. $Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(g)}$

Given: balanced equilibrium equations

Asked for: expressions for K and K_p

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution:

1. This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their concentrations do not appear in the equilibrium constant expression because they do not change significantly. So

$$K = \frac{1}{[Cl_2]}$$

and

$$K_p = \frac{1}{P_{Cl_2}}$$

2. This reaction contains two pure solids (Fe_3O_4 and Fe), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

$$K = \frac{[H_2O]^4}{[H_2]^4}$$

Exercise

Write the expressions for K and K_p for the following reactions.

1. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
2. $\underset{glucose}{C_6H_{12}O_{6(s)}} + 6O_{2(g)} \rightleftharpoons 6CO_{2(g)} + 6H_2O_{(g)}$

Answer

1. K = [CO_2]; and Kp = P(CO_2)
2. $K = \dfrac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \dfrac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that pure water is about 55.5 M, and pure ethanol is about 17 M). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

Note the Pattern

The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

Equilibrium Constant Expressions for the Sums of Reactions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of N_2 with O_2 to give NO_2. As we stated in Section 15.1, this reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (2). The equilibrium constant for each reaction at 100°C is also given.

1. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad K_1 = 2.0 \times 10^{-25}$
2. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_2 = 6.4 \times 10^{9}$
3. Summing reactions (1) and (2) gives the overall reaction of N_2 with O_2:
4. $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_3 = ?$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

v

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, Δ*H* for the sum of two or more reactions is the *sum* of the Δ*H* values for the individual reactions.

Note the Pattern

To determine *K* for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.

Example 15.2.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)}) \qquad K_2 = 3.3 \times 10^{4}$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of *K*, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of *K* for that equation. Calculate *K* for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^{4}) = 3.03 \times 10^{3}$$

Exercise

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \qquad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_3 = ?$

Answer: $K_3 = 1.1 \times 10^{66}$

Summary

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the **equilibrium constant (*K*)**, a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same *K*. For a system at equilibrium, the **law of mass action** relates *K* to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the **equilibrium equation**. The ratio is called the **equilibrium constant expression**. When a reaction is written in the reverse direction, *K* and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to *K* by the ideal gas constant (*R*), the temperature (*T*), and the change in the number of moles of gas during the reaction. An equilibrium system that contains products and reactants in a single phase is a **homogeneous equilibrium**; a system whose reactants, products, or both are in more than one phase is a **heterogeneous equilibrium**. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

Key Takeaways

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.

Key Equations

Definition of equilibrium constant in terms of forward and reverse rate constants

Equation 15.2.5: $K = \frac{k_f}{k_r}$

Equilibrium constant expression (law of mass action)

Equation 15.2.7: <$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$

Equilibrium constant expression for reactions involving gases using partial pressures

Equation 15.2.1617: $K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$

Relationship between K_p and K

Equation 15.2.18: $K_p = K\,(RT)^{\Delta n}$

Conceptual Problems

1. For an equilibrium reaction, what effect does reversing the reactants and products have on the value of the equilibrium constant?

2. Which of the following equilibriums are homogeneous and which are heterogeneous?

    1. $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$
    2. $C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)}$
    3. $\mathrm{H_2C{=}CH_{2(g)}} + H_{2(g)} \rightleftharpoons C_2H_{6(g)}$
    4. $2Hg_{(l)} + O_{2(g)} \rightleftharpoons 2HgO_{(s)}$

3. Classify each equilibrium system as either homogeneous or heterogeneous.

1. $NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$
2. $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$
3. $2Mg_{(s)} + O_{2(g)} \rightleftharpoons 2MgO_{(s)}$
4. $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

4. If an equilibrium reaction is endothermic, what happens to the equilibrium constant if the temperature of the reaction is increased? if the temperature is decreased?

5. Industrial production of NO by the reaction $\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2NO(g)}$ is carried out at elevated temperatures to drive the reaction toward the formation of product. After sufficient product has formed, the reaction mixture is quickly cooled. Why?

6. How would you differentiate between a system that has reached chemical equilibrium and one that is reacting so slowly that changes in concentration are difficult to observe?

7. What is the relationship between the equilibrium constant, the concentration of each component of the system, and the rate constants for the forward and reverse reactions?

8. Write the equilibrium constant expressions for *K* and K_p for each reaction.

   1. $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$
   2. $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$
   3. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$

9. Write the equilibrium constant expressions for *K* and K_p as appropriate for each reaction.

   1. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$
   2. $\frac{1}{2}H_{2(g)} + 12I_{2(g)} \rightleftharpoons HI_{(g)}$
   3. $cis - stilbene_{(soln)} \rightleftharpoons trans - stilbene_{(soln)}$

10. Why is it incorrect to state that pure liquids, pure solids, and solvents are not part of an equilibrium constant expression?

11. Write the equilibrium constant expressions for *K* and K_p for each equilibrium reaction.

    1. $2S_{(s)} + 3O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
    2. $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$
    3. $2ZnS_{(s)} + 3O_{2(g)} \rightleftharpoons 2ZnO_{(s)} + 2SO_{2(g)}$

12. Write the equilibrium constant expressions for *K* and K_p for each equilibrium reaction.

    1. $2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + O_{2(g)}$
    2. $H_{2(g)} + I_{2(s)} \rightleftharpoons 2HI_{(g)}$
    3. $NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$

13. At room temperature, the equilibrium constant for the reaction $\mathrm{2A(g) \rightleftharpoons B(g)}$ is 1. What does this indicate about the concentrations of A and B at equilibrium? Would you expect *K* and K_p to vary significantly from each other? If so, how would their difference be affected by temperature?

14. For a certain series of reactions, if $[OH^-][HCO_3^-]/[CO_3^{2-}] = K_1$ and $[OH^-][H_2CO_3]/[HCO_3^-] = K_2$, what is the equilibrium constant expression for the overall reaction? Write the overall equilibrium equation.

15. In the equation for an enzymatic reaction, ES represents the complex formed between the substrate S and the enzyme protein E. In the final step of the following oxidation reaction, the product P dissociates from the ESO_2 complex, which regenerates the active enzyme:

$$E + S \rightleftharpoons ES \qquad K_1 \tag{10.3.4}$$

$$ES + O_2 \rightleftharpoons ESO_2 \qquad K_2 \tag{10.3.5}$$

$$ESO_2 \rightleftharpoons E + P \qquad K_3 \tag{10.3.6}$$

Give the overall reaction equation and show that $K = K_1 \times K_2 \times K_3$.

Answers

1. The equilibrium constant for the reaction written in reverse: $K' = 1/K$.
2.
3. Each system is heterogeneous.
4.
5. Rapid cooling “quenches” the reaction mixture and prevents the system from reverting to the low-temperature equilibrium composition that favors the reactants.
6.
7. \(K=\dfrac{k_f}{k_r}\;\;\; K=\dfrac{[C]^c[D]^d}{[A]^a[B]^b}\)
8.
9.
    1. $K = \dfrac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_p = \dfrac{(P_{N_2O})^2}{(P_{NO})^2(P_{O_2}})$
    2. $K = \dfrac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} \qquad K_p = \dfrac{P_{HI}}{(P_{H_2})^{1/2}(P_{I_2})}$
    3. $K = \dfrac{[\text{trans-stilbene}]}{[\text{cis-stilbene}]}$
10.
11.
    1. $K = \dfrac{[SO_3]^2}{[O_2]^3} \qquad K_p = \dfrac{(P_{SO_3})^2}{(P_{O_2})^3}$
    2. $K = \dfrac{[CO]^2}{[CO_2]} \qquad K_p = \dfrac{(P_{CO})^2}{P_{CO_2}}$
    3. $K = \dfrac{[SO_2]^2}{[O_2]^3} \qquad K_p = \dfrac{(P_{SO_2})^2}{(P_{O_2})^3}$
12.
13. At equilibrium,

$$[A] = \sqrt{B} \text{ and } \Delta n = -1 \text{ so } K_p = K(RT)^{\Delta n} = \frac{K}{RT}$$

    the difference increases as T increases.

14.
15.

Numerical Problems

1. Explain what each of the following values for K tells you about the relative concentrations of the reactants versus the products in a given equilibrium reaction: $K = 0.892$; $K = 3.25 \times 10^8$; $K = 5.26 \times 10^{-11}$. Are products or reactants favored at equilibrium?
2. Write the equilibrium constant expression for each reaction. Are these equilibrium constant expressions equivalent? Explain.
    1. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
    2. $\frac{1}{2}N_2O_{4(g)} \rightleftharpoons NO_{2(g)}$
3. Write the equilibrium constant expression for each reaction.
    1. $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$
    2. $\frac{1}{3}N_{2(g)} + H_{2(g)} \rightleftharpoons \frac{2}{3}NH_{3(g)}$

How are these two expressions mathematically related to the equilibrium constant expression for

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}?$$

4. Write an equilibrium constant expression for each reaction.

    1. $C_{(s)} + 2H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 2H_{2(g)}$
    2. $SbCl_{3(g)} + Cl_{2(g)} \rightleftharpoons SbCl_{5(g)}$
    3. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$

5. Give an equilibrium constant expression for each reaction.

    1. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$
    2. $\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)}$
    3. $CaCO_{3(s)} + 2HOCl_{(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OCl^{-}_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

6. Calculate K and K_p for each reaction.

    1. $2NOBr_{(g)} \rightleftharpoons 2NO_{(g)} + Br_{(g)}$ at 727°C, the equilibrium concentration of NO is 1.29 M, Br_2 is 10.52 M, and NOBr is 0.423 M.
    2. $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$: at 1200 K, a 2.00 L vessel at equilibrium has partial pressures of 93.5 atm CO_2 and 76.8 atm CO, and the vessel contains 3.55 g of carbon.

7. Calculate K and K_p for each reaction.

    1. $N_2O4_{(g)} \rightleftharpoons 2NO_{2(g)}$: at the equilibrium temperature of –40°C, a 0.150 M sample of N_2O_4 undergoes a decomposition of 0.456%.
    2. $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$: an equilibrium is reached at 227°C in a 15.5 L reaction vessel with a total pressure of 6.71 × 10^2 atm. It is found to contain 37.8 g of hydrogen gas, 457.7 g of carbon monoxide, and 7193 g of methanol.

8. Determine K and K_p (where applicable) for each reaction.

    1. $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$: at 1065°C, an equilibrium mixture consists of 1.00×10^{-3} M H_2, 1.20×10^{-3} M S_2, and 3.32×10^{-3} M H_2S.
    2. $Ba(OH)_{2(s)} \rightleftharpoons 2OH^{-}_{(aq)} + Ba^{2+}_{(aq)}$: at 25°C, a 250 mL beaker contains 0.330 mol of barium hydroxide in equilibrium with 0.0267 mol of barium ions and 0.0534 mol of hydroxide ions.

9. Determine K and K_p for each reaction.

    1. $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$: at 500 K, a 24.3 mM sample of $NOCl$ has decomposed, leaving an equilibrium mixture that contains 72.7% of the original amount of $NOCl$.
    2. $Cl_{2(g)} + PCl_{3(g)} \rightleftharpoons PCl_{5(g)}$: at 250°C, a 500 mL reaction vessel contains 16.9 g of Cl_2 gas, 0.500 g of PCl_3, and 10.2 g of PCl_5 at equilibrium.

10. The equilibrium constant expression for a reaction is $[CO_2]^2/[SO_2]^2[O_2]$. What is the balanced chemical equation for the overall reaction if one of the reactants is Na_2CO_3(s)?

11. The equilibrium constant expression for a reaction is $[NO][H_2O]^{3/2}/[NH_3][O_2]^{5/4}$. What is the balanced chemical equation for the overall reaction?

12. Given $K = k_f/k_r$, what happens to the magnitude of the equilibrium constant if the reaction rate of the forward reaction is doubled? What happens if the reaction rate of the reverse reaction for the overall reaction is decreased by a factor of 3?

13. The value of the equilibrium constant for

$$2H_{2(g)} + S_{2(g)} \rightleftharpoons 2H_2S_{(g)}$$

is 1.08 × 10^7 at 700°C. What is the value of the equilibrium constant for the following related reactions?

1. $H_{2(g)} + 12S_{2(g)} \rightleftharpoons H_2S_{(g)}$
2. $4H_{2(g)} + 2S_{2(g)} \rightleftharpoons 4H_2S_{(g)}$
3. $H_2S_{(g)} \rightleftharpoons H_{2(g)} + 12S_{2(g)}$

Answers

1. K = 0.892: the concentrations of the products and the reactants are approximately equal at equilibrium so neither is favored; K = 3.25 × 10^{8}: the ratio of the concentration of the products to the reactants at equilibrium is very large so the formation of products is favored; K = 5.26 × 10^{-11}: the ratio of the concentration of the products to the reactants at equilibrium is very small so the formation of products is not favored.
2.
3.
   1. $K' = \dfrac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$
   2. $K'' = \dfrac{[NH_3]^{2/3}}{[N_2]^{1/3}[H_2]} \qquad K = \dfrac{[NH_3]^2}{[N_2][H_2]^3} \qquad K' = K^{1/2}, \text{ and} K'' = K^{1/3}$
4.
5.
   1. $K = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$
   2. $K = \dfrac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}}$
   3. $K = \dfrac{[Ca^{2+}][OCl^-]^2[P_{CO_2}]}{[HOCl]^2}$
6.
7.
   1. $K = 1.25 \times 10^{-5} \qquad K_p = 2.39 \times 10^{-4}$
   2. $K = 9.43 \qquad K_p = 5.60 \times 10^{-3}$
8.
9.
   1. $K = \dfrac{[Cl_2][NO]^2}{[NOCl]^2} = 4.59 \times 10^{-4} \qquad K_p = 1.88 \times 10^{-2}$
   2. $K = \dfrac{[PCl_5]}{[PCl_3][Cl_2]} = 28.3 \qquad K_p = 0.658$
10.
11. $NH_3 + \frac{5}{4}O_2 \rightleftharpoons NO + \frac{3}{2}H_2O$, which can also be written as follows:

$$4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)} \tag{10.3.7}$$

12.
13.
    1. 3.29 × 10^{3}
    2. 1.17 × 10^{14}
    3. 3.04 × 10^{-4}

- Anonymous

Modified by Joshua B. Halpern

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10.4: Solving Equilibrium Problems

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Determine the equilibrium composition of a mixture from a balanced chemical equation and initial amounts.

There are two fundamental kinds of equilibrium problems: (1) those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and (2) those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

We saw in the exercise in Example 6 in Section 15.2 that the equilibrium constant for the decomposition of $CaCO_3$(s) to CaO(s) and CO_2(g) is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is 2.5×10^{-3} M. Thus K at 800°C is 2.5×10^{-3}. (Remember that equilibrium constants are unitless.)



A more complex example of this type of problem is the conversion of *n*-butane, an additive used to increase the volatility of gasoline, to isobutane (2-methylpropane). This reaction can be written as follows:

$$n-butane\,(g) \rightleftharpoons isobutane\,(g)$$

and the equilibrium constant K = [isobutane]/[*n*-butane]. At equilibrium, a mixture of *n*-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M *n*-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{isobutane}{n-butane} = \frac{0.041\ \cancel{M}}{0.016\ \cancel{M}} = 2.6$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 15.3.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained 5.0

× 10^{-2} M SO_3, 3.5 × 10^{-3} M O_2, and 3.0 × 10^{-3} M SO_2. Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy:

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution:

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(5.0 \times 10^{-2}\right)^2}{\left(3.0 \times 10^{-3}\right)^2\left(3.5 \times 10^{-3}\right)} = 7.9 \times 10^4$$

To solve for K_p, we use Equation 15.2.17, where $\Delta n = 2 - 3 = -1$:

$$\begin{aligned} K_p &= K(RT)^{\Delta n} \\ &= 7.9 \times 10^4 \left[\left(0.082606\ L \cdot atm/mol \cdot \cancel{K}\right)\left(800\ \cancel{K}\right)\right] \\ &= 1.2 \times 10^3 \end{aligned}$$

Exercise

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained 1.37 × 10^{-2} M HI, 6.47 × 10^{-3} M H_2, and 5.94 × 10^{-4} M I_2. Calculate K and K_p for this reaction.

Answer: K = 48.8; K_p = 48.8

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example 9 shows one way to do this.

Example 15.3.2

A 1.00 mol sample of NOCl was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of NOCl to NO and Cl_2 is as follows:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).

B Calculate all possible initial concentrations from the data given and insert them in the table.

C Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.

D Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution:

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO_2]^2\,[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of NOCl, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

2NOCl(g) ⇌ 2NO(g) + Cl_2			
	[NOCl]	[NO]	[Cl_2]
initial			
change			
final			

B Initially, the system contains 1.00 mol of NOCl in a 2.00 L container. Thus $[NOCl]_i$ = 1.00 mol/2.00 L = 0.500 M. The initial concentrations of NO and Cl_2 are 0 M because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f$ = 0.056 mol/2.00 L = 0.028 M. We insert these values into the following table:

2NOCl(g) ⇌ 2NO(g) + Cl_2			
	[NOCl]	[NO]	[Cl_2]
initial	0.500	0	0
change			
final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$\Delta[Cl_2]$ = [0.028 M (final) − 0.00 M (initial)] = +0.028 M

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta\,[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ \ M$$

Similarly, 2 mol of NOCl are consumed for every 1 mol of Cl_2 produced, so the change in the NOCl concentration is as follows:

$$\Delta\,[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ \ M$$

We insert these values into our table:

2NOCl(g) ⇌ 2NO(g) + Cl_2			
	[NOCl]	[NO]	[Cl_2]
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final			0.028

D We sum the numbers in the [NOCl] and [NO] columns to obtain the final concentrations of NO and NOCl:

$[NO]_f$ = 0.000 M + 0.056 M = 0.056 M $[NOCl]_f$ = 0.500 M + (−0.056 M) = 0.444 M

We can now complete the table:

2NOCl(g) ⇌ 2NO(g) + Cl_2			
	[NOCl]	[NO]	[Cl_2]
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO_2]^2\,[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2\,(0.028)}{0.444}^2 = 4.5 \times 10^{-4}$$

Exercise

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting 0.1248 M H_2 and 0.0416 M N_2 at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction N_2 + 3 H_2 ⇌ 2NH_3at this temperature? What is K_p?

Answer: K = 0.105; K_p = 2.61 × 10^{-5}



The original laboratory apparatus designed by Fritz Haber and Robert Le Rossignol in 1908 for synthesizing ammonia from its elements. A metal catalyst bed, where ammonia was produced, is in the large cylinder at the left. The Haber-Bosch process used for the industrial production of ammonia uses essentially the same process and components but on a much larger scale. Unfortunately, Haber's process enabled Germany to prolong World War I when German supplies of nitrogen compounds, which were used for explosives, had been exhausted in 1914.

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of *n*-butane to isobutane (Equation 15.26), for which $K = 2.6$ at 25°C. If we begin with a 1.00 M sample of *n*-butane, we can determine the concentration of *n*-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 9.

nbutane(g) ⇌ isobutane(g)		
	[*n*-Butane]	[Isobutane]
initial		
change		
final		

The initial concentrations of the reactant and product are both known: $[n\text{-butane}]_i = 1.00$ M and $[\text{isobutane}]_i = 0$ M. We need to calculate the equilibrium concentrations of both *n*-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the *change* in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as $+x$, then the change in the concentration of *n*-butane is $\Delta[n\text{-butane}] = -x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of *n*-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

nbutane(g) ⇌ isobutane(g)		
	[*n*-Butane]	[Isobutane]
initial	1.00	0
change	$-x$	$+x$
final	$(1.00 - x)$	$(0 + x) = x$

Substituting the expressions for the final concentrations of *n*-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[isobutane]}{[n-butane]} = \frac{x}{1.00 - x} = 2.6$$

Rearranging and solving for *x*,

$$\begin{gathered} x = 2.6\,(1.00 - x) = 2.6 - 2.6x \\ x + 2.6x = 2.6 \\ x = 0.72 \end{gathered}$$

We obtain the final concentrations by substituting this *x* value into the expressions for the final concentrations of *n*-butane and isobutane listed in the table:

$[n\text{-butane}]_f = (1.00 - x)$ M = (1.00 − 0.72) M = 0.28 M $[\text{isobutane}]_f = (0.00 + x)$ M = (0.00 + 0.72) M = 0.72 M

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same *K* that we used in the calculation:

$$K = \frac{[isobutane]}{[n-butane]} = \frac{0.72 \cancel{M}}{0.28 \cancel{M}} = 2.6$$

This is the same *K* we were given, so we can be confident of our results.

Example 10 illustrates a common type of equilibrium problem that you are likely to encounter.

Example 15.3.3

The *water–gas shift reaction* is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:

$$H_2\,(g) + CO_2\,(g) \rightleftharpoons H_2O\,(g) + CO\,(g)$$

K = 0.106 at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, *K*, and initial concentrations

Asked for: final concentrations

Strategy:

A Construct a table showing what is known and what needs to be calculated. Define *x* as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of *x*. From the values in the table, calculate the final concentrations.

B Write the equilibrium equation for the reaction. Substitute appropriate values from the table to obtain *x*.

C Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain *K*.

Solution:

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i$ = 0.0150 M. Just as before, we will focus on the *change* in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as *x*, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of *x*. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$H_2(g) + CO_2(g) \diamondsuit H_2O(g) + CO(g)$				
	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
initial	0.0150	0.0150	0	0
change	$-x$	$-x$	$+x$	$+x$
final	(0.0150 – *x*)	(0.0150 – *x*)	*x*	*x*

B We can now use the equilibrium equation and the given *K* to solve for *x*:

$$K = \frac{[H_2O]\,[CO]}{[H_2]\,[CO_2]} = \frac{(x)\,(x)}{(0.0150-x)\,(0.0150-x)} = \frac{x^2}{(0.0150-x)^2} = 0.160$$

We could solve this equation with the quadratic formula, but it is far easier to solve for *x* by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150-x)^2} = \left(\frac{x}{0.0150-x}\right)^2 = 0.106$$

(The quadratic formula is presented in Essential Skills 7 in Section 15.7 .) Taking the square root of the middle and right terms,

$$\frac{x^2}{(0.0150-x)^2} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this *K* is the same as the value given in the problem, so our answer is confirmed.

Exercise

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

K = 54 at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer: $[HI]_f$ = 0.270 M; $[H_2]_f = [I_2]_f$ = 0.037 M

In Example 10, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example 11.

Example 15.3.4

In the water–gas shift reaction shown in Example 10, a sample containing 0.632 M CO_2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, *K* = 0.106. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and *K*

Asked for: composition of reaction mixture at equilibrium

Strategy:

A Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (*x*) and the final concentrations.

B Write the equilibrium constant expression for the reaction. Substitute the known *K* value and the final concentrations to solve for *x*.

C Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain *K*.

Solution:

A $[CO_2]_i$ = 0.632 M and $[H_2]_i$ = 0.570 M. Again, *x* is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H_2O, so $\Delta[CO] = +x$. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \tag{10.4.1}$$

	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
initial	0.570	0.632	0	0
change	$-x$	$-x$	$+x$	$+x$
final	(0.570 − *x*)	(0.632 − *x*)	*x*	*x*

B We can now use the equilibrium equation and the known *K* value to solve for *x*:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 10, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.20x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148$ M, and $\Delta[H_2] = \Delta[CO_2] = -0.148$ M.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f[= [H_2]_i + \Delta[H_2] = 0.570\ M - 0.148\ M = 0.422M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = 0.632\ M - 0.148\ M = 0.484M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = 0\ M + 0.148\ M = 0.148\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = 0M + 0.148\ M = 0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because *K* is essentially the same as the value given in the problem, our calculations are confirmed.

Exercise

The exercise in Example 8 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer: $[HI]_f = 0.0882$ M; $[H_2]_f = 0.156$ M; $[I_2]_f = 9.2 \times 10^{-4}$ M

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \le 10^{-3}$) or very large ($K \ge 10^{3}$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 12.

Example 15.3.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

$K_p = 2.0 \times 10^{-31}$ at 25°C. What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm, P{N_2} = 0.78 atm and P{O_2} = 0.21 atm

Given: balanced equilibrium equation and values of K_p, P{O_2} and P{N_2}

Asked for: partial pressure of NO

Strategy:

A Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.

B Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (x).

C Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution:

A Because we are given K_p and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in the partial pressure of O_2 and of N_2 is $-x$ because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \tag{10.4.2}$$

	P{N_2}	P{N_2}	P{NO}
initial P	0.78	0.21	0
change in P	$-x$	$-x$	$+2x$
final P	$(0.78 - x)$	$(0.21 - x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very

small; therefore, the *x* value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, (0.78 – *x*) = 0.78 and (0.21 – *x*) = 0.21. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x^{=}9.1 \times 10^{-17}$$

C Substituting this value of *x* into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x \ \ atm = 1.8 \times 10^{-16} \ \ atm$
- $P_{N_2} = (0.78 - x) \ \ atm = 0.78 \ \ atm$
- $P_{O_2} = (0.21 - x) \ \ atm = 0.21 \ \ atm$

From these calculations, we see that our initial assumption regarding *x* was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if *x* is less than about 5% of the total, or $10^{-3} > K > 10^{3}$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

Exercise

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

$K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere $P(O_2)$ =0.21 atm?

Answer: 4.8×10^{-31} atm

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^{3}$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the *products* side of the reaction rather than the reactants side. This approach is illustrated in Example 13.

Example 15.3.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

$K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, *K*, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.

B Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for *x* (the change in concentration).

C Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 12. If we define *–x* as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is *+x*. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)} \tag{10.4.3}$$

	[H₂]	[C₂H₄]	[C₂H₆]
initial	0.200	0.155	0
assuming 100% reaction	0.045	0	0.155
change	*+x*	*+x*	*–x*
final	(0.045 + *x*)	(0 + *x*)	(0.155 – *x*)

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus *x* is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified [(0.045 + *x*) = 0.045 and (0.155 – *x*) = 0.155] as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small *x* value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x) \;\; M = 0.155 \;\; M$
- $[C_2H_4]_f = x \;\; M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x) \;\; M = 0.045 \;\; M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This *K* value agrees with our initial value at the beginning of the example.

Exercise

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

K_p = 4.0 × 10^{31} at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer:

- $[H_2]_f = 4.8 \times 10^{-32}\ \ M$
- $[Cl_2]_f = 0.135\ \ M$
- $[HCl]_f = 0.514\ \ M$

Summary

When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

Key Takeaway

- Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture.

Conceptual Problems

1. Describe how to determine the magnitude of the equilibrium constant for a reaction when not all concentrations of the substances are known.

2. Calculations involving systems with very small or very large equilibrium constants can be dramatically simplified by making certain assumptions about the concentrations of products and reactants. What are these assumptions when *K* is (a) very large and (b) very small? Illustrate this technique using the system A + 2B ⇌ C for which you are to calculate the concentration of the product at equilibrium starting with only A and B. Under what circumstances should simplifying assumptions not be used?

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 7 (Section 15.7) before proceeding to the Numerical Problems.

1. In the equilibrium reaction A + B ⇌C, what happens to *K* if the concentrations of the reactants are doubled? tripled? Can the same be said about the equilibrium reaction A ⇌B + C?

2. The following table shows the reported values of the equilibrium P{O_2} at three temperatures for the reaction Ag_2O(s) ⇌ 2 Ag(s) + 1/2 O_2(g) for which $\Delta H°$ = 31 kJ/mol. Are these data consistent with what you would expect to occur? Why or why not?

T (°C)	P(O_2) mm Hg
150	182

T (°C)	$P(O_2)$ mm Hg
184	143
191	126

3. Given the equilibrium system $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$, what happens to K_p if the initial pressure of N_2O_4 is doubled? If K_p is 1.7×10^{-1} at 2300°C, and the system initially contains 100% N_2O_4 at a pressure of 2.6×10^{2} atm, what is the equilibrium pressure of each component?

4. At 430°C, 4.20 mol of HI in a 9.60 L reaction vessel reaches equilibrium according to the following equation: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ At equilibrium, $[H_2] = 0.047$ M and $[HI] = 0.345$ M. What are K and K_p for this reaction?

5. Methanol, a liquid used as an automobile fuel additive, is commercially produced from carbon monoxide and hydrogen at 300°C according to the following reaction: $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ and $K_p = 1.3 \times 10^{-4}$. If 56.0 g of CO is mixed with excess hydrogen in a 250 mL flask at this temperature, and the hydrogen pressure is continuously maintained at 100 atm, what would be the maximum percent yield of methanol? What pressure of hydrogen would be required to obtain a minimum yield of methanol of 95% under these conditions?

6. Starting with pure A, if the total equilibrium pressure is 0.969 atm for the reactionA(s $\rightleftharpoons$ 2 B(g) + C(g), what is K_p?

7. The decomposition of ammonium carbamate to NH_3 and CO_2 at 40°C is written as $NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2$ If the partial pressure of NH_3 at equilibrium is 0.242 atm, what is the equilibrium partial pressure of CO_2? What is the total gas pressure of the system? What is K_p?

8. At 375 K, K_p for the reaction $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2g)$ is 2.4, with pressures expressed in atmospheres. At 303 K, K_p is 2.9×10^{-2}.

    1. What is K for the reaction at each temperature?
    2. If a sample at 375 K has 0.100 M Cl_2 and 0.200 M SO_2 at equilibrium, what is the concentration of SO_2Cl_2?
    3. If the sample given in part b is cooled to 303 K, what is the pressure inside the bulb?

9. For the gas-phase reaction $aA \rightleftharpoons bB$, show that $K_p = K(RT)^{\Delta n}$ assuming ideal gas behavior.

10. For the gas-phase reaction $I_2 \rightleftharpoons 2I$, show that the total pressure is related to the equilibrium pressure by the following equation:

$$P_T = \sqrt{K_p P_{I_2}} + P_{I_2}$$

11. Experimental data on the system Br2(l) $\rightleftharpoons$ $Br_2(aq)$ are given in the following table. Graph $[Br_2]$ versus moles of $Br_2(l)$ present; then write the equilibrium constant expression and determine K.

Grams Br_2 in 100 mL Water	$[Br_2]$ (M)
1.0	0.0626
2.5	0.156
3.0	0.188
4.0	0.219
4.5	0.219

12. Data accumulated for the reaction n-butane(g) $\rightleftharpoons$ isobutane(g) at equilibrium are shown in the following table. What is the equilibrium constant for this conversion? If 1 mol of *n*-butane is allowed to equilibrate under the same reaction conditions, what is the final number of moles of *n*-butane and isobutane?

Moles *n*-butane	Moles Isobutane
0.5	1.25
1.0	2.5
1.50	3.75

13. Solid ammonium carbamate ($NH_4CO_2NH_2$) dissociates completely to ammonia and carbon dioxide when it vaporizes:

$$NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$$

At 25°C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium partial pressure of each gas? What is K_p? If the concentration of CO_2 is doubled and then equilibrates to its initial equilibrium partial pressure $+x$ atm, what change in the NH_3 concentration is necessary for the system to restore equilibrium?

14. The equilibrium constant for the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ is $K_p = 2.2 \times 10^{-10}$ at 100°C. If the initial concentration of $COCl_2$ is 3.05×10^{-3} M, what is the partial pressure of each gas at equilibrium at 100°C? What assumption can be made to simplify your calculations?

15. Aqueous dilution of IO_4^- results in the following reaction:

$$IO^-_{4(aq)} + 2H_2O_{(l)} \rightleftharpoons H_4IO^-_{6(aq)}$$

and $K = 3.5 \times 10^{-2}$. If you begin with 50 mL of a 0.896 M solution of IO_4^- that is diluted to 250 mL with water, how many moles of $H_4IO_6^-$ are formed at equilibrium?

16. Iodine and bromine react to form IBr, which then sublimes. At 184.4°C, the overall reaction proceeds according to the following equation:

$$I_{2(g)} + Br_{2(g)} \rightleftharpoons 2IBr_{(g)}$$

$K_p = 1.2 \times 10^2$. If you begin the reaction with 7.4 g of I_2 vapor and 6.3 g of Br_2 vapor in a 1.00 L container, what is the concentration of IBr(g) at equilibrium? What is the partial pressure of each gas at equilibrium? What is the total pressure of the system?

17. For the reaction

$$C_{(s)} + 12N_{2(g)} + \frac{5}{2}H_{2(g)} \rightleftharpoons CH3NH2(g)$$

$K = 1.8 \times 10^{-6}$. If you begin the reaction with 1.0 mol of N_2, 2.0 mol of H_2, and sufficient C(s) in a 2.00 L container, what are the concentrations of N_2 and CH_3NH_2 at equilibrium? What happens to K if the concentration of H_2 is doubled?

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10.5: Non-equilibrium Conditions

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Evaluate the direction of reaction (left to right, right to left, or at equilibrium) based on the reaction quotient.
- Predict how stresses in concentration, temperature, and pressure affect a mixture's equilibrium composition.

Knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a quantity called the reaction quotient (Q)A quantity derived from a set of values measured at any time during the reaction of any mixture of reactants and products, regardless of whether the system is at equilibrium: Q = $[C]^c[D]^d/[A]^a[B]^b$ for the general balanced chemical equation aA + bB ⇳ cC + dD. The expression for the reaction quotient has precisely the same form as the equilibrium constant expression, except that Q may be derived from a set of values measured at *any* time during the reaction of *any* mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightarrow cC + dD$$

the reaction quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.4.1}$$

The reaction quotient Q_p analogous to K_p, can be written for any reaction that involves gases by using the partial pressures of the components.

To understand how information is obtained using a reaction quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \tag{15.4.2}$$

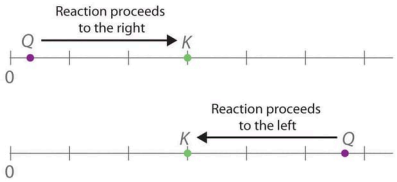
The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Experiment	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$Q = [NO_2]^2/[N_2O_4]$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$

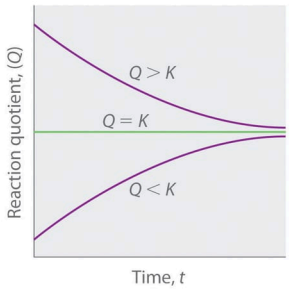
Experiment	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$Q = [NO_2]^2/[N_2O_4]$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K. If $Q = K$, for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is *less* than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is *greater* than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure 15.4.1



(a) Q versus K, t_0 to t



(b) Q versus K, t_0 to t_∞

Figure 15.4.1 Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

Note the Pattern

If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.

Example 15.4.1

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a *steam-reforming* reaction:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0×10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Given: balanced chemical equation, *K*, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A Calculate the molar concentrations of the reactants and the products.

B Use Equation 15.4.1 to determine Q. Compare *Q* and *K* to determine in which direction the reaction will proceed.

Solution:

A We must first find the initial concentrations of the substances present. For example, we have 1.2 × 10^{-2} mol of CH_4 in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2} mol}{2.0\ L} = 6.0 \times 10^{-3} M$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

B We now compute *Q* and compare it with *K*:

$$Q = \frac{[CO][H_2]^3}{[CH_4][H_2O} = \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} = 9.0 \times 10^{-6}$$

Because *K* = 2.4 × 10^{-4}, we see that *Q* < *K*. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4.

Exercise

In the water–gas shift reaction introduced in Example 10, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

K = 0.64 at 900 K. If 0.010 mol of both CO and H_2O, 0.0080 mol of CO_2, and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer: *Q* = 0.96 (*Q* > *K*), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which *Q* = *K*. Such a graph allows us to predict what will happen to a reaction when conditions change so that *Q* no longer equals *K*, such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$PbCO_{3(s)} \rightleftharpoons PbO_{(s)} + CO_{2(g)} \tag{15.4.3}$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply *K* = [CO_2]. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 15.4.2, which shows a plot of [CO_2] versus the amount

of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to *K*. Thus the left portion of the graph represents a system that is *not* at equilibrium because it contains only CO_2(g) and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line. Thus any CO_2 concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled *A* in Figure 15.4.2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of CO_2 ($Q > K$). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting CO_2 with solid PbO to form solid $PbCO_3$. Thus the reaction in Equation 15.4.3 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled *B* in Figure 15.4.2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of CO_2 ($Q < K$). To reach equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form CO_2 and solid PbO. The reaction in Equation 15.4.2 will therefore proceed to the right as written, until $[CO_2] = K$.

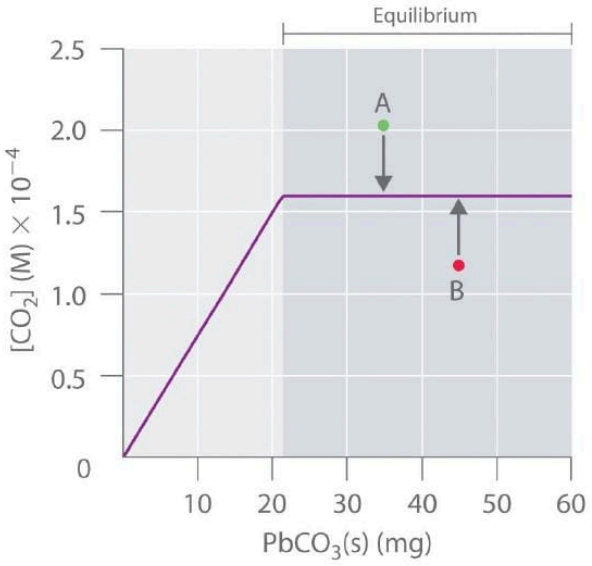


Figure 15.4.2 The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ **Added** Initially the concentration of CO_2(g) increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to CO_2(g) and solid PbO. Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)} \tag{15.4.4}$$

and the equilibrium constant *K* is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then $[H_2]$ must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of *K* (Figure 15.4.3). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 15.4.4 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point *A* in Figure 15.4.3 lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture ($Q < K$). Thus the reaction in Equation 15.4.3 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point *B* in Figure 15.4.3 lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction in Equation 15.4.3 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

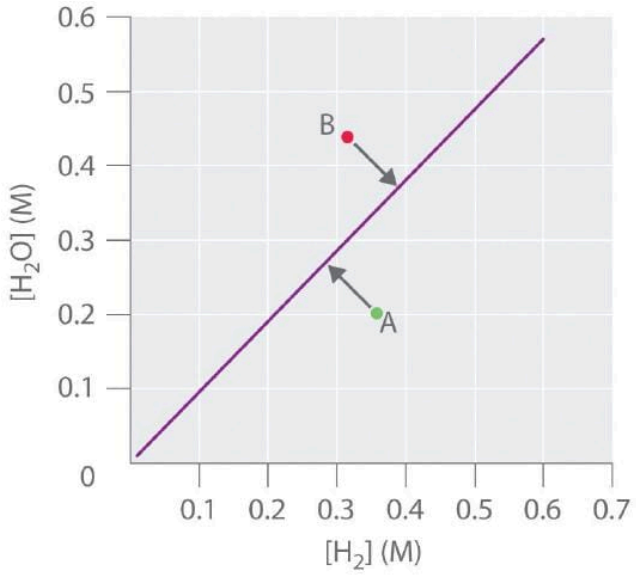


Figure 15.4.3 The Concentration of Water Vapor versus the Concentration of Hydrogen for the CdO(s) + H_2(g) ⇄ Cd(s) + H_2O(g) System at **Equilibrium**For any equilibrium concentration of H_2O(g), there is only one equilibrium concentration of H_2(g). Because the magnitudes of the two concentrations are directly proportional, a large [H_2O] at equilibrium requires a large [H_2] and vice versa. In this case, the slope of the line is equal to *K*.

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)} \tag{15.4.5}$$

For this system, *K* is equal to the product of the concentrations of the two products: [NH_3][HI]. If we double the concentration of NH_3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 15.4.4. As a result, for a given concentration of either HI or NH_3, only a *single* equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which [NH_3] = [HI] = $K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point *A* in Figure 15.4.4) corresponds to *Q* < *K*, and the reaction in Equation 15.4.4 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point *B* in Figure 15.4.3) corresponds to *Q* > *K*, and the reaction in Equation 15.4.4 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

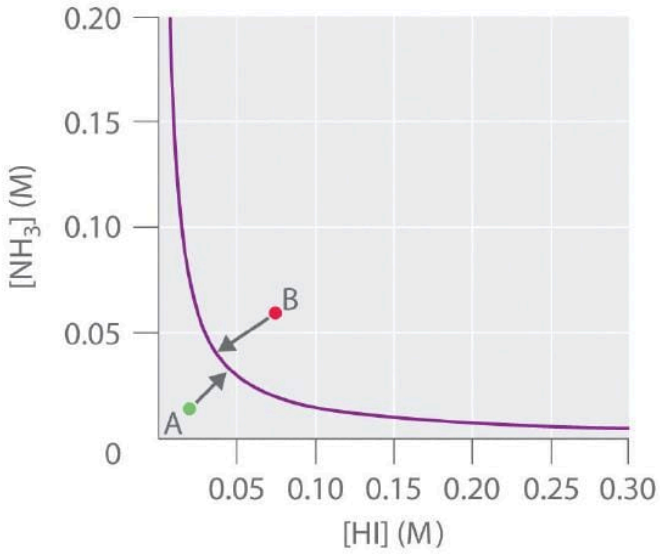


Figure 15.4.4 The Concentration of $NH_3(g)$ versus the Concentration of HI(g) for the $NH_4I(s) \diamond NH_3(g) + HI(g)$ System at **Equilibrium**Only one equilibrium concentration of $NH_3(g)$ is possible for any given equilibrium concentration of HI(g). In this case, the two are inversely proportional. Thus a large [HI] at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.

Le Chatelier's Principle

When a system at equilibrium is perturbed in some way, the effects of the perturbation can be predicted qualitatively using Le Chatelier's principleIf a stress is applied to a system at equilibrium, the composition of the system will change to relieve the applied stress. (named after the French chemist Henri Louis Le Chatelier, 1850–1936).The name is pronounced "Luh SHOT-lee-ay." This principle can be stated as follows: *if a stress is applied to a system at equilibrium, the composition of the system will change to counteract the applied stress*. Stress occurs when any change in a system affects the magnitude of *Q* or *K*. In Equation 15.4.4, for example, increasing $[NH_3]$ produces a stress on the system that requires a decrease in [HI] for the system to return to equilibrium. As a further example, consider esters, which are one of the products of an equilibrium reaction between a carboxylic acid and an alcohol. (For more information on this type of reaction, see Section 7.5 .) Esters are responsible for the scents we associate with fruits (such as oranges and bananas), and they are also used as scents in perfumes. Applying a stress to the reaction of a carboxylic acid and an alcohol will change the composition of the system, leading to an increase or a decrease in the amount of ester produced. In Section 15.5 and Section 15.6 , we explore how chemists control reactions conditions to affect equilibrium concentrations.

Note the Pattern

In all reactions, if a stress is applied to a system at equilibrium, the composition of the system will change to counteract the applied stress (Le Chatelier's principle).

Example 15.4.2

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

1. $2HgO(s) \diamond 2Hg(l) + \mathbf{O_2(g)}$: the amount of HgO is doubled.
2. $NH_4HS(s) \diamond \mathbf{NH_3(g)} + H_2S(g)$: the concentration of H_2S is tripled.
3. ***n*-butane(g)** $\diamond$ isobutane(g): the concentration of isobutane is halved.

Given: equilibrium systems and changes

Asked for: equilibrium constant expressions and effects of changes

Strategy:

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

Solution:

1. Because HgO(s) and Hg(l) are pure substances, they do not appear in the equilibrium constant expression. Thus, for this reaction, $K = [O_2]$. The equilibrium concentration of O_2 is a constant and does not depend on the amount of HgO present. Hence adding more HgO will not affect the equilibrium concentration of O_2, so no compensatory change is necessary.
2. NH_4HS does not appear in the equilibrium constant expression because it is a solid. Thus $K = [NH_3][H_2S]$, which means that the concentrations of the products are inversely proportional. If adding H_2S triples the H_2S concentration, for example, then the NH_3 concentration must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations equals K.
3. For this reaction, K = [isobutane]/[*n*-butane], so halving the concentration of isobutane means that the *n*-butane concentration must also decrease by about half if the system is to maintain equilibrium.

Exercise

Write an equilibrium constant expression for each reaction. What must happen to the concentration of the substance in bold when the indicated change occurs if the system is to maintain equilibrium?

1. HBr(g) + NaH(s) ⇌ NaBr(s) + **H_2(g)**: the concentration of HBr is decreased by a factor of 3.
2. 6Li(s) + **N_2(g)** ⇌ $2Li_3N$(s): the amount of Li is tripled.
3. **SO_2(g)** + Cl_2(g) ⇌ SO_2Cl_2(l): the concentration of Cl_2 is doubled.

Answer

1. $K = [H_2]/[HBr]$; $[H_2]$ must decrease by about a factor of 3.
2. $K = 1/[N_2]$; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.
3. $K = 1/[SO_2][Cl_2]$; $[SO_2]$ must decrease by about half.

Summary

The **reaction quotient (*Q* or Q_p)** has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium. **Le Chatelier's principle** states that if a stress is applied to a system at equilibrium, the composition of the system will adjust to counteract the stress.

Key Takeaway

- The reaction quotient (*Q*) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction.

Key Equation

Reaction quotient

Equation 15.4.1:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{10.5.1}$$

Conceptual Problems

1. During a set of experiments, graphs were drawn of [reactants] versus [products] at equilibrium. Using Figure 15.4.4 and Figure 15.4.4 as your guides, sketch the shape of each graph using appropriate labels.

    1. $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$
    2. $2MgO_{(s)} \rightleftharpoons 2Mg_{(s)} + O_{2(g)}$
    3. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$
    4. $2PbS_{(s)} + 3O_{2(g)} \rightleftharpoons 2PbO_{(s)} + 2SO_{2(g)}$

2. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

    1. $2NaHCO_3(s) \diamondsuit Na_2CO_3(s) + CO_2(g) + \mathbf{H_2O(g)}$: $[CO_2]$ is doubled.
    2. $\mathbf{N_2F_4(g)} \diamondsuit 2NF_2(g)$: [NF] is decreased by a factor of 2.
    3. $H_2(g) + I_2(g) \diamondsuit \mathbf{2HI(g)}$: $[I_2]$ is doubled.

3. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

    1. $CS_2(g) + \mathbf{4H_2(g)} \diamondsuit CH_4(g) + 2H_2S(g)$: $[CS_2]$ is doubled.
    2. $\mathbf{PCl_5(g)} \diamondsuit PCl_3(g) + Cl_2(g)$: $[Cl_2]$ is decreased by a factor of 2.
    3. $4NH_3(g) + 5O_2(g) \diamondsuit 4NO(g) + \mathbf{6H_2O(g)}$: [NO] is doubled.

Answer

1.
2.
3.
    1. $K = \frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}$; doubling $[CS_2]$ would require decreasing $[H_2]$ by a factor of 2√4≅ 1.189.
    2. $K = \frac{[PCl_3]}{[Cl_2][PCl_5]}$; if $[Cl_2]$ is halved, $[PCl_5]$ must also be halved.
    3. $K = \frac{[NO]^4[H_2O]^6}{[NH_3][O_2]^5}$; if $[NO]$ is doubled, $[H_2O]$ is multiplied by 22/3≅1.587.

Numerical Problems

1. The data in the following table were collected at 450°C for the reaction

    $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

	Equilibrium Partial Pressure (atm)		
***P* (atm)**	**NH_3**	**N_2**	**H_2**
30 (equilibrium)	1.740	6.588	21.58
100	15.20	19.17	65.13
600	321.6	56.74	220.8

    The reaction equilibrates at a pressure of 30 atm. The pressure on the system is first increased to 100 atm and then to 600 atm. Is the system at equilibrium at each of these higher pressures? If not, in which direction will the reaction proceed to reach equilibrium?

2. For the reaction 2A ⇄ B + 3 C, *K* at 200°C is 2.0. A 6.00 L flask was used to carry out the reaction at this temperature. Given the experimental data in the following table, all at 200°C, when the data for each experiment were collected, was the reaction at equilibrium? If it was not at equilibrium, in which direction will the reaction proceed?

Experiment	A	B	C
1	2.50 M	2.50 M	2.50 M
2	1.30 atm	1.75 atm	14.15 atm
3	12.61 mol	18.72 mol	6.51 mol

3. The following two reactions are carried out at 823 K:

$$CoO_{(s)} + H_{2(g)} \rightleftharpoons Co_{(s)} + H_2O_{(g)} \text{ with } K = 67$$

$$CoO_{(s)} + CO_{(g)} \rightleftharpoons Co_{(s)} + CO_{2(g)} \text{ with } K = 490$$

   1. Write the equilibrium expression for each reaction.
   2. Calculate the partial pressure of both gaseous components at equilibrium in each reaction if a 1.00 L reaction vessel initially contains 0.316 mol of H_2 or CO plus 0.500 mol CoO.
   3. Using the information provided, calculate K_p for the following reaction: $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$
   4. Describe the shape of the graphs of [reactants] versus [products] as the amount of CoO changes.

4. Hydrogen iodide (HI) is synthesized via $H_2(g) + I_2(g) \diamondsuit 2HI(g)$, for which $K_p = 54.5$ at 425°C. Given a 2.0 L vessel containing 1.12×10^{-2} mol of H_2 and 1.8×10^{-3} mol of I_2 at equilibrium, what is the concentration of HI? Excess hydrogen is added to the vessel so that the vessel now contains 3.64×10^{-1} mol of H_2. Calculate Q and then predict the direction in which the reaction will proceed. What are the new equilibrium concentrations?

Answers

1. Not at equilibrium; in both cases, the sum of the equilibrium partial pressures is *less* than the total pressure, so the reaction will proceed to the right to decrease the pressure.

2.

3.
   1. $K = [H_2O][H_2]$; K=[CO2][CO]
   2. $P_{H_2O} = 21.0\ atm$; $P_{H_2} = 0.27\ atm$; $P_{CO_2} = 21.3\ atm$; $P_{CO} = 0.07\ atm$
   3. $K_p = 0.14$
   4. The amount of CoO has no effect on the shape of a graph of products versus reactants *as long as some solid CoO is present*.

4.

Contributors

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Modified by Joshua B. Halpern

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10.6: Factors That Affect Equilibrium

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Predict how stresses in concentration, temperature, and pressure affect a mixture's equilibrium composition.

Chemists use various strategies to increase the yield of the desired products of reactions. When synthesizing an ester, for example, how can a chemist control the reaction conditions to obtain the maximum amount of the desired product? Only three types of stresses can change the composition of an equilibrium mixture: (1) a change in the concentrations (or partial pressures) of the components by adding or removing reactants or products, (2) a change in the total pressure or volume, and (3) a change in the temperature of the system. In this section, we explore how changes in reaction conditions can affect the equilibrium composition of a system. We will explore each of these possibilities in turn.

Changes in Concentration

If we add a small volume of carbon tetrachloride (CCl_4) solvent to a flask containing crystals of iodine, we obtain a saturated solution of I_2 in CCl_4, along with undissolved crystals:

$$I_{2(s)} \rightleftharpoons I_{2(soln)} \tag{15.5.1}$$

The system reaches equilibrium, with $K = [I_2]$. If we add more CCl_4, thereby diluting the solution, Q is now less than K. Le Chatelier's principle tells us that the system will react to relieve the stress—but how? Adding solvent stressed the system by decreasing the concentration of dissolved I_2. Hence more crystals will dissolve, thereby increasing the concentration of dissolved I_2 until the system again reaches equilibrium if enough solid I_2 is available (Figure 15.5.1). By adding solvent, we drove the reaction shown in Equation 15.5.1 to the right as written.

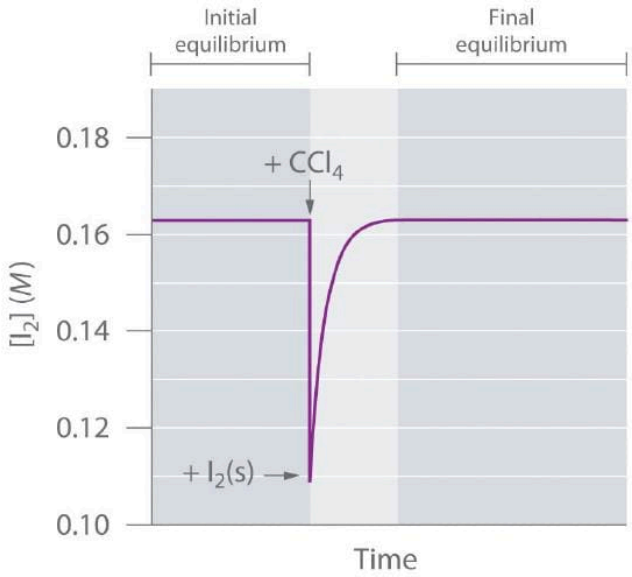


Figure 15.5.1 The Concentration of Dissolved I_2 as a Function of Time Following the Addition of More Solvent to a Saturated Solution in Contact with Excess Solid I_2 The concentration of I_2 decreases initially due to dilution but returns to its original value as long as solid I_2 is present.

We encounter a more complex system in the reaction of hydrogen and nitrogen to form ammonia:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{15.5.2}$$

The K_p for this reaction is 2.14×10^{-2} at about 540 K. Under one set of equilibrium conditions, the partial pressure of ammonia is $P(NH_3) = 0.454$ atm, that of hydrogen is $P(H_2) = 2.319$ atm, and that of nitrogen is $P(N_2) = 0.773$ atm. If an additional 1 atm of hydrogen is added to the reactor to give $P(H_2) = 3.319$ atm, how will the system respond? Because the stress is an increase in $P(H_2)$ the system must respond in some way that decreases the partial pressure of hydrogen to counteract the stress. The reaction will therefore proceed to the right as written, consuming H_2 and N_2 and forming additional NH_3. Initially, the partial pressures of H_2 and N_2 will decrease, and the partial pressure of NH_3 will increase until the system eventually reaches a new equilibrium composition, which will have a net increase in $P(H_2)$

We can confirm that this is indeed what will happen by evaluating Q_p under the new conditions and comparing its value with K_p. The equations used to evaluate K_p and Q_p have the same form: substituting the values after adding hydrogen into the expression for Q_p results in the following:

$$Q_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{(0.454)^2}{(0.773)(2.319 + 1.00)^3} = 7.29 \times 10^{-3} \tag{10.6.1}$$

Thus $Q_p < K_p$, which tells us that the ratio of products to reactants is less than at equilibrium. To reach equilibrium, the reaction must proceed to the right as written: the partial pressures of the products will increase, and the partial pressures of the reactants will decrease. Q_p will thereby increase until it equals K_p, and the system will once again be at equilibrium. Changes in the partial pressures of the various substances in the reaction mixture (Equation 15.5.2) as a function of time are shown in Figure 15.5.2.

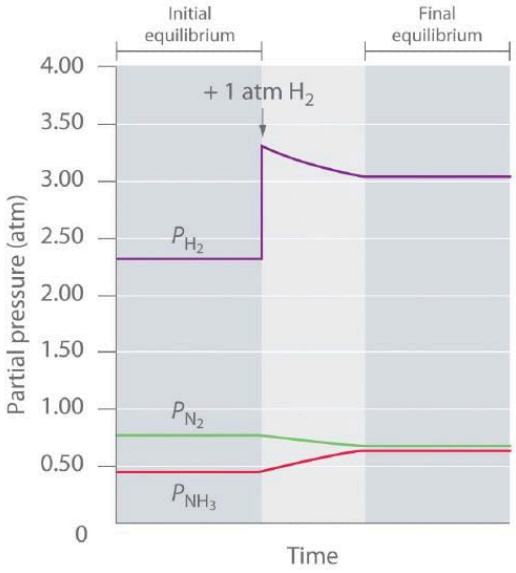


Figure 15.5.2 The Partial Pressures of H_2, N_2, and NH_3 as a Function of Time Following the Addition of More H_2 to an Equilibrium **Mixture**Some of the added hydrogen is consumed by reacting with nitrogen to produce more ammonia, allowing the system to reach a new equilibrium composition.

We can force a reaction to go essentially to completion, regardless of the magnitude of K, by continually removing one of the products from the reaction mixture. Consider, for example, the *methanation* reaction, in which hydrogen reacts with carbon monoxide to form methane and water:

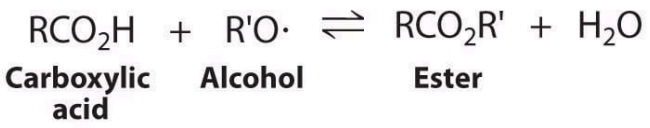
$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \tag{15.5.3}$$

This reaction is used for the industrial production of methane, whereas the reverse reaction is used for the production of H_2 (Example 14). The expression for Q has the following form:

$$Q = \frac{[CH_4][H_2O]}{[CO][H_2]^3} \tag{15.5.4}$$

Regardless of the magnitude of K, if either H_2O or CH_4 can be removed from the reaction mixture so that $[H_2O]$ or $[CH_4]$ is approximately zero, then $Q \approx 0$. In other words, when product is removed, the system is stressed ($Q << K$), and more product will form to counter the stress. Because water (bp = 100°C) is much less volatile than methane, hydrogen, or carbon monoxide (all of

which have boiling points below –100°C), passing the gaseous reaction mixture through a cold coil will cause the water vapor to condense to a liquid that can be drawn off. Continuing to remove water from the system forces the reaction to the right as the system attempts to equilibrate, thus enriching the reaction mixture in methane. This technique, referred to as *driving a reaction to completion*, can be used to force a reaction to completion even if K is relatively small. For example, esters are usually synthesized by removing water. The products of the condensation reaction are shown here. In Chapter 19, we will describe the thermodynamic basis for the change in the equilibrium position caused by changes in the concentrations of reaction components.



Example 15.5.1

For each equilibrium system, predict the effect of the indicated stress on the specified quantity.

1. $2SO_2(g) + O_2(g) \diamondsuit 2SO_3(g)$:
   (1) the effect of removing O_2 on $P(SO_2)$
   (2) the effect of removing O_2 on $P(SO_3)$
2. $CaCO_3(s) \diamondsuit CaO(s) + CO_2(g)$:
   (1) the effect of removing CO_2 on the amount of $CaCO_3$;
   (2) the effect of adding $CaCO_3$ on $P(CO_2)$

Given: balanced chemical equations and changes

Asked for: effects of indicated stresses

Strategy:

Use Q and K to predict the effect of the stress on each reaction.

Solution:

1. (1) Removing O_2 will decrease $P(O_2)$thereby decreasing the denominator in the reaction quotient and making $Q_p > K_p$. The reaction will proceed to the left as written, increasing the partial pressures of SO_2 and O_2 until Q_p once again equals K_p.
   (2) Removing O_2 will decrease $P(O_2)$ and thus increase Q_p, so the reaction will proceed to the left. The partial pressure of SO_3 will decrease.
2. K_p and Q_p are both equal to $P(CO_2)$.
   (1) Removing CO_2 from the system causes more $CaCO_3$ to react to produce CO_2, which increases $P(CO_2)$ to the partial pressure required by K_p. (2) Adding (or removing) solid $CaCO_3$ has no effect on $P(CO_2)$ because it does not appear in the expression for K_p (or Q_p).

Exercise

For each equilibrium system, predict the effect that the indicated stress will have on the specified quantity.

1. $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$:
   1. the effect of adding CO on $[H_2]$;
   2. the effect of adding CO_2 on $[H_2]$
2. $CuO_{(s)} + CO_{(g)} \rightleftharpoons Cu_{(s)} + CO_{2(g)}$:
   1. the effect of adding CO on the amount of Cu;
   2. the effect of adding CO_2 on $[CO]$

Answer

1. (1) $[H_2]$ increases; (2) $[H_2]$ decreases.

2. (1) the amount of Cu increases; (2) [CO] increases.

Changes in Total Pressure or Volume

Because liquids are relatively incompressible, changing the pressure above a liquid solution has little effect on the concentrations of dissolved substances. Consequently, changes in external pressure have very little effect on equilibrium systems that contain only solids or liquids. In contrast, because gases are highly compressible, their concentrations vary dramatically with pressure. From the ideal gas law, *PV* = *nRT*, described in Chapter 10, the concentration (*C*) of a gas is related to its pressure as follows:

$$C = \frac{n}{V} = \frac{P}{RT} \tag{15.5.5}$$

Hence the concentration of any gaseous reactant or product is directly proportional to the applied pressure (*P*) and inversely proportional to the total volume (*V*). Consequently, the equilibrium compositions of systems that contain gaseous substances are quite sensitive to changes in pressure, volume, and temperature.

These principles can be illustrated using the reversible dissociation of gaseous N_2O_4 to gaseous NO_2 (Equation 15.2.1).

$$N_2O_4 \rightleftharpoons 2NO_2 \tag{15.1.1}$$

The syringe shown in Figure 15.5.3 initially contains an equilibrium mixture of colorless N_2O_4 and red-brown NO_2. Decreasing the volume by 50% causes the mixture to become darker because all concentrations have doubled. Decreasing the volume also constitutes a stress, however, as we can see by examining the effect of a change in volume on *Q*. At equilibrium,

$$Q = K = \frac{[NO_2]^2}{[N_2O_4]} \tag{15.5.6a}$$

If the volume is decreased by half, the concentrations of the substances in the mixture are doubled, so the new reaction quotient is as follows:

$$Q = \frac{(2[NO_2]_i)^2}{2[N_2O_4]_i} = \frac{4([NO_2]_i)^2}{2[N_2O_4]_i} = 2K \tag{15.5.6b}$$

Because *Q* is now greater than *K*, the system is no longer at equilibrium. The stress can be relieved if the reaction proceeds to the left, consuming 2 mol of NO_2 for every 1 mol of N_2O_4 produced. This will decrease the concentration of NO_2 and increase the concentration of N_2O_4, causing *Q* to decrease until it once again equals *K*. Thus, as shown in part (c) in Figure 15.5.3, the intensity of the brown color due to NO_2 decreases with time following the change in volume.

Figure 15.5.3 The Effect of Changing the Volume (and Thus the Pressure) of an Equilibrium Mixture of N_2O_4 and NO_2 at Constant Temperature(a) The syringe with a total volume of 15 mL contains an equilibrium mixture of N_2O_4 and NO_2; the red-brown color is proportional to the NO_2 concentration. (b) If the volume is rapidly decreased by a factor of 2 to 7.5 mL, the initial effect is to double the concentrations of all species present, including NO_2. Hence the color becomes more intense. (c) With time, the system adjusts its composition in response to the stress as predicted by Le Chatelier's principle, forming colorless N_2O_4 at the expense of red-brown NO_2, which decreases the intensity of the color of the mixture.

Note the Pattern

Increasing the pressure of a system (or decreasing the volume) favors the side of the reaction that has fewer gaseous molecules and vice versa.

In general, *if a balanced chemical equation contains different numbers of gaseous reactant and product molecules, the equilibrium will be sensitive to changes in volume or pressure*. Increasing the pressure on a system (or decreasing the volume) will favor the side of the reaction that has fewer gaseous molecules and vice versa.

Example 15.5.2

For each equilibrium system, write the reaction quotient for the system if the pressure is decreased by a factor of 2 (i.e., if the

volume is doubled) at constant temperature and then predict the direction of the reaction.

1. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
2. $C_2H_{2(g)} + C_2H_{6(g)} \rightleftharpoons 2C_2H_{4(g)}$
3. $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$

Given: balanced chemical equations

Asked for: direction of reaction if pressure is halved

Strategy:

Use Le Chatelier's principle to predict the effect of the stress.

Solution:

1. Two moles of gaseous products are formed from 4 mol of gaseous reactants. Decreasing the pressure will cause the reaction to shift to the left because that side contains the larger number of moles of gas. Thus the pressure increases, counteracting the stress. *K* for this reaction is $[NH_3]^2/[N_2][H_2]^3$. When the pressure is decreased by a factor of 2, the concentrations are halved, which means that the new reaction quotient is as follows:

$$Q = \frac{[1/2\ NH_3]^2}{[1/2\ N_2][1/2H_2]^3} = \frac{1/4\ [NH_3]^2}{1/16\ [N_2][H_2]^3} = 4K$$

2. Two moles of gaseous products form from 2 mol of gaseous reactants. Decreasing the pressure will have no effect on the equilibrium composition because both sides of the balanced chemical equation have the same number of moles of gas. Here $K = [C_2H_4]^2/[C_2H_2][C_2H_6]$. The new reaction quotient is as follows:

$$Q = \frac{[C_2H_4]^2}{[C_2H_2][C_2H_6]} = \frac{[1/2C_2H_4]^2}{[1/2C_2H_2][1/2C_2H_6]} = \frac{1/4[C_2H_4]^2}{1/4[C_2H_2][C_2H_6]} = K$$

3. Three moles of gaseous products are formed from 2 mol of gaseous reactants. Decreasing the pressure will favor the side that contains more moles of gas, so the reaction will shift toward the products to increase the pressure. For this reaction $K = [NO]^2[O_2]/[NO_2]^2$. Under the new reaction conditions the reaction quotient is as follows:

$$Q = \frac{[1/2NO]^2[1/2O_2]}{[1/2NO_2]^2} = \frac{1/8[NO]^2[O_2]}{1/4[NO_2]^2} = 1/2K$$

Exercise

For each equilibrium system, write a new reaction quotient for the system if the pressure is increased by a factor of 2 (i.e., if the volume is halved) at constant temperature and then predict the direction in which the reaction will shift.

1. $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$
2. $H_{2(g)} + C_2H_{4(g)} \rightleftharpoons C_2H_{6(g)}$
3. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

Answer

1. $Q = K$; no effect
2. $Q = 1/2\ K$; to the right
3. $Q = 1/2\ K$; to the right

Changes in Temperature

In all the cases we have considered so far, the magnitude of the equilibrium constant, *K* or K_p, was constant. Changes in temperature can, however, change the value of the equilibrium constant without immediately affecting the reaction quotient ($Q \neq K$). In this case, the system is no longer at equilibrium; the composition of the system will change until *Q* equals *K* at the new

temperature.

To predict how an equilibrium system will respond to a change in temperature, we must know something about the enthalpy change of the reaction (ΔH_{rxn}). As you learned in Chapter 9 , heat is released to the surroundings in an exothermic reaction ($\Delta H_{rxn} < 0$), and heat is absorbed from the surroundings in an endothermic reaction ($\Delta H_{rxn} > 0$). We can express these changes in the following way:

- Exothermic ($\Delta H<0$):

$$\text{reactants} \rightleftharpoons \text{products} + \text{heat} \tag{15.5.7}$$

- Endothermic ($\Delta H>0$):

$$\text{reactants} + \text{heat} \rightleftharpoons \text{products} \tag{15.5.8}$$

Thus heat can be thought of as a product in an exothermic reaction and as a reactant in an endothermic reaction. Increasing the temperature of a system corresponds to adding heat. Le Chatelier's principle predicts that an exothermic reaction will shift to the left (toward the reactants) if the temperature of the system is increased (heat is added). Conversely, an endothermic reaction will shift to the right (toward the products) if the temperature of the system is increased. If a reaction is thermochemically neutral ($\Delta H_{rxn} = 0$), then a change in temperature will not affect the equilibrium composition.

We can examine the effects of temperature on the dissociation of N_2O_4 to NO_2, for which ΔH = +58 kJ/mol. This reaction can be written as follows:

$$58\ kJ + N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \tag{15.5.9}$$

Increasing the temperature (adding heat to the system) is a stress that will drive the reaction to the right, as illustrated in Figure 15.5.4. Thus increasing the temperature increases the ratio of NO_2 to N_2O_4 at equilibrium, which increases K.



Figure 15.5.4 The Effect of Temperature on the Equilibrium between Gaseous N_2O_4 and NO_2 The value of K changes with temperature of the same 99.9% pure NO_2/N_2O_4 sealed in an ampoule. From left to right -196° C, 0° C, 23° C, 35° C, 50° C. In the endothermic reaction , the equilibrium position can be shifted by changing the temperature. When heat is added and the temperature increases, the reaction shifts to the right and the flask turns reddish brown due to an increase in NO_2. When heat is removed and the temperature decreases, the reaction shifts to the left and flask turns colorless due to an increase in N_2O_4. This demonstrates Le Chatelier's Principle because the equilibrium shifts in the direction that consumes energy. Figure used with permission from Wikipedia.

The effect of increasing the temperature on a system at equilibrium can be summarized as follows: *increasing the temperature increases the magnitude of the equilibrium constant for an endothermic reaction, decreases the equilibrium constant for an exothermic reaction, and has no effect on the equilibrium constant for a thermally neutral reaction*. Table 15.5.1 shows the temperature dependence of the equilibrium constants for the synthesis of ammonia from hydrogen and nitrogen, which is an exothermic reaction with $\Delta H°$ = −91.8 kJ/mol. The values of both K and K_p decrease dramatically with increasing temperature, as predicted for an exothermic reaction.

Table 15.5.1 Temperature Dependence of K and K_p for $N_2(g) + 3\ H_2\ (g) \diamondsuit 2\ NH_3(g)$

Temperature (K)	K	K_p
298	3.3×10^{8}	5.6×10^{5}
400	3.9×10^{4}	3.6×10^{1}
450	2.6×10^{3}	1.9
500	1.7×10^{2}	1.0×10^{-1}
550	2.6×10^{1}	1.3×10^{-2}
600	4.1	1.7×10^{-3}

Note the Pattern

Increasing the temperature causes endothermic reactions to favor products and exothermic reactions to favor reactants.

Example 15.5.3

For each equilibrium reaction, predict the effect of decreasing the temperature:

1. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H_{rxn} = -91.8 \ \ kJ/mol$
2. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \quad \Delta H_{rxn} = 178 \ \ kJ/mol$

Given: balanced chemical equations and values of ΔH_{rxn}

Asked for: effects of decreasing temperature

Strategy:

Use Le Chatelier's principle to predict the effect of decreasing the temperature on each reaction.

Solution:

1. The formation of NH_3 is exothermic, so we can view heat as one of the products:
$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 91.8\ kJ$$
2. If the temperature of the mixture is decreased, heat (one of the products) is being removed from the system, which causes the equilibrium to shift to the right. Hence the formation of ammonia is favored at lower temperatures.
3. The decomposition of calcium carbonate is endothermic, so heat can be viewed as one of the reactants:
$$CaCO_{3(s)} + 178\ kJ \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$
If the temperature of the mixture is decreased, heat (one of the reactants) is being removed from the system, which causes the equilibrium to shift to the left. Hence the thermal decomposition of calcium carbonate is less favored at lower temperatures.

Exercise

For each equilibrium system, predict the effect of increasing the temperature on the reaction mixture:

1. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ with $\Delta H_{rxn} = -198 \ \ kJ/mol$
2. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ with $\Delta H_{rxn} = +181 \ \ kJ/mol$

Answer

1. Reaction shifts to the left.
2. Reaction shifts to the right.

Summary

Three types of stresses can alter the composition of an equilibrium system: adding or removing reactants or products, changing the total pressure or volume, and changing the temperature of the system. A reaction with an unfavorable equilibrium constant can be driven to completion by continually removing one of the products of the reaction. Equilibriums that contain different numbers of gaseous reactant and product molecules are sensitive to changes in volume or pressure; higher pressures favor the side with fewer gaseous molecules. Removing heat from an exothermic reaction favors the formation of products, whereas removing heat from an endothermic reaction favors the formation of reactants.

Key Takeaway

- Equilibriums are affected by changes in concentration, total pressure or volume, and temperature.

Conceptual Problems

1. If an equilibrium reaction is endothermic in the forward direction, what is the expected change in the concentration of each component of the system if the temperature of the reaction is increased? If the temperature is decreased?

2. Write the equilibrium equation for the following system:

   \[4NH_{3(g)} +5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}\

   Would you expect the equilibrium to shift toward the products or reactants with an increase in pressure? Why?

3. The reaction rate approximately doubles for every 10°C rise in temperature. What happens to K?

4. The formation of $A_2B_2(g)$ via the equilibrium reaction $2AB(g) \diamondsuit A_2B_2(g)$ is exothermic. What happens to the ratio k_f/k_r if the temperature is increased? If both temperature and pressure are increased?

5. In each system, predict the effect that the indicated change will have on the specified quantity at equilibrium:

   1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$:

      H_2 is removed; what is the effect on $P(I_2)$?

   2. $2NOBr_{(g)} \rightleftharpoons 2NO_{(g)} + Br_{2(g)}$

      If Br_2 is removed; what is the effect on P_{NOBr}?

   3. $2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(g)} + CO_{2(g)} + H_2O_{(g)}$

      If CO_2 is removed; what is the effect on $P(NaHCO_3)$?

6. What effect will the indicated change have on the specified quantity at equilibrium?

   1. $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$

      If NH_4Cl is increased; what is the effect on P_{HCl}?

   2. $2H2O_{(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$

      If O_2 is added; what is the effect on $P(H_2)$?<

   3. $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

If Cl_2 is removed; what is the effect on $P(PCl_5)$?

Numerical Problems

1. For each equilibrium reaction, describe how Q and *K* change when the pressure is increased, the temperature is increased, the volume of the system is increased, and the concentration(s) of the reactant(s) is increased.

    1. A(g) ⇌ B(g) Δ H = −20.6 kJ/mol
    2. 2A(g) ⇌ B(g) Δ H = −0.3 kJ/mol
    3. A(g) + B(g) ⇌ 2C(g) Δ H = 46 kJ/mol

2. For each equilibrium reaction, describe how Q and *K* change when the pressure is decreased, the temperature is increased, the volume of the system is decreased, and the concentration(s) of the reactant(s) is increased.

    1. 2A(g) ⇌ B(g) Δ H = −80 kJ/mol
    2. A(g) ⇌ 2B(g) Δ H = 0.3 kJ/mol
    3. 2A(g) ⇌ 2B(g) + C(g) Δ H = 46 kJ/mol

3. Le Chatelier's principle states that a system will change its composition to counteract stress. For the system $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, write the equilibrium constant expression K_p. What changes in the values of Q and *K* would you anticipate when (a) the volume is doubled, (b) the pressure is increased by a factor of 2, and (c) $COCl_2$ is removed from the system?

4. For the equilibrium system $3O_2(g) \rightleftharpoons 2\ O_3(g)$, $\Delta H° = 284$ kJ, write the equilibrium constant expression K_p. What happens to the values of Q and *K* if the reaction temperature is increased? What happens to these values if both the temperature and pressure are increased?

5. Carbon and oxygen react to form CO_2 gas via $C(s) + O_2(g) \rightleftharpoons CO_2(g)$, for which $K = 1.2 \times 10^{69}$. Would you expect *K* to increase or decrease if the volume of the system were tripled? Why?

6. The reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2\ (g)$ has $K = 2.2 \times 10^{-10}$ at 100°C. Starting with an initial $P(\ COCl_2)$ of 1.0 atm, you determine the following values of P_{CO} at three successive time intervals: 6.32×10^{-6} atm, 1.78×10^{-6} atm, and 1.02×10^{-5} atm. Based on these data, in which direction will the reaction proceed after each measurement? If chlorine gas is added to the system, what will be the effect on Q?

7. The following table lists experimentally determined partial pressures at three temperatures for the reaction $Br_2(g) \rightleftharpoons 2\ Br(g)$

T (K)	1123	1173	1273
$P(Br_2)$ (atm)	3.000	0.3333	6.755×10^{-2}
P(Br) (atm)	3.477×10^{-2}	2.159×10^{-2}	2.191×10^{-2}

    Is this an endothermic or an exothermic reaction? Explain your reasoning.

8. The dissociation of water vapor proceeds according to the following reaction:$H_2O(g) \rightleftharpoons 1/2\ O_2(g) + H_2\ (g)$. At 1300 K, there is 0.0027% dissociation, whereas at 2155 K, the dissociation is 1.18%. Calculate *K* and K_p. Is this an endothermic reaction or an exothermic reaction? How do the magnitudes of the two equilibriums compare? Would increasing the pressure improve the yield of H_2 gas at either temperature? (Hint: assume that the system initially contains 1.00 mol of H_2O in a 1.00 L container.)

9. When 1.33 mol of CO_2 and 1.33 mol of H_2 are mixed in a 0.750 L container and heated to 395°C, they react according to the following equation: $CO_2(g) + H_2\ (g) \rightleftharpoons CO(g) + H_2O(g)$ If $K = 0.802$, what are the equilibrium concentrations of each component of the equilibrium mixture? What happens to *K* if H_2O is removed during the course of the reaction?

10. The equilibrium reaction $H_2(g) + Br_2(g) \rightleftharpoons 2\ HBr(g)$ has $K_p = 2.2 \times 10^9$ at 298 K. If you begin with 2.0 mol of Br_2 and 2.0 mol of H_2 in a 5.0 L container, what is the partial pressure of HBr at equilibrium? What is the partial pressure of H_2 at equilibrium? If H_2 is removed from the system, what is the effect on the partial pressure of Br_2?

11. Iron(II) oxide reacts with carbon monoxide according to the following equation: FeO(s) + CO(g) ⇌ Fe(s) + CO_2(g) At 800°C, K = 0.34; at 1000°C, K = 0.40.

    1. A 20.0 L container is charged with 800.0 g of CO_2, 1436 g of FeO, and 1120 g of iron. What are the equilibrium concentrations of all components of the mixture at each temperature?
    2. What are the partial pressures of the gases at each temperature?
    3. If CO were removed, what would be the effect on P(CO_2) at each temperature?

12. The equilibrium constant K for the reaction C(s) + CO_2 g) >⇌ 2 CO(g) is 1.9 at 1000 K and 0.133 at 298 K.

    1. If excess C is allowed to react with 25.0 g of CO_2 in a 3.00 L flask, how many grams of CO are produced at each temperature?
    2. What are the partial pressures of each gas at 298 K? at 1000 K?
    3. Would you expect K to increase or decrease if the pressure were increased at constant temperature and volume?

13. Data for the oxidation of methane, CH_4(g) + 2 O_2(g) ⇌ CO_2(g) + 2 H_2O(g), in a closed 5.0 L vessel are listed in the following table. Fill in the blanks and determine the missing values of Q and K (indicated by ?) as the reaction is driven to completion.

	CH_4	O_2	CO_2	H_2O	Q	K
initial (moles)	0.45	0.90	0	0	?	
at equilibrium						1.29
add 0.50 mol of methane	0.95				?	
new equilibrium						?
remove water				0	?	
new equilibrium						1.29

Answers

1.
2.
3. K_p = P($COCl_2$)/(P(CO) P(Cl_2)) P

   None of the changes would affect K; (a) Q doubles; (b) Q is halved; Q decreases.

4.

5. K would not change; it does not depend on volume.

6.
7.
8.

9. [CO] = [H_2O] = 0.839 M, [CO_2] = [H_2] = 0.930 M; no effect on K

10.
11.
    1. At 800°C, [CO] = 0.678 M, [CO_2] = 0.231 M; at 1000°C, [CO] = 0.645 M, [CO_2] = 0.264 M
    2. At 800°C, PCO = 59.7 atm, P(CO_2) = 20.3 atm; at 1000°C, P(CO) = 67.4 atm, P(CO_2) = 27.6 atm.
    3. Removing CO would cause the reaction to shift to the right, causing P(CO_2) to decrease.
12.
13.

	CH_4	O_2	CO_2	H_2O	Q	K
initial (moles)	0.45	0.90	0	0	0	1.29

	CH_4	O_2	CO_2	H_2O	Q	K
at equilibrium	0.215	0.43	0.235	0.47	K	1.29
add 0.50 mol of methane	0.715	0.43	0.235	0.47	**0.39**	1.29
new equilibrium	0.665	0.33	0.285	0.57	K	**1.29**
remove water	0.665	0.33	0.285	0	**0**	1.29
new equilibrium	0.57	0.14	0.38	0.19	K	1.29

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10.7: Spontaneity and Equilibrium

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Compare and contrast product-favored equilibria to reactant-favored equilibria in terms of equilibrium composition, ΔG, and *K*.

We have identified three criteria for whether a given reaction will occur spontaneously: $\Delta S_{univ} > 0$, $\Delta G_{sys} < 0$, and the relative magnitude of the reaction quotient *Q* versus the equilibrium constant *K*. (For more information on the reaction quotient and the equilibrium constant, see Chapter 15.) Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 18.6.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes. Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. The relationship between ΔS_{univ} and ΔG_{sys} was described in Section 18.5. In this section, we explore the relationship between the standard free energy of reaction ($\Delta G°$) and the equilibrium constant (*K*).

Table 18.6.1 Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
$Q < K$	$Q = K$	$Q > K$
***Spontaneous in the *reverse* direction.**		

Free Energy and the Equilibrium Constant

Because $\Delta H°$ and $\Delta S°$ determine the magnitude of $\Delta G°$ (Equation 18.5.5), and because *K* is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express *K* in terms of $\Delta G°$ and vice versa. As you learned in Section 18.5, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. Using higher math, the general relationship can be shown as follows:

$$\Delta G = V\Delta P - S\Delta T$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 18.29 simplifies to

$$\Delta G = V\Delta P$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important. What Equation 18.6.2 tells us is how the free energy changes as the pressure changes at constant temperature.

Assuming ideal gas behavior, we can replace the *V* in Equation 18.6.2 by *nRT*/*P* (where *n* is the number of moles of gas and *R* is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively) as in Equation 18.4.1.

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P = nRT\frac{\Delta P}{P} = nRTln\left(\frac{P_f}{P_i}\right)$$

To actually show the final step one has to consider infinitesmal changes in both the free energy and the pressure and then integrate both sides of the equation using calculus, which is beyond the scope of this course. If the initial state is the standard state with P_i = 1 atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^o = nRTln\ \ P$$

This can be rearranged as follows:

$$G = G^o + nRTln\ \ P$$

As you will soon discover, Equation 18.6.5 allows us to relate $\Delta G°$ and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum mG_{products} - \sum mG_{reactants} = (cG_C + dG_D) - (aG_A + bG_B)$$

Substituting Equation 18.6.5 for each term into Equation 18.6.7,

$$\Delta G = [(cG_C + cRTln\ P_C) + (dG_D + dRTln\ P_D)] - [(aG_A + aRTln\ P_A) + (bG_B + bRTln\ P_B)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^o + RTln\left(\frac{P_C^c P_D^d}{P_A^a P_B^b}\right) = \Delta G^o + RTln\ \ Q$$

where $\Delta G°$ indicates that all reactants and products are in their standard states. In Chapter 15, you learned that for gases Q = K_p at equilibrium, and as you've learned in this chapter, ΔG = 0 for a system at equilibrium. Therefore, we can describe the relationship between $\Delta G°$ and K_p for gases as follows:

$$0 = \Delta G^o + RTln\ \ K_P$$

$$\Delta G^o = -RTln\ \ K_P$$

If the products and reactants are in their standard states and $\Delta G° < 0$, then $K_p > 1$, and products are favored over reactants. Conversely, if $\Delta G° > 0$, then $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, then $K_p = 1$, and neither reactants nor products are favored: the system is at equilibrium.

Note the Pattern

For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.

Example 18.6.1

In Example 18.5.3, we calculated that $\Delta G°$ = –32.7 kJ/mol of N_2 for the reaction $N_2(g)+3H_2(g \diamond 2NH_3(g)$ This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions: $P(N_2)$ = 2.00 atm, $P(H_2)$ = 7.00 atm, $P(NH_3)$ = 0.021 atm, and T = 100°C. Does the reaction favor products or reactants?

Given: balanced chemical equation, partial pressure of each species, temperature, and $\Delta G°$

Asked for: whether products or reactants are favored

Strategy:

A Using the values given and Equation 18.6.8, calculate *Q*.

B Substitute the values of Δ*G*° and *Q* into Equation 18.6.8 to obtain Δ*G* for the reaction under nonstandard conditions.

Solution:

A The relationship between Δ*G*° and Δ*G* under nonstandard conditions is given in Equation 18.6.8. Substituting the partial pressures given, we can calculate *Q*:

$$Q = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{(0.021)^2}{(2.00)\,(7.00)^3} = 6.4 \times 10^{-7}$$

B Substituting the values of Δ*G*° and *Q* into Equation 18.6.8,

$$\Delta G = \Delta G^o + RTln\ \ Q = -32.7\ \ kJ + \left[\left(8.314\ \cancel{J}\ \cancel{K}\right)\left(373\ \cancel{K}\right)\left(1\ kJ/1000\ \cancel{kJ}\right) ln\left(6.4 \times 10^{-7}\right)\right]$$

$$= -32.7\ \ kJ + (-44\ kJ) = -77\ \ kJ/mol\ \ N_2$$

Because Δ*G* < 0 and *Q* < 1.0, the reaction is spontaneous to the right as written, so products are favored over reactants.

Exercise

Calculate Δ*G* for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: *T* = 50°C, *P(NO)* = 0.0100 atm, *P(O2)* = 0.200 atm, and *P(NO2)* = 1.00 × 10^{-4} atm. The value of Δ*G*° for this reaction is –72.5 kJ/mol of O_2. Are products or reactants favored?

Answer: –92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written, so products are favored.

Example 18.6.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. As calculated in Example 18.5.3 , Δ*G*° for this reaction is –32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 10, Δ*G*°, and temperature

Asked for: K_p

Strategy:

Substitute values for Δ*G*° and *T* (in kelvins) into Equation 18.6.9 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution:

In Example 18.5.3 , we used tabulated values of ΔG° to calculate Δ*G*° for this reaction (–32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 18.6.9,

$$\Delta G^o = -RTln\ \ K_P$$

$$\frac{-\Delta G^o}{RT} = ln\ \ K_P$$

Inserting the value of Δ*G*° and the temperature (25°C = 298 K) into this equation,

$$ln\ K_P = -\frac{\left(-32.7\ \cancel{kJ}\right)\left(1000\ \cancel{J}/\cancel{kJ}\right)}{8.314\ \cancel{J}/\cancel{K}\left(298\ \cancel{K}\right)} = 13.2$$

$$K_P = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. As we saw in Chapter 15, however, the *rate* at which the reaction occurs at room temperature is too slow to be useful.

Exercise

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. As calculated in the exercise in Example 10, $\Delta G°$ for this reaction is –70.5 kJ/mol of O_2.

Answer: 2.2×10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of K_p and K in Chapter 15 and showed that they are related:

$$K_P = K\,(RT)^{\Delta n}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 18.36 can be written in a more general form:

$$\Delta G^o = -RTln\ K$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 18.38 for the difference between K_p and K.Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of activities or fugacities in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equation 18.26 and Equation 18.6.11 provides insight into how the components of $\Delta G°$ influence the magnitude of the equilibrium constant:

$$\Delta G^o = \Delta H^o - T\Delta S^o = -RTln\ K$$

Notice that K becomes larger as $\Delta S°$ becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as $\Delta H°$ decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

Note the Pattern

The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder and seek the lowest energy state possible.

Temperature Dependence of the Equilibrium Constant

The fact that $\Delta G°$ and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 18.6.12, which can be rearranged as follows:

$$ln\ K = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

Assuming $\Delta H°$ and $\Delta S°$ are temperature independent, for an exothermic reaction ($\Delta H° < 0$), the magnitude of K decreases

with increasing temperature, whereas for an endothermic reaction ($\Delta H° > 0$), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 18.6.13 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 18.6.13 also shows that the *magnitude* of $\Delta H°$ dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of $\Delta S°$ affect the magnitude of K but not its temperature dependence.

There is a mathematical equation describing the relationship between K, ΔH, and ΔS called the *van't Hoff equation,* but it is beyond the scope of this class and not included here.

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If $\Delta G° < 0$, then K or $K_p > 1$, and products are favored over reactants. If $\Delta G° > 0$, then K or $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, then K or $K_p = 1$, and the system is at equilibrium. We can use the measured equilibrium constant K at one temperature and $\Delta H°$ to estimate the equilibrium constant for a reaction at any other temperature.

Key Takeaway

- The change in free energy of a reaction can be expressed in terms of the standard free-energy change and the equilibrium constant K or K_p and indicates whether a reaction will occur spontaneously under a given set of conditions.

Key Equations

Relationship between standard free-energy change and equilibrium constant

Equation 18.6.9: $\Delta G^o = -RTln\ \ K$

Temperature dependence of equilibrium constant

Equation 18.6.11: $ln\ \ K = \dfrac{-\Delta H^o}{RT} + \dfrac{-\Delta S^o}{R}$

Calculation of K at second temperature

Equation 18.6.11: $ln\ \ \dfrac{K_2}{K_1} = \dfrac{-\Delta H^o}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

Conceptual Problems

1. Do you expect products or reactants to dominate at equilibrium in a reaction for which $\Delta G°$ is equal to

    1. 1.4 kJ/mol?
    2. 105 kJ/mol?
    3. −34 kJ/mol?

2. The change in free energy enables us to determine whether a reaction will proceed spontaneously. How is this related to the extent to which a reaction proceeds?

3. What happens to the change in free energy of the reaction $N_2(g) + 3F_2(g) \rightarrow 2NF_3(g)$ if the pressure is increased while the temperature remains constant? if the temperature is increased at constant pressure? Why are these effects not so important for reactions that involve liquids and solids?

4. Compare the expressions for the relationship between the change in free energy of a reaction and its equilibrium constant where the reactants are gases versus liquids. What are the differences between these expressions?

Numerical Problems

1. Carbon monoxide, a toxic product from the incomplete combustion of fossil fuels, reacts with water to form CO_2 and H_2, as shown in the equation $CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$, for which $\Delta H° = -41.0$ kJ/mol and $\Delta S° = -42.3$ J cal/(mol·K) at 25°C and 1 atm.

    1. What is $\Delta G°$ for this reaction?
    2. What is ΔG if the gases have the following partial pressures: $P(CO) = 1.3$ atm, $P(H_2O) = 0.8$ atm, $P(CO_2) = 2.0$ atm, and $P(H_2) = 1.3$ atm?
    3. What is ΔG if the temperature is increased to 150°C assuming no change in pressure?

2. Methane and water react to form carbon monoxide and hydrogen according to the equation $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

    1. What is the standard free energy change for this reaction?
    2. What is K_p for this reaction?
    3. What is the carbon monoxide pressure if 1.3 atm of methane reacts with 0.8 atm of water, producing 1.8 atm of hydrogen gas?
    4. What is the hydrogen gas pressure if 2.0 atm of methane is allowed to react with 1.1 atm of water?
    5. At what temperature does the reaction become spontaneous?

3. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.

    1. $CCl_4(g) + 6\ H_2O(l) \rightleftharpoons CO_2(g) + 4HCl(aq)$; $\Delta G° = -377$ kJ/mol
    2. $Xe(g) + 2F_2(g) \rightleftharpoons XeF_4(s)$; $\Delta H° = -66.3$ kJ/mol, $\Delta S° = -102.3$ J/(mol·K)
    3. $PCl_3(g) + S \rightleftharpoons PSCl_3(l)$; $\Delta G_f°(PCl_3) = -272.4$ kJ/mol, $\Delta G_f°(PSCl_3) = -363.2$ kJ/mol

4. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.

    1. $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$; $\Delta G° = -225.8$ kJ/mol
    2. $CoCl2(s) + 6\ H_2O(l) \rightleftharpoons 6CoCl_2 \cdot 6\ H_2O(s)$; $\Delta H_{rxn}° = -352$ kJ/mol, $\Delta S_{rxn}° = -899$ J/(mol·K)
    3. $PCl_3(g) + O_2(g) \rightleftharpoons 2POCl_3(g)$; (PCl_3); $\Delta G_f°(PCl_3) = -272.4$ kJ/mol, $\Delta G_f°(POCl_3) = -558.5$ kJ/mol

5. The gas-phase decomposition of N_2O_4 to NO_2 is an equilibrium reaction with $K_p = 4.66 \times 10^{-3}$. Calculate the standard free-energy change for the equilibrium reaction between N_2O_4 and NO_2.

6. The standard free-energy change for the dissolution $K_4Fe(CN)_6 \cdot H_2O(s) \rightleftharpoons 4K^+(aq) + Fe(CN)_6^{4-}(aq) + H_2O(l)$ is 26.1 kJ/mol. What is the equilibrium constant for this process at 25°C?

7. Ammonia reacts with water in liquid ammonia solution (am) according to the equation $NH_3(g) + H_2O(am) \rightleftharpoons NH_4^+(am) + OH^-(am)$ The change in enthalpy for this reaction is 21 kJ/mol, and $\Delta S° = -303$ J/(mol·K). What is the equilibrium constant for the reaction at the boiling point of liquid ammonia (–31°C)?

8. At 25°C, a saturated solution of barium carbonate is found to have a concentration of $[Ba^{2+}] = [CO_3^{2-}] = 5.08 \times 10^{-5}$ M. Determine $\Delta G°$ for the dissolution of $BaCO_3$.

9. Lead phosphates are believed to play a major role in controlling the overall solubility of lead in acidic soils. One of the dissolution reactions is $Pb_3(PO_4)_2(s) + 4H^+(aq) \rightleftharpoons 3Pb^{2+}(aq) + 2H_2PO_4^-(aq)$ for which $\log K = -1.80$. What is $\Delta G°$ for this reaction?

10. The conversion of butane to 2-methylpropane is an equilibrium process with $\Delta H° = -2.05$ kcal/mol and $\Delta G° = -0.89$ kcal/mol.

1. What is the change in entropy for this conversion?
2. Based on structural arguments, are the sign and magnitude of the entropy change what you would expect? Why?
3. What is the equilibrium constant for this reaction?

11. The reaction of $CaCO_3(s)$ to produce $CaO(s)$ and $CO_2(g)$ has an equilibrium constant at 25°C of 2×10^{-23}. Values of ΔH_f° are as follows: $CaCO_3$, −1207.6 kJ/mol; CaO, −634.9 kJ/mol; and CO_2, −393.5 kJ/mol.

    1. What is ΔG° for this reaction?
    2. What is the equilibrium constant at 900°C?
    3. What is the partial pressure of $CO_2(g)$ in equilibrium with CaO and $CaCO_3$ at this temperature?
    4. Are reactants or products favored at the lower temperature? at the higher temperature?

12. In acidic soils, dissolved Al^{3+} undergoes a complex formation reaction with SO_4^{2-} to form $[AlSO_4^+]$. The equilibrium constant at 25°C for the reaction $Al^{3+}(aq) + SO_4^{2-}(aq) \rightleftharpoons AlSO_4^+(aq)$ is 1585.

    1. What is ΔG° for this reaction?
    2. How does this value compare with ΔG° for the reaction $Al^{3+}(aq) + F^-(aq) \rightleftharpoons AlF^{2+}(aq)$ for which $K = 10^7$ at 25°C?
    3. Which is the better ligand to use to trap Al^{3+} from the soil?

Answers

1.
    1. −28.4 kJ/mol
    2. −26.1 kJ/mol
    3. −19.9 kJ/mol
2.
3.
    1. 1.21×10^{66}; equilibrium lies far to the right.
    2. 1.89×10^{6}; equilibrium lies to the right.
    3. 5.28×10^{16}; equilibrium lies far to the right.
4.
5. 13.3 kJ/mol
6.
7. 5.1×10^{-21}
8.
9. 10.3 kJ/mol
10.
11.
    1. 129.5 kJ/mol
    2. 6
    3. 6.0 atm
    4. Products are favored at high *T*; reactants are favored at low *T*.
12.

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10.8: Comparing Thermodynamics and Kinetics

Learning Objectives

- To understand the differences between the information that thermodynamics and kinetics provide about a system.

Because thermodynamics deals with state functions, it can be used to describe the overall properties, behavior, and equilibrium composition of a system. It is not concerned with the particular pathway by which physical or chemical changes occur, however, so it cannot address the rate at which a particular process will occur. Although thermodynamics provides a significant constraint on what can occur during a reaction process, it does not describe the detailed steps of what actually occurs on an atomic or a molecular level.

Note
Thermodynamics focuses on the energetics of the products and the reactants, whereas kinetics focuses on the pathway from reactants to products.

Table 18.4 gives the numerical values of the equilibrium constant (K) that correspond to various approximate values of ΔG°. Note that ΔG° ≥ +10 kJ/mol or ΔG° ≤ −10 kJ/mol ensures that an equilibrium lies essentially all the way to the left or to the right, respectively, under standard conditions, corresponding to a reactant-to-product ratio of approximately 10,000:1 (or vice versa). Only if ΔG° is quite small (±10 kJ/mol) are significant amounts of both products and reactants present at equilibrium. Most reactions that we encounter have equilibrium constants substantially greater or less than 1, with the equilibrium strongly favoring either products or reactants. In many cases, we will encounter reactions that are strongly favored by thermodynamics but do not occur at a measurable rate. In contrast, we may encounter reactions that are not thermodynamically favored under standard conditions but nonetheless do occur under certain nonstandard conditions.

Table 18.4 The Relationship between K and ΔG° at 25°C

ΔG° (kJ/mol)	K	Physical Significance
500	3×10^{-88}	For all intents and purposes, the reaction does not proceed in the forward direction: only reactants are present at equilibrium.
100	3×10^{-18}	
10	2×10^{-2}	Both forward and reverse reactions occur: significant amounts of both products and reactants are present at equilibrium.
0	1	
−10	60	
−100	3×10^{17}	For all intents and purposes, the forward reaction proceeds to completion: only products are present at equilibrium.
−500	4×10^{87}	

A typical challenge in industrial processes is a reaction that has a large negative value of ΔG° and hence a large value of K but that is too slow to be practically useful. In such cases, mixing the reactants results in only a physical mixture, not a chemical reaction. An example is the reaction of carbon tetrachloride with water to produce carbon dioxide and hydrochloric acid, for which ΔG° is −232 kJ/mol:

$$CCl_4(l) + 2H_2O(l) \rightleftharpoons CO_2(g) + 2HCl(g) \tag{18.42}$$

The value of K for this reaction is 5×10^{49} at 25°C, yet when CCl_4 and water are shaken vigorously at 25°C, nothing happens: the two immiscible liquids form separate layers, with the denser CCl_4 on the bottom. In comparison, the analogous reaction of $SiCl_4$ with water to give SiO_2 and HCl, which has a similarly large equilibrium constant, occurs almost explosively. Although the two reactions have comparable thermodynamics, they have very different kinetics!

There are also many reactions for which $\Delta G° << 0$ but that do not occur as written because another possible reaction occurs more rapidly. For example, consider the reaction of lead sulfide with hydrogen peroxide. One possible reaction is as follows:

$$PbS(s) + 4H_2O_2(l) \rightleftharpoons PbO2(s) + SO_2(g) + 4H_2O(l) \tag{18.43}$$

for which $\Delta G°$ is –886 kJ/mol and K is 10^{161}. Yet when lead sulfide is mixed with hydrogen peroxide, the ensuing vigorous reaction does not produce PbO_2 and SO_2. Instead, the reaction that actually occurs is as follows:

$$PbS(s) + 4H_2O_2(l) \rightleftharpoons PbSO_4(s) + 4H_2O(l) \tag{10.8.1}$$

This reaction has a $\Delta G°$ value of –1181 kJ/mol, within the same order of magnitude as the reaction in Equation 18.43, but it occurs much more rapidly.

Now consider reactions with $\Delta G° > 0$. Thermodynamically, such reactions do not occur spontaneously under standard conditions. Nonetheless, these reactions can be made to occur under nonstandard conditions. An example is the reduction of chromium(III) chloride by hydrogen gas:

$$\mathrm{CrCl_3(s)} + \frac{1}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{CrCl_2(s)} + \mathrm{HCl(g)}$$

At 25°C, $\Delta G° = 35$ kJ/mol and $K_p = 7 \times 10^{-7}$. However, at 730°C, $\Delta G° = -52$ kJ/mol and $K_p = 5 \times 10^{2}$; at this elevated temperature, the reaction is a convenient way of preparing chromium(II) chloride in the laboratory. Moreover, removing HCl gas from the system drives the reaction to completion, as predicted by Le Chatelier's principle. Although the reaction is not thermodynamically spontaneous under standard conditions, it becomes spontaneous under nonstandard conditions.

There are also cases in which a compound whose formation appears to be thermodynamically prohibited can be prepared using a different reaction. The reaction for the preparation of chlorine monoxide from its component elements, for example, is as follows:

$$\frac{1}{2}\mathrm{O_2(g)} + \mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2O(g)}$$

for which $\Delta G°_f$ is 97.9 kJ/mol. The large positive value of $\Delta G°_f$ for this reaction indicates that mixtures of chlorine and oxygen do not react to any extent to form Cl_2O. Nonetheless, Cl_2O is easily prepared using the reaction

$$\mathrm{HgO(s)} + 2\mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2O(g)} + \mathrm{HgCl_2(s)}$$

which has a $\Delta G°$ of –22.2 kJ/mol and a K_p of approximately 1×10^{4}.

Finally, the $\Delta G°$ values for some reactions are so positive that the only way to make them proceed in the desired direction is to supply external energy, often in the form of electricity. Consider, for example, the formation of metallic lithium from molten lithium chloride:

$$\mathrm{LiCl(l)} \rightleftharpoons \mathrm{Li(l)} + \frac{1}{2}\mathrm{Cl_2(g)}$$

Even at 1000°C, ΔG is very positive (324 kJ/mol), and there is no obvious way to obtain lithium metal using a different reaction. Hence in the industrial preparation of metallic lithium, electrical energy is used to drive the reaction to the right.

Note
A reaction that does not occur under standard conditions can be made to occur under nonstandard conditions, such as by driving the reaction to completion using Le Chatelier's principle or by providing external energy.

Often reactions that are not thermodynamically spontaneous under standard conditions can be made to occur spontaneously if coupled, or connected, in some way to another reaction for which $\Delta G° << 0$. Because the overall value of $\Delta G°$ for a series of

reactions is the sum of the ΔG° values for the individual reactions, virtually any unfavorable reaction can be made to occur by chemically coupling it to a sufficiently favorable reaction or reactions. In the preparation of chlorine monoxide from mercuric oxide and chlorine (Equation 18.47), we have already encountered one example of this phenomenon of coupled reactions, although we did not describe it as such at the time. We can see how the chemical coupling works if we write Equation 18.47 as the sum of three separate reactions:

$$\frac{1}{2}\mathrm{O_2(g)} + \mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2O(g)} \qquad \Delta G^\circ = 97.9\ \mathrm{kJ/mol} \qquad (1)$$

$$\mathrm{HgO(s)} \rightleftharpoons \mathrm{Hg(l)} + \frac{1}{2}\mathrm{O_2(g)} \qquad \Delta G^\circ = 58.5\ \mathrm{kJ/mol} \qquad (2)$$

$$\mathrm{Hg(l)} + \mathrm{Cl_2(g)} \rightleftharpoons \mathrm{HgCl_2(s)} \qquad \Delta G^\circ = -178.6\ \mathrm{kJ/mol} \qquad (3)$$

$$\mathrm{HgO(s)} + 2\mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2O(g)} + \mathrm{HgCl_2(s)} \qquad \Delta G^\circ_{\mathrm{rxn}} = -22.2\ \mathrm{kJ/mol} \qquad (10.8.2)$$

Comparing the ΔG° values for the three reactions shows that reaction 3 is so energetically favorable that it more than compensates for the other two energetically unfavorable reactions. Hence the overall reaction is indeed thermodynamically spontaneous as written.

Note
By coupling reactions, a reaction that is thermodynamically nonspontaneous can be made spontaneous.

Example 15

Bronze Age metallurgists were accomplished practical chemists who unknowingly used coupled reactions to obtain metals from their ores. Realizing that different ores of the same metal required different treatments, they heated copper oxide ore in the presence of charcoal (carbon) to obtain copper metal, whereas they pumped air into the reaction system if the ore was copper sulfide. Assume that a particular copper ore consists of pure cuprous oxide (Cu_2O). Using the ΔG°_f values given for each, calculate

a. $\Delta G°$ and K_p for the decomposition of Cu_2O to metallic copper and oxygen gas [$\Delta G^\circ_f(Cu_2O)$=–146.0 kJ/mol].
b. $\Delta G°$ and K_p for the reaction of Cu_2O with carbon to produce metallic copper and carbon monoxide [ΔG°_f (CO)=–137.2 kJ/mol].

Given: reactants and products, ΔG°_f values for Cu_2O and CO, and temperature

Asked for: $\Delta G°$ and K_p for the formation of metallic copper from Cu_2O in the absence and presence of carbon

Strategy:

A. Write the balanced equilibrium equation for each reaction. Using the “products minus reactants” rule, calculate $\Delta G°$ for the reaction.
B. Substitute appropriate values into Equation 18.36 to obtain K_p.

Solution

A The chemical equation for the decomposition of cuprous oxide is as follows:

$$\mathrm{Cu_2O(s) \rightleftharpoons 2Cu(s) + \tfrac{1}{2}O_2(g)}$$

The substances on the right side of this equation are pure elements in their standard states, so their ΔG°_f values are zero. $\Delta G°$ for the reaction is therefore

$$\Delta G^\circ = \left[2\Delta G^\circ_f(\mathrm{Cu}) + \frac{1}{2}\Delta G^\circ_f(\mathrm{O_2})\right] - \Delta G^\circ_f(\mathrm{Cu_2O}) \tag{10.8.3}$$

$$= \left[(2\text{ mol})(0\text{ kJ/mol}) + \left(\frac{1}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] - [(1\text{ mol})(-146.0\text{ kJ/mol})] \tag{10.8.4}$$

$$= 146.0\text{ kJ} \tag{10.8.5}$$

B Rearranging and substituting the appropriate values into Equation 18.36,

$$\ln K_\mathrm{p} = -\frac{\Delta G^\circ}{RT} = -\frac{(146.0\text{ kJ})(1000\text{ J/kJ})}{(8.314\text{ J/K})(298.15\text{ K})} = -58.90 \tag{10.8.6}$$

$$K_\mathrm{p} = 2.6 \times 10^{-26} \tag{10.8.7}$$

This is a very small number, indicating that Cu_2O does not spontaneously decompose to a significant extent at room temperature.
b.

A The O_2 produced in the decomposition of Cu_2O can react with carbon to form CO:

$$\mathrm{\tfrac{1}{2}O_2(g) + C(s) \rightleftharpoons CO(g)}$$

Because $\Delta G°$ for this reaction is equal to ΔG°_f for CO (–137.2 kJ/mol), it is energetically more feasible to produce metallic copper from cuprous oxide by coupling the two reactions:

$$\mathrm{Cu_2O(s) \rightleftharpoons 2Cu(s) + \frac{1}{2}O_2(g)} \qquad \Delta G^\circ = 146.0\text{ kJ/mol} \tag{10.8.8}$$

$$\mathrm{\frac{1}{2}O_2(g) + C(s) \rightleftharpoons CO(g)} \qquad \Delta G^\circ = -137.2\text{ kJ/mol} \tag{10.8.9}$$

$$\mathrm{Cu_2O(s) + C(s) \rightleftharpoons 2Cu(s) + CO(g)} \qquad \Delta G^\circ_f = 8.8\text{ kJ/mol} \tag{10.8.10}$$

B We can find the corresponding value of K_p:

$$\ln K_{\mathrm{p}} = -\frac{\Delta G^\circ}{RT} = -\frac{(8.8\ \mathrm{kJ})(1000\ \mathrm{J/kJ})}{(8.314\ \mathrm{J/K})(298.15\ \mathrm{K})} = -3.6 \tag{10.8.11}$$

$$K_{\mathrm{p}} = 0.03 \tag{10.8.12}$$

Although this value is still less than 1, indicating that reactants are favored over products at room temperature, it is about 24 orders of magnitude greater than K_p for the production of copper metal in the absence of carbon. Because both ΔH° and ΔS° are positive for this reaction, it becomes thermodynamically feasible at slightly elevated temperatures (greater than about 80°C). At temperatures of a few hundred degrees Celsius, the reaction occurs spontaneously, proceeding smoothly and rapidly to the right as written and producing metallic copper and carbon monoxide from cuprous oxide and carbon.

Exercise 1

Use the ΔG°_f values given to calculate ΔG° and K_p for each reaction.

a. the decomposition of cuprous sulfide to copper metal and elemental sulfur [ΔG°_f (Cu_2S)=−86.2 kJ/mol]
b. the reaction of cuprous sulfide with oxygen gas to produce sulfur dioxide and copper metal [ΔG°_f [$SO_2(g)$] = −300.1 kJ/mol]

Answer:

a. ΔG° = 86.2 kJ/mol; $K_p = 7.90 \times 10^{-16}$
b. ΔG° = −213.9 kJ/mol; $K_p = 2.99 \times 10^{37}$

Contributors and Attributions

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11: ACIDS AND BASES HAVE COMMON PROPERTIES AND REACTIONS

11.1: Overview and Objectives

11.2: Definitions of Acids and Bases

11.3: Acid-Base Reactions

11.4: The Autoionization of Water and Solution pH

11.5: Equilibria and pH of Weak Acid and Salt Solutions

11.6: Buffers

11.7: Acid-Base Titrations

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11.1: Overview and Objectives

> "It is therefore natural to define acids and bases as substances which are able to split off or take up hydrogen ions, respectively. By this scheme, an acid and a base are related by the fundamental equation: $\mathrm{Acid} \rightleftharpoons \mathrm{Base} + H^+$. This definition marks a major advance, because it frees our concept of acids and bases from any dependency on a solvent." (Johannes Nicholas Brønsted)

Although there are several different definitions of acids and bases, Brønsted and Lowry's definition stands out for its simplicity and generality. Earlier theories of acids and bases were tied to water - if you didn't have water, you couldn't have acid-base chemistry. Now, we recognize that acids and bases have inherent structural characteristics that govern their behavior. We'll look at that behavior in this chapter, learning the Brønsted-Lowry definitions of acids and bases and exploring qualitative and quantitative applications of those definitions to acid, base, and salt solutions; reactions with water; general acid-base reactions; and a special class of acid-base solution known as *buffers*.

Chapter Objectives

- Classify substances as acids (strong or weak), bases (strong or weak), amphoteric, or neither according to Brønsted-Lowry theory.
- Write balanced acid-base reactions; predict, identify, and name conjugate pairs.
- Determine the pH and pOH of a solution containing a single acid, base, or salt.
- Identify buffer solutions and calculate their pH.
- For any titration process, write the neutralization reaction and determine concentration, moles, or pH at the end of the titration.

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11.2: Definitions of Acids and Bases

Learning Objectives

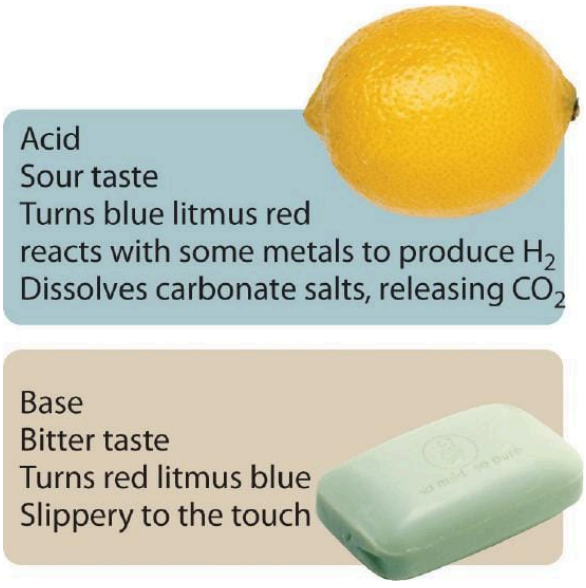
By the end of this section, you will have background information that will help you to be able to:

- Classify substances as acids (strong or weak), bases (strong or weak), amphoteric, or neither according to Brønsted-Lowry theory.

Acid–base reactions are essential in both biochemistry and industrial chemistry. Moreover, many of the substances we encounter in our homes, the supermarket, and the pharmacy are acids or bases. For example, aspirin is an acid (acetylsalicylic acid), and antacids are bases. In fact, every amateur chef who has prepared mayonnaise or squeezed a wedge of lemon to marinate a piece of fish has carried out an acid–base reaction. Before we discuss the characteristics of such reactions, let's first describe some of the properties of acids and bases.

Definitions of Acids and Bases

Although the general properties of acids and bases have been known for more than a thousand years, the definitions of *acid* and *base* have changed dramatically as scientists have learned more about them. In ancient times, an acid was any substance that had a sour taste (e.g., vinegar or lemon juice), caused consistent color changes in dyes derived from plants (e.g., turning blue litmus paper red), reacted with certain metals to produce hydrogen gas and a solution of a salt containing a metal cation, and dissolved carbonate salts such as limestone ($CaCO_3$) with the evolution of carbon dioxide. In contrast, a base was any substance that had a bitter taste, felt slippery to the touch, and caused color changes in plant dyes that differed diametrically from the changes caused by acids (e.g., turning red litmus paper blue). Although these definitions were useful, they were entirely descriptive.



The Arrhenius Definition of Acids and Bases (not used in this class)

The first person to define acids and bases in detail was the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry, 1903). According to the *Arrhenius definition*, an acid is a substance like hydrochloric acid that dissolves in water to produce H^+ ions (protons; Equation $11.2.1$), and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide (OH^-) ions (Equation $11.2.2$):

$$\underset{an\ Arrhenius\ acid}{HCl_{(g)}} \xrightarrow{H_2O_{(l)}} H^+_{(aq)} + Cl^-_{(aq)} \tag{11.2.1}$$

$$\underset{an\ Arrhenius\ base}{NaOH_{(s)}} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + OH^-_{(aq)} \tag{11.2.2}$$

According to Arrhenius, the characteristic properties of acids and bases are due exclusively to the presence of H^+ and OH^- ions, respectively, in solution. Although Arrhenius's ideas were widely accepted, his definition of acids and bases had two major limitations:

1. First, because acids and bases were defined in terms of ions obtained from water, the Arrhenius concept applied only to substances in aqueous solution.
2. Second, and more important, the Arrhenius definition predicted that *only* substances that dissolve in water to produce H^+ and OH^- ions should exhibit the properties of acids and bases, respectively. For example, according to the Arrhenius definition, the reaction of ammonia (a base) with gaseous HCl (an acid) to give ammonium chloride (Equation $11.2.3$) is not an acid–base reaction because it does not involve H^+ and OH^-:

$$NH_{3\ (g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)} \tag{11.2.3}$$

The Brønsted–Lowry Definition of Acids and Bases (used in this class)

Because of the limitations of the Arrhenius definition, a more general definition of acids and bases was needed. One was proposed independently in 1923 by the Danish chemist J. N. Brønsted (1879–1947) and the British chemist T. M. Lowry (1874–1936), who defined acid–base reactions in terms of the transfer of a proton (H^+ ion) from one substance to another.

According to Brønsted and Lowry, an acid (A substance with at least one hydrogen atom that can dissociate to form an anion and an H^+ ion (a proton) in aqueous solution, thereby forming an acidic solution) is any substance that can donate a proton, and a base (a substance that produces one or more hydroxide ions (OH^- and a cation when dissolved in aqueous solution, thereby forming a basic solution) is any substance that can accept a proton. The Brønsted–Lowry definition of an acid is essentially the same as the Arrhenius definition, except that it is not restricted to aqueous solutions. The Brønsted–Lowry definition of a base, however, is far more general because the hydroxide ion is just one of many substances that can accept a proton. Ammonia, for example, reacts with a proton to form NH_4^+, so in Equation $11.2.3$, NH_3 is a Brønsted–Lowry base and HCl is a Brønsted–Lowry acid. Because of its more general nature, the Brønsted–Lowry definition is used throughout this text unless otherwise specified.

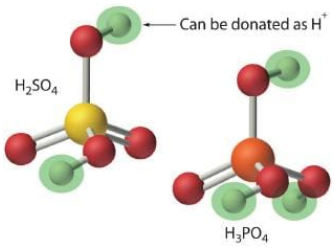
Polyprotic Acids

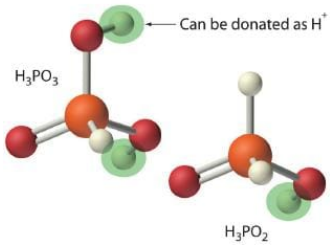
Acids differ in the number of protons they can donate. For example, monoprotic acids (a compound that is capable of donating one proton per molecule) are compounds that are capable of donating a single proton per molecule. Monoprotic acids include HF, HCl, HBr, HI, HNO_3, and HNO_2. All carboxylic acids that contain a single $–CO_2H$ group, such as acetic acid (CH_3CO_2H), are monoprotic acids, dissociating to form RCO_2^- and H^+ (section 4.6). A compound that can donate more than one proton per molecule. can donate more than one proton per molecule. For example, H_2SO_4 can donate two H^+ ions in separate steps, so it is a diprotic acid (a compound that can donate two protons per molecule in separate steps) and H_3PO_4, which is capable of donating three protons in successive steps, is a triprotic acid (a compound that can donate three protons per molecule in separate steps), (Equation $11.2.4$, Equation $11.2.5$, and Equation $11.2.6$):

$$H_3PO_4(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + H_2PO_4^-(aq) \tag{8.7.4}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \tag{8.7.5}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \tag{8.7.6}$$





In chemical equations such as these, a double arrow is used to indicate that both the forward and reverse reactions occur simultaneously, so the forward reaction does not go to completion. Instead, the solution contains significant amounts of both reactants and products. Over time, the reaction reaches a state in which the concentration of each species in solution remains constant. The reaction is then said to be in equilibrium (the point at which the rates of the forward and reverse reactions become the same, so that the net composition of the system no longer changes with time).

Strengths of Acids and Bases

Strong acids react essentially completely with water) to give H^+ and the corresponding anion. The equilibrium constant for the reaction of a strong acid with water is much larger than 1. See Table $11.2.1$ a list of six (6) strong acids to memorize.

Similarly, strong bases dissociates essentially completely in water) to give OH^- and the corresponding cation. Strong bases are the hydroxides of the alkali metals and the heavier alkaline earths (Ca, Sr, and Ba).

Table $11.2.1$ Common Strong Acids and Bases

Strong Acids		Strong Bases	
Hydrogen Halides	Oxoacids	Group 1 Hydroxides	Hydroxides of the Heavier Group 2 Elements
HCl	HNO_3	LiOH	$Ca(OH)_2$
HBr	H_2SO_4	NaOH	$Sr(OH)_2$
HI	$HClO_4$	KOH	$Ba(OH)_2$
		RbOH	
		CsOH	

All other acids and bases are considered *weak acids* or *weak bases*. These do not dissociate completely in water and the equilibrium constant for the dissolution process is less than one. Note that an acid's strength or weakness is not correlated with its solubility. For example, acetic acid is *very* soluble in water, but almost all of the acetic acid in solution exists in the form of neutral molecules (less than 1% dissociates). Another example is the common weak base ammonia, which reacts with water to form small amounts of hydroxide ion:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{11.2.4}$$

Most of the ammonia (>99%) is present in the form of $NH_3(g)$. Amines, which are organic analogues of ammonia, are also weak bases, as are ionic compounds that contain anions derived from weak acids (such as S^{2-}).

Example 11.2.1

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

1. $CH_3CH_2CO_2H$
2. CH_3OH
3. $Sr(OH)_2$
4. $CH_3CH_2NH_2$
5. $HBrO_4$

Given: compound

Asked for: acid or base strength

Strategy:

A Determine whether the compound is organic or inorganic.

B If inorganic, determine whether the compound is acidic or basic by the presence of dissociable H^+ or OH^- ions, respectively. If organic, identify the compound as a weak base or a weak acid by the presence of an amine or a carboxylic acid group, respectively. Recall that all polyprotic acids except H_2SO_4 are weak acids.

Solution

1. **A** This compound is propionic acid, which is organic. **B** It contains a carboxylic acid group analogous to that in acetic acid, so it must be a weak acid.
2. **A** CH_3OH is methanol, an organic compound that contains the –OH group. **B** As a covalent compound, it does not dissociate to form the OH^- ion. Because it does not contain a carboxylic acid ($–CO_2H$) group, methanol also cannot dissociate to form $H^+(aq)$ ions. Thus we predict that in aqueous solution methanol is neither an acid nor a base.
3. **A** $Sr(OH)_2$ is an inorganic compound that contains one Sr^{2+} and two OH^- ions per formula unit. **B** We therefore expect it to be a strong base, similar to $Ca(OH)_2$.
4. **A** $CH_3CH_2NH_2$ is an amine (ethylamine), an organic compound in which one hydrogen of ammonia has been replaced by an R group. **B** Consequently, we expect it to behave similarly to ammonia (Equation 8.6.7), reacting with water to produce small amounts of the OH^- ion. Ethylamine is therefore a weak base.
5. **A** $HBrO_4$ is perbromic acid, an inorganic compound. **B** It is not listed in Table 8.3 as one of the common strong acids, but that does not necessarily mean that it is a weak acid. If you examine the periodic table, you can see that Br lies directly below Cl in group 17. We might therefore expect that $HBrO_4$ is chemically similar to $HClO_4$, a strong acid—and, in fact, it is.

Exercise 11.2.1

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

1. $Ba(OH)_2$
2. HIO_4
3. $CH_3CH_2CH_2CO_2H$
4. $(CH_3)_2NH$
5. CH_2O

Answer available at the end of this section.

Summary

Acid–base reactions require both an acid and a base. In Brønsted–Lowry terms, an **acid** is a substance that can donate a proton (H^+), and a **base** is a substance that can accept a proton. All acid–base reactions contain two acid–base pairs: the reactants and the products. Acids can donate one proton (**monoprotic acids**), two protons (**diprotic acids**), or three protons (**triprotic acids**). Compounds that are capable of donating more than one proton are generally called **polyprotic acids**. Acids also differ in their tendency to donate a proton, a measure of their acid strength. **Strong acids** react completely with water to produce $H_3O^+(aq)$ (the **hydronium ion**), whereas **weak acids** dissociate only partially in water. Conversely, **strong bases** react completely with water to produce the hydroxide ion, whereas **weak bases** react only partially with water to form hydroxide ions.

Conceptual Problems

1. Why was it necessary to expand on the Arrhenius definition of an acid and a base? What specific point does the Brønsted–Lowry definition address?

2. State whether each compound is an acid, a base, or a salt.

   a. $CaCO_3$
   b. $NaHCO_3$
   c. H_2SO_4
   d. $CaCl_2$
   e. $Ba(OH)_2$

3. State whether each compound is an acid, a base, or a salt.

   a. NH_3
   b. NH_4Cl
   c. H_2CO_3
   d. CH_3COOH
   e. NaOH

4. Classify each compound as a strong acid, a weak acid, a strong base, or a weak base in aqueous solution.

   a. sodium hydroxide
   b. acetic acid
   c. magnesium hydroxide
   d. tartaric acid
   e. sulfuric acid
   f. ammonia
   g. hydroxylamine (NH_2OH)
   h. hydrocyanic acid

5. Decide whether each compound forms an aqueous solution that is strongly acidic, weakly acidic, strongly basic, or weakly basic.

   a. propanoic acid
   b. hydrobromic acid
   c. methylamine
   d. lithium hydroxide
   e. citric acid
   f. sodium acetate
   g. ammonium chloride
   h. barium hydroxide

6. What is the relationship between the strength of an acid and the strength of the conjugate base derived from that acid? Would you expect the $CH_3CO_2^-$ ion to be a strong base or a weak base? Why? Is the hydronium ion a strong acid or a weak acid? Explain your answer.

Answer

1.
2.
3.
4.
5. a. weakly acidic
   b. strongly acidic
   c. weakly basic
   d. strongly basic
   e. weakly acidic
   f. weakly basic
   g. weakly acidic
   h. strongly basic
6.

Contributors

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Modified by Joshua Halpern (Howard University)

Video from Colin McKay @ YouTube

Answers

Exercise 11.2.1

1. strong base
2. strong acid
3. weak acid
4. weak base
5. none of these; formaldehyde is a neutral molecule

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11.3: Acid-Base Reactions

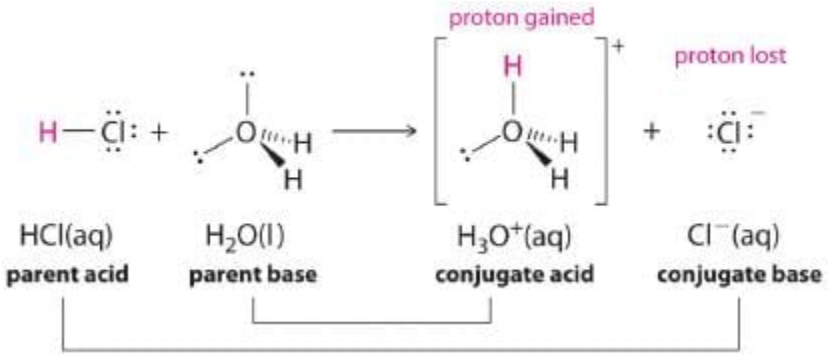
Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Classify substances as acids (strong or weak), bases (strong or weak), amphoteric, or neither according to Brønsted-Lowry theory.
- Write balanced acid-base reactions; predict, identify, and name conjugate pairs.

Conjugate Acid–Base Pairs

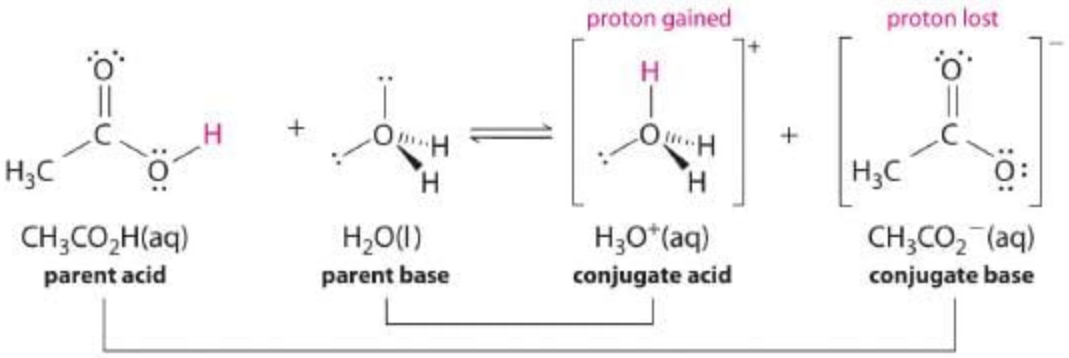
Recall that acids and bases can be defined in terms of the transfer of a proton from an acid to a base. Thus for every acidic species in an aqueous solution, there exists a species derived from the acid by the loss of a proton. These two species that differ by only a proton constitute a conjugate acid–base pair. For example, in the reaction of HCl with water (Equation 16.1.1), HCl, the *parent acid*, donates a proton to a water molecule, the *parent base*, thereby forming Cl^-. Thus HCl and Cl^- constitute a conjugate acid–base pair. By convention, we always write a conjugate acid–base pair as the acid followed by its conjugate base. In the reverse reaction, the Cl^- ion in solution acts as a base to accept a proton from H_3O^+, forming H_2O and HCl. Thus H_3O^+ and H_2O constitute a second conjugate acid–base pair. In general, any acid–base reaction must contain *two* conjugate acid–base pairs, which in this case are HCl/Cl^- and H_3O^+/H_2O.



Note the Pattern

All acid–base reactions contain *two* conjugate acid–base pairs.

Similarly, in the reaction of acetic acid with water, acetic acid donates a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base. Once again, we have two conjugate acid–base pairs: the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and the parent base and its conjugate acid (H_3O^+/H_2O).



In the reaction of ammonia with water to give ammonium ions and hydroxide ions (Equation 16.1.3), ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-. Some common conjugate acid–base pairs are shown in Figure 16.2.1.

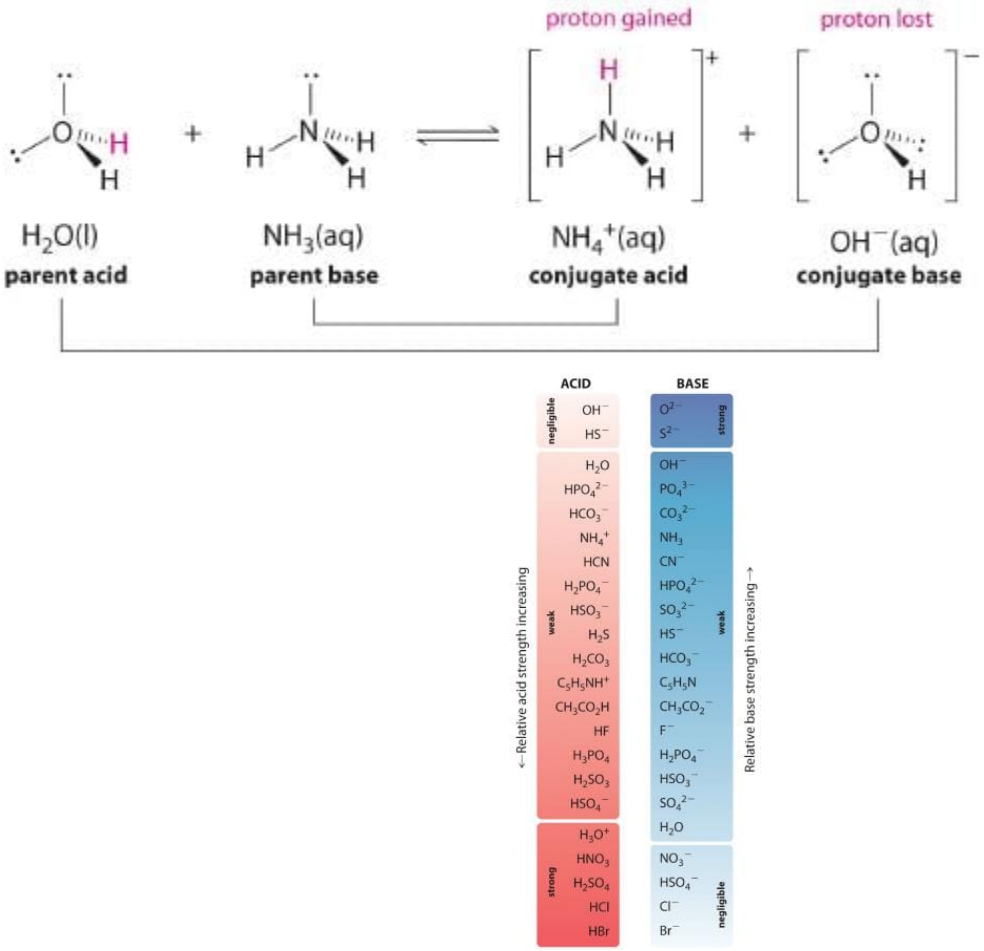


Figure 16.2.1 The Relative Strengths of Some Common Conjugate Acid–Base **Pairs** The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Acid–Base Equilibrium Constants: K_a, K_b, pK_a, and pK_b

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids

and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A^- is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{16.2.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{16.2.2}$$

As we noted earlier, the concentration of water is essentially constant for all reactions in aqueous solution, so [H_2O] in Equation 16.2.2 can be incorporated into a new quantity, the acid ionization constant (K_a)An equilibrium constant for the ionization (dissociation) of a weak acid (HA) with water, HA(aq) + H_2O(l) ⇌ $H_3O(aq)^+$ + A^-(aq), in which the concentration of water is treated as a constant: Ka = [$H_3O(aq)^+$][A^-(aq)]/[HA], also called the *acid dissociation constant*:

$$K_a = K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]} \tag{16.2.3}$$

Thus the numerical values of K and K_a differ by the concentration of water (55.3 M). Again, for simplicity, H_3O^+ can be written as H^+ in Equation 16.2.3. Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form H_3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium.Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the *activities* of H^+ or OH^-, thus making them unitless. The values of K_a for a number of common acids are given in Table 16.2.1.

Table 16.2.1 Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA) and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^{9}	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^{2}	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^{1}	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	NO_2^-	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2^-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	HOCl	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
***The number in parentheses indicates the ionization step referred to for a polyprotic acid.**						

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0
***The number in parentheses indicates the ionization step referred to for a polyprotic acid.**						

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH^+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{16.2.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b)An equilibrium constant for the reaction of a weak base (B) with water, B(aq) + H_2O(l) ⇌ BH^+(aq) + OH^-(aq), in which the concentration of water is treated as a constant: Kb = $[BH^+][OH^-]/[B]$, also called the *base dissociation constant*:

$$K_b = K[H_2O] = [BH^+][OH^-][B] \tag{16.2.5}$$

Once again, the concentration of water is constant, so it does not appear in the equilibrium constant expression; instead, it is included in the K_b. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 16.2.2

Table 16.2.2 Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH^+)

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0*	0.00
***As in Table 16.2.**						

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{16.2.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{16.2.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{16.2.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{16.2.9}$$

If we add Equation 16.2.8 and Equation 16.2.9, we obtain the following (recall from Chapter 15 that the equilibrium constant for the *sum* of two reactions is the *product* of the equilibrium constants for the individual reactions):

$$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}} \quad K_a = [H^+]\,\cancel{[CN^-]} \,/\, \cancel{[HCN]}$$

$$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}} \quad K_b = [OH^-]\,\cancel{[HCN]} \,/\, \cancel{[CN^-]}$$

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \quad K = K_a \times K_b = [H^+][OH^-]$$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_aK_b = K_w \tag{16.2.10}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pK_w, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{16.2.11}$$

$$K_a = 10^{-pK_a} \tag{16.2.12}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{16.2.13}$$

$$K_b = 10^{-pK_b} \tag{16.2.14}$$

Similarly, Equation 16.2.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{16.2.15}$$

At 25°C, this becomes

$$pK_a + pK_b = 14.00 \tag{16.2.16}$$

The values of pK_a and pK_b are given for several common acids and bases in Table 16.2.1 and Table 16.2.2 , respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a 1000 times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 16.2.1 . The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 16.2 are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

Note the Pattern

The conjugate base of a strong acid is a weak base and vice versa.

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: *an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows*:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow\rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{16.2.17}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3CO_2{}_{(aq)}^-}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

Note the Pattern

All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.

Example 16.2.1

1. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
2. Calculate K_a and pK_a of the dimethylammonium ion [$(CH_3)_2NH_2^+$]. The base ionization constant K_b of dimethylamine [$(CH_3)_2NH$] is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 16.2.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equation 16.2.15 and Equation 16.2.16. Use the relationships $pK = -\log K$ and $K = 10^{-pK}$ (Equation 16.24 and Equation 16.26) to convert between K_a and pK_a or K_b and pK_b.

Solution:

1. We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 16.2.16: $pK_a + pK_b = pK_w = 14.00$. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

2. In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 16.23: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

Because $pK_a = -\log K_a$, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27$$

$$pKa + pK_b = 14.00$$

$$pK_a = 10.73$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

Exercise

Lactic acid [$CH_3CH(OH)CO_2H$] is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer: $K_a = 1.4 \times 10^{-4}$ for lactic acid; $pK_b = 10.14$ and $K_b = 7.2 \times 10^{-11}$ for the lactate ion

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table 16.2.1 that acids like H_2SO_4 and HNO_3 lie *above* the hydronium ion, meaning that they have pK_a values less than zero and are stronger acids than the H_3O^+ ion. The acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving HNO_3 instead. In fact, all six of the common strong acids have pK_a values less than zero, which means that they have a greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibriums for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 10^8 greater than K_a for HNO_3, the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I^- or NO_3^-. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, *regardless of the identity of the strong acid*. This phenomenon is called the leveling effectThe phenomenon that makes H_3O^+ the strongest acid that can exist in water. Any species that is a stronger acid than H_3O^+ is leveled to the strength of H_3O^+ in aqueous solution.: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO_3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O. Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like

a weak acid *in this solvent*. This result clearly tells us that HI is a stronger acid than HNO_3. The relative order of acid strengths and approximate K_a and pK_a values for the strong acids at the top of Table 16.2.1 were determined using measurements like this and different nonaqueous solvents.

Note the Pattern

In aqueous solutions, $[H_3O^+]$ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O.

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH^- is leveled to the strength of OH^- because OH^- is the strongest base that can exist in equilibrium with water. Salts such as K_2O, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table 16.3, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + 2K^+_{(aq)} \tag{16.2.18}$$

$$NaOCH_{3(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + CH_3OH_{(aq)} \tag{16.2.19}$$

$$NaNH_{2(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + NH_{3(aq)} \tag{16.2.20}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).

Polyprotic Acids and Bases

Polyprotic acids such as H_2SO_4, H_3PO_4, and H_2CO_3 contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases. Consider H_2SO_4, for example:

$$HSO^-_{4(aq)} \rightleftharpoons SO^{2-}_{4(aq)} + H^+_{(aq)} \quad pK_a = -2$$

The equilibrium in the first reaction lies far to the right, consistent with H_2SO_4 being a strong acid. In contrast, in the second reaction, appreciable quantities of both HSO_4^- and SO_4^{2-} are present at equilibrium.

Note the Pattern

For a polyprotic acid, acid strength decreases and the pK_a increases with the sequential loss of each proton.

The hydrogen sulfate ion (HSO_4^-) is both the conjugate base of H_2SO_4 and the conjugate acid of SO_4^{2-}. Just like water, HSO_4^- can therefore act as *either* an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion (SO_4^{2-}) is a *polyprotic base* that is capable of accepting two protons in a stepwise manner:

$$SO^{2-}_{4(aq)} + H_2O_{(aq)} \rightleftharpoons HSO^-_{4(aq)} + OH^-_{(aq)}$$

$$HSO^-_{4(aq)} + H_2O_{(aq)} \rightleftharpoons H_2SO_{4(aq)} + OH^-_{(aq)}$$

Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by $pK_a + pK_b = pK_w$. Consider, for example, the HSO_4^-/ SO_4^{2-} conjugate acid–base pair. From Table 16.2.1, we see that the pK_a of HSO_4^- is 1.99. Hence the pK_b of SO_4^{2-} is 14.00 − 1.99 = 12.01. Thus sulfate is a rather weak base, whereas OH^- is a strong base, so the equilibrium shown above lies to the left. The HSO_4^- ion is also a very weak base [pK_a of H_2SO_4 = 2.0, pK_b of HSO_4^- = 14 − (−2.0) = 16], which is consistent with what we expect for the conjugate base of a strong acid. Thus the equilibrium also lies almost completely to the left. Once again, equilibrium favors the formation of the weaker acid–base pair.

Example 16.2.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $NH^{+}_{4(aq)} + PO^{3-}_{4(aq)} \rightleftharpoons NH_{3(aq)} + HPO^{2-}_{4(aq)}$
- $CH_3CH_2CO_2H_{(aq)} + CN^{-}_{(aq)} \rightleftharpoons CH_3CH_2CO^{-}_{2(aq)} + HCN_{(aq)}$

Given: balanced chemical equation

Asked for: equilibrium position

Strategy:

Identify the conjugate acid–base pairs in each reaction. Then refer to Table 16.2.1 Table 16.2.2, and Figure 16.2.1 to determine which is the stronger acid and base. Equilibrium always favors the formation of the weaker acid–base pair.

Solution:

1. The conjugate acid–base pairs are NH_4^+/NH_3 and HPO_4^{2-}/PO_4^{3-}. According to Table 16.2 and Table 16.3, NH_4^+ is a stronger acid (pK_a = 9.25) than HPO_4^{2-} (pK_a = 12.32), and PO_4^{3-} is a stronger base (pK_b = 1.68) than NH_3 (pK_b = 4.75). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{NH^{+}_{4(aq)}} + \underset{\text{stronger base}}{PO^{3-}_{4(aq)}} \rightleftharpoons \underset{\text{weaker base}}{NH_{3(aq)}} + \underset{\text{weaker acid}}{HPO^{2-}_{4(aq)}}$$

2. The conjugate acid–base pairs are $CH_3CH_2CO_2H/CH_3CH_2CO_2^-$ and HCN/CN^-. According to Table 16.2.1, HCN is a weak acid (pK_a = 9.21) and CN^- is a moderately weak base (pK_b = 4.79). Propionic acid ($CH_3CH_2CO_2H$) is not listed in Table 16.2.1, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties *are* listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ($–CH_2CH_3$ versus $–CH_3$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the pK_a of propionic acid to be similar in magnitude to the pK_a of acetic acid. (In fact, the pK_a of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{CH_3CH_2CO_2H_{(aq)}} + \underset{\text{stronger base}}{CN^{-}_{(aq)}} \rightleftharpoons \underset{\text{weaker base}}{CH_3CH_2CO^{-}_{2(aq)}} + \underset{\text{weaker acid}}{HCN_{(aq)}}$$

Exercise

Predict whether the equilibrium for each reaction lies to the left or the right as written.

1. $H_2O_{(l)} + HS^{-}_{(aq)} \rightleftharpoons OH^{-}_{(aq)} + H_2S_{(aq)}$
2. $HCO^{-}_{2(aq)} + HSO^{-}_{4(aq)} \rightleftharpoons HCO_2H_{(aq)} + SO^{2-}_{4(aq)}$

Answer

1. left
2. left

Acid–Base Properties of Solutions of Salts

We can also use the relative strengths of conjugate acid–base pairs to understand the acid–base properties of solutions of salts. A *neutralization reaction* can be defined as the reaction of an acid and a base to produce a salt and water. That is, another cation,

such as Na^+, replaces the proton on the acid. An example is the reaction of CH_3CO_2H, a weak acid, with NaOH, a strong base:

$$\underset{acid}{CH_3CO_2H_{(l)}} + \underset{base}{NaOH_{(s)}} \xrightarrow{H_2O} \underset{salt}{H_2OCH_3CO_2Na_{(aq)}} + \underset{water}{H_2O_{(l)}} \tag{16.2.22}$$

Depending on the acid–base properties of its component ions, however, a salt can dissolve in water to produce a neutral solution, a basic solution, or an acidic solution.

When a salt such as NaCl dissolves in water, it produces Na^+(aq) and Cl^-(aq) ions. Using a Lewis approach, the Na^+ ion can be viewed as an acid because it is an electron pair acceptor, although its low charge and relatively large radius make it a very weak acid. The Cl^- ion is the conjugate base of the strong acid HCl, so it has essentially no basic character. Consequently, dissolving NaCl in water has no effect on the pH of a solution, and the solution remains neutral.

Now let's compare this behavior to the behavior of aqueous solutions of potassium cyanide and sodium acetate. Again, the cations (K^+ and Na^+) have essentially no acidic character, but the anions (CN^- and $CH_3CO_2^-$) are weak bases that can react with water because they are the conjugate bases of the weak acids HCN and acetic acid, respectively.

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)} \tag{16.2.23}$$

$$CH_3CO^2_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)} \tag{16.2.24}$$

Neither reaction proceeds very far to the right as written because the formation of the weaker acid–base pair is favored. Both HCN and acetic acid are stronger acids than water, and hydroxide is a stronger base than either acetate or cyanide, so in both cases, the equilibrium lies to the left. Nonetheless, each of these reactions generates enough hydroxide ions to produce a basic solution. For example, the pH of a 0.1 M solution of sodium acetate or potassium cyanide at 25°C is 8.8 or 11.1, respectively. From Table 16.2.2 and Figure 16.2.1, we can see that CN^- is a stronger base (pK_b = 4.79) than acetate (pK_b = 9.24), which is consistent with KCN producing a more basic solution than sodium acetate at the same concentration.

In contrast, the conjugate acid of a weak base should be a weak acid (Figure 16.2.1). For example, ammonium chloride and pyridinium chloride are salts produced by reacting ammonia and pyridine, respectively, with HCl. As you already know, the chloride ion is such a weak base that it does not react with water. In contrast, the cations of the two salts are weak acids that react with water as follows:

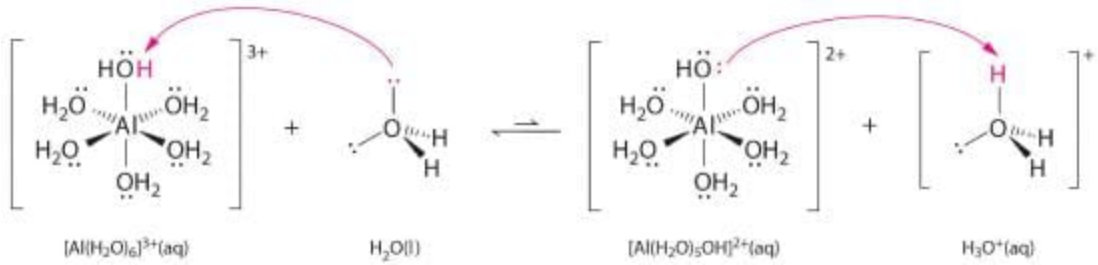
$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons HH_{3(aq)} + H_3O^+_{(aq)} \tag{16.2.25}$$

$$C_5H_5NH^+_{(aq)} + H_2O_{(l)} \rightleftharpoons C_5H_5NH_{(aq)} + H_3O^+_{(aq)} \tag{16.2.26}$$

Figure 16.2.1 shows that H_3O^+ is a stronger acid than either NH_4^+ or $C_5H_5NH^+$, and conversely, ammonia and pyridine are both stronger bases than water. The equilibrium will therefore lie far to the left in both cases, favoring the weaker acid–base pair. The H_3O^+ concentration produced by the reactions is great enough, however, to decrease the pH of the solution significantly: the pH of a 0.10 M solution of ammonium chloride or pyridinium chloride at 25°C is 5.13 or 3.12, respectively. This is consistent with the information shown in Figure 16.2.1, indicating that the pyridinium ion is more acidic than the ammonium ion.

What happens with aqueous solutions of a salt such as ammonium acetate, where both the cation *and* the anion can react separately with water to produce an acid and a base, respectively? According to Eq 16.2.25, the ammonium ion will lower the pH, while according to Eq 16.2.24, the acetate ion will raise the pH. This particular case is unusual, in that the cation is as strong an acid as the anion is a base ($pK_a \approx pK_b$). Consequently, the two effects cancel, and the solution remains neutral. With salts in which the cation is a stronger acid than the anion is a base, the final solution has a pH < 7.00. Conversely, if the cation is a weaker acid than the anion is a base, the final solution has a pH > 7.00.

Solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion (part (a) in Figure 16.2.2), as discussed in Chapter 8 . A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.



Second, the positive charge on the Al^{3+} ion attracts electron density from the oxygen atoms of the water molecules, which decreases the electron density in the O–H bonds, as shown in part (b) in Figure 16.2.2. With less electron density between the O atoms and the H atoms, the O–H bonds are weaker than in a free H_2O molecule, making it easier to lose a H^+ ion.

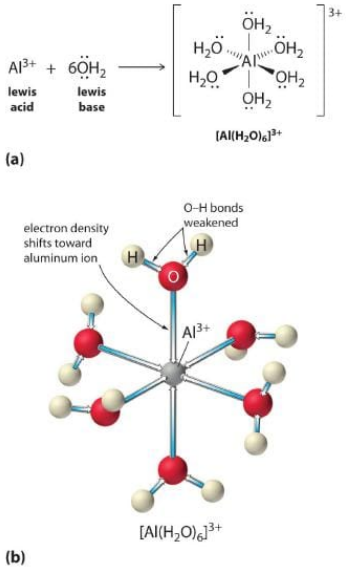


Figure 16.2.2 Effect of a Metal Ion on the Acidity of Water(a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton.

The magnitude of this effect depends on the following two factors (Figure 16.2.3):

1. **The *charge* on the metal ion.** A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^+) of the same radius.
2. **The *radius* of the metal ion.** For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

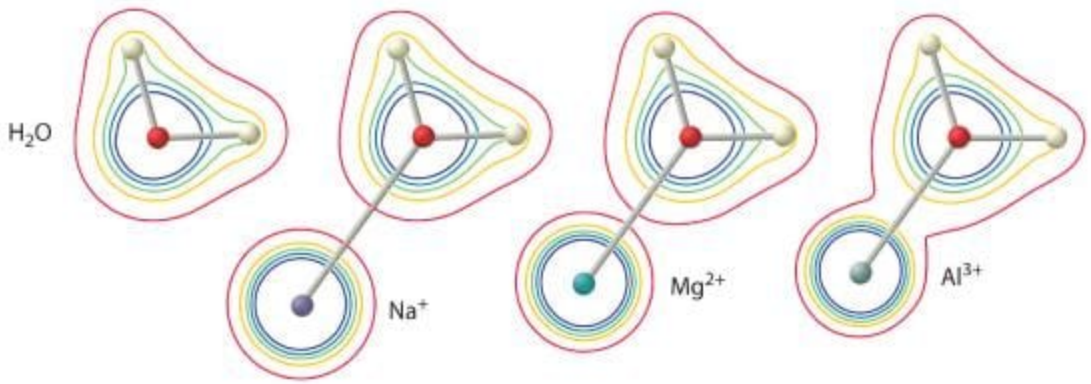


Figure 16.2.3 The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^+, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases.

Thus aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+}, are acidic:

$$[Al(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)} \tag{16.2.27}$$

The $[Al(H_2O)_6]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameter for predicting the effect of a metal ion on the acidity of coordinated water molecules is the *charge-to-radius ratio* of the metal ion. A number of pairs of metal ions that lie on a diagonal line in the periodic table, such as Li^+ and Mg^{2+} or Ca^{2+} and Y^{3+}, have different sizes and charges but similar charge-to-radius ratios. As a result, these pairs of metal ions have similar effects on the acidity of coordinated water molecules, and they often exhibit other significant similarities in chemistry as well.

Note the Pattern

Solutions of small, highly charged metal ions in water are acidic.

Reactions such as those discussed in this section, in which a salt reacts with water to give an acidic or basic solution, are often called hydrolysis reactionsA chemical reaction in which a salt reacts with water to yield an acidic or a basic solution.. Using a separate name for this type of reaction is unfortunate because it suggests that they are somehow different. In fact, hydrolysis reactions are just acid–base reactions in which the acid is a cation or the base is an anion; they obey the same principles and rules as all other acid–base reactions.

Note the Pattern

A hydrolysis reaction is an acid–base reaction.

Example 16.2.3

Predict whether aqueous solutions of these compounds are acidic, basic, or neutral.

1. KNO_3
2. $CrBr_3{\cdot}6H_2O$
3. Na_2SO_4

Given: compound

Asked for: acidity or basicity of aqueous solution

Strategy:

A Assess the acid–base properties of the cation and the anion. If the cation is a weak Lewis acid, it will not affect the pH of the solution. If the cation is the conjugate acid of a weak base or a relatively highly charged metal cation, however, it will react with water to produce an acidic solution.

B If the anion is the conjugate base of a strong acid, it will not affect the pH of the solution. If, however, the anion is the conjugate base of a weak acid, the solution will be basic.

Solution:

1. **A** The K^+ cation has a small positive charge (+1) and a relatively large radius (because it is in the fourth row of the periodic table), so it is a very weak Lewis acid.

   B The NO_3^- anion is the conjugate base of a strong acid, so it has essentially no basic character (Table 16.1). Hence neither the cation nor the anion will react with water to produce H^+ or OH^-, and the solution will be neutral.

2. **A** The Cr^{3+} ion is a relatively highly charged metal cation that should behave similarly to the Al^{3+} ion and form the $[Cr(H_2O)_6]^{3+}$ complex, which will behave as a weak acid:

   $$Cr(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons Cr(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(}aq)$$

   B The Br^- anion is a very weak base (it is the conjugate base of the strong acid HBr), so it does not affect the pH of the solution. Hence the solution will be acidic.

3. **A** The Na^+ ion, like the K^+, is a very weak acid, so it should not affect the acidity of the solution.

   B In contrast, SO_4^{2-} is the conjugate base of HSO_4^-, which is a weak acid. Hence the SO_4^{2-} ion will react with water as shown in Figure 16.6 to give a slightly basic solution.

Exercise

Predict whether aqueous solutions of the following are acidic, basic, or neutral.

1. KI
2. $Mg(ClO_4)_2$
3. NaHS

Answer

1. neutral
2. acidic
3. basic (due to the reaction of HS^- with water to form H_2S and OH^-)

Summary

Two species that differ by only a proton constitute a **conjugate acid–base pair**. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the **acid ionization constant (K_a)**. Similarly, the equilibrium constant for the reaction of a weak base with water is the **base ionization constant (K_b)**. For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, pK_a + pK_b = 14.00. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the **leveling effect**. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base. A salt can dissolve in water to produce a neutral, a basic, or an acidic solution, depending on whether it contains the

conjugate base of a weak acid as the anion (A^-), the conjugate acid of a weak base as the cation (BH^+), or both. Salts that contain small, highly charged metal ions produce acidic solutions in water. The reaction of a salt with water to produce an acidic or a basic solution is called a **hydrolysis reaction**.

Key Takeaways

- Acid–base reactions always contain two conjugate acid–base pairs.
- Each acid and each base has an associated ionization constant that corresponds to its acid or base strength.

Key Equations

Acid ionization constant

Equation 16.2.13: $K_a = K[H_2O] = \dfrac{[H_3O^+][A^-]}{[HA]}$

Base ionization constant

Equation 16.2.15: $K_b = K[H_2O] = [BH^+][OH^-][B]$

Relationship between K_a and K_b of a conjugate acid–base pair

Equation 16.2.20: $K_a K_b = K_w$

Definition of pK_a

Equation 16.2.21: $pKa = -\log_{10} K_a$

Equation 16.2.22: $K_a = 10^{-pK_a}$

Definition of pK_b

Equation 16.2.23: $pK_b = -\log_{10} K_b$

Equation 16.2.25: $K_b = 10^{-pK_b}$

Relationship between pK_a and pK_b of a conjugate acid–base pair

Equation 16.2.25: $pK_a + pK_b = pK_w$

Equation 16.29: $pK_a + pK_b = 14.00 \text{ at } 25^\circ\text{C}$

Conceptual Problems

1. Identify the conjugate acid–base pairs in each equilibrium.
    1. $HSO^-_{4(aq)} + H_2O_{(l)} \rightleftharpoons SO^{2-}_{4(aq)} + H_3O^+_{(aq)}$
    2. $C_3H_7NO_{2(aq)} + H_3O^+_{(aq)} \rightleftharpoons C_3H_8NO^+_{2(aq)} + H_2O_{(l)}$
    3. $CH_3CO_2H_{(aq)} + NH_{3(aq)} \rightleftharpoons CH_3CO^-_{2(aq)} + NH^+_{4(aq)}$
    4. $SbF_{5(aq)} + 2HF_{(aq)} \rightleftharpoons H_2F^+_{(aq)} + SbF^-_{6(aq)}$
2. Identify the conjugate acid–base pairs in each equilibrium.
    1. $HF(aq) + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$
    2. $CH_3CH_2NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CH_2NH^+_{3(aq)} + OH^-_{(aq)}$
    3. $C_3H_7NO_{2(aq)} + OH^-_{(aq)} \rightleftharpoons C_3H_6NO^-_{2(aq)} + H_2O_{(l)}$

4. $CH_3CO_2H_{(aq)} + 2HF_{(aq)} \rightleftharpoons CH_3C(OH)_2 + (aq) + HF^-_{2(aq)}$

3. Salts such as NaH contain the hydride ion (H^-). When sodium hydride is added to water, it produces hydrogen gas in a highly vigorous reaction. Write a balanced chemical equation for this reaction and identify the conjugate acid–base pairs.

4. Write the expression for K_a for each reaction.

   1. $HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons CO^{2-}_{3(aq)} + H_3O^+_{(aq)}$
   2. $formic\ \ acid_{(aq)} + H_2O_{(l)} \rightleftharpoons formate_{(aq)} + H_3O^+_{(aq)}$
   3. $H_3PO_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_2PO^-_{4(aq)} + H_3O^+_{(aq)}$

5. Write an expression for the ionization constant K_b for each reaction.

   1. $OCH^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons HOCH_{3(aq)} + OH - (aq)$
   2. $NH^-_{2(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + OH^-_{(aq)}$
   3. $S^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons HS^-_{(aq)} + OH^-_{(aq)}$

6. Predict whether each equilibrium lies primarily to the left or to the right.

   1. $HBr_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Br^-_{(aq)}$
   2. $NaH_{(soln)} + NH_{3(l)} \rightleftharpoons H2(soln) + NaNH_{2(soln)}$
   3. $OCH^-_{3(aq)} + NH_{3(aq)} \rightleftharpoons CH3OH(aq) + NH^-_{2(aq)}$
   4. $NH_{3(aq)} + HCl_{(aq)} \rightleftharpoons NH^+_{4(aq)} + Cl^-_{(aq)}$

7. Species that are strong bases in water, such as CH_3^-, NH_2^-, and S^{2-}, are leveled to the strength of OH^-, the conjugate base of H_2O. Because their relative base strengths are indistinguishable in water, suggest a method for identifying which is the strongest base. How would you distinguish between the strength of the acids HIO_3, H_2SO_4, and $HClO_4$?

8. Is it accurate to say that a 2.0 M solution of H_2SO_4, which contains two acidic protons per molecule, is 4.0 M in H^+? Explain your answer.

9. The alkalinity of soil is defined by the following equation: alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$. The source of both HCO_3^- and CO_3^{2-} is H_2CO_3. Explain why the basicity of soil is defined in this way.

10. Why are aqueous solutions of salts such as $CaCl_2$ neutral? Why is an aqueous solution of $NaNH_2$ basic?

11. Predict whether aqueous solutions of the following are acidic, basic, or neutral.

    1. Li_3N
    2. NaH
    3. KBr
    4. $C_2H_5NH_3^+Cl^-$

12. When each compound is added to water, would you expect the pH of the solution to increase, decrease, or remain the same?

    1. $LiCH_3$
    2. $MgCl_2$
    3. K_2O
    4. $(CH_3)_2NH_2^+Br^-$

13. Which complex ion would you expect to be more acidic—$Pb(H_2O)_4^{2+}$ or $Sn(H_2O)_4^{2+}$? Why?

14. Would you expect $Sn(H_2O)_4^{2+}$ or $Sn(H_2O)_6^{4+}$ to be more acidic? Why?

15. Is it possible to arrange the hydrides LiH, RbH, KH, CsH, and NaH in order of increasing base strength in aqueous solution?

Why or why not?

Answer

1. 1. $\underset{\text{base 2}}{HSO^-_{4(aq)}} + H_2O_{(l)} \rightleftharpoons \underset{\text{acid 2}}{SO^{2-}_{4(aq)}} + H_3O^+_{(aq)}$
   2. $\underset{\text{base 2}}{C_3H_7NO_{2(aq)}} + H_3O^+_{(aq)} \rightleftharpoons C_3H_8NO^+_{2(aq)} + H_2O_{(l)}$
   3. $HOAc_{(aq)} + \underset{\text{base 2}}{NH_{3(aq)}} \rightleftharpoons \underset{\text{acid 2}}{CH_3CO^-_{2(aq)}} + NH^+_{4(aq)}$
   4. $SbF_{5(aq)} + \underset{\text{base 2}}{2HF_{(aq)}} \rightleftharpoons \underset{\text{acid 2}}{H_2F^+_{(aq)}} + SbF^-_6(aq)$
2.
3.
4.
5.
6.
7.
8.
9.
10.
11.
12.
13.
14.
15.

Numerical Problems

1. Arrange these acids in order of increasing strength.

   - acid A: pK_a = 1.52
   - acid B: pK_a = 6.93
   - acid C: pK_a = 3.86

   Given solutions with the same initial concentration of each acid, which would have the highest percent ionization?

2. Arrange these bases in order of increasing strength:

   - base A: pK_b = 13.10
   - base B: pK_b = 8.74
   - base C: pK_b = 11.87

   Given solutions with the same initial concentration of each base, which would have the highest percent ionization?

3. Calculate the K_a and the pK_a of the conjugate acid of a base with each pK_b value.

   1. 3.80
   2. 7.90
   3. 13.70
   4. 1.40
   5. −2.50

4. Benzoic acid is a food preservative with a pK_a of 4.20. Determine the K_b and the pK_b for the benzoate ion.

5. Determine K_a and pK_a of boric acid [$B(OH)_3$], solutions of which are occasionally used as an eyewash; the pK_b of its conjugate

base is 4.80.

Answers

1. acid B < acid C < acid A (strongest)
2.
3.
    1. $K_a = 6.3 \times 10^{-11}$; $pK_a = 10.20$
    2. $K_a = 7.9 \times 10^{-7}$; $pK_a = 6.10$
    3. $K_a = 0.50$; $pK_a = 0.30$
    4. $K_a = 2.5 \times 10^{-13}$; $pK_a = 12.60$
    5. $K_a = 3.2 \times 10^{-17}$; $pK_a = 16.50$
4.
5. $K_a = 6.3 \times 10^{-10}$ $pK_a = 9.20$

Contributors

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Modified by Joshua B. Halpern

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11.4: The Autoionization of Water and Solution pH

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Classify substances as acids (strong or weak), bases (strong or weak), amphoteric, or neither according to Brønsted-Lowry theory.
- Determine the pH and pOH of a solution containing a single acid, base, or salt.

In the previous section, we discussed several different definitions of acids and bases. going forward, we will use the *Brønsted–Lowry definition*. In Brønsted–Lowry terms, a base is any substance that can *accept* a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton . Consequently, all Brønsted–Lowry acid–base reactions actually involve *two* conjugate acid–base pairs and the transfer of a *proton* from one substance (the acid) to another (the base).

Water is Amphoteric and Undergoes *Autoionization*

The water molecule has two polar O–H bonds and two lone pairs of electrons on the oxygen atom. Liquid water is a network of water molecules connected by hydrogen bonding. Because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton).

Water can act as a base in reactions with stronger acids by accepting an H^+ ion. One example is the dissolution of a strong acid such as HCl into chloride ions (Cl^-) and protons (H^+). The proton, in turn, reacts with a water molecule to form the *hydronium ion* (H_3O^+):

$$\underset{aicd}{HCl_{(aq)}} + \underset{base}{H_2O_{(l)}} \rightarrow \underset{acid}{H_3O^+_{(aq)}} + \underset{base}{Cl^-_{(aq)}} \tag{16.1.1}$$

The reaction in Equation 16.1.1 is often written in a simpler form by removing H_2O from each side:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \tag{16.1.2}$$

In Equation 16.1.2, the hydronium ion is represented by H^+, although free H^+ ions do not exist in liquid water.

Water can also act as an acid in reactions with stronger bases, as shown in Equation 16.1.3. In this equilibrium reaction, H_2O donates a proton to NH_3, which acts as a base:

$$\underset{aicd}{H_2O_{(aq)}} + \underset{base}{NH_{3(aq)}} \rightleftharpoons \underset{acid}{NH^+_{4(aq)}} + \underset{base}{OH^-_{(aq)}} \tag{16.1.3}$$

Thus, water is **amphiprotic**, which is the word for the class of substances that can behave as either an acid or a base in a chemical reaction, depending on the nature of the other reactant(s).

Because water is amphiprotic, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an autoionization process:

$$2H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{16.1.4}$$

The equilibrium constant *K* for this reaction can be written as follows:

$$K = \frac{[H_3O^+(aq)][OH^-(aq)]}{[H_2O(l)]^2} \tag{16.1.5}$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25°C, the concentrations of the hydronium ion and the hydroxide ion are equal: $[H_3O^+] = [OH^−] = 1.003 \times 10^{-7}$ M. Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb. We can calculate $[H_2O]$ at 25°C from the density of water at this temperature (0.997 g/mL):

$$[H_2O(l)] = mol/L = (0.997\ \cancel{g}/mL)\left(\frac{1\ mol}{18.02\ \cancel{g}}\right)\left(\frac{1000\ \cancel{mL}}{L}\right) = 55.3\ M \tag{16.1.6}$$

With so few water molecules dissociated, the equilibrium of the autoionization reaction (Equation 16.4) lies far to the left. Consequently, $[H_2O]$ is essentially unchanged by the autoionization reaction and can be treated as a constant. Incorporating this constant into the equilibrium expression allows us to rearrange Equation 16.1.5 to define a new equilibrium constant, the ion-product constant of liquid water (K_w)

$$K = \frac{K_w}{[H_2O(l)]^2} \tag{16.1.7a}$$

with

$$K_w = [H_3O^+(aq)][OH^−(aq)] = [H_3O^+(aq)][OH^−(aq)] \tag{16.1.7b}$$

Substituting the values for $[H_3O^+]$ and $[OH^−]$ at 25°C into this expression,

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14} \tag{16.1.8}$$

Thus, to three significant figures, $K_w = 1.01 \times 10^{-14}$ M. Like any other equilibrium constant, K_w varies with temperature, ranging from 1.15×10^{-15} at 0°C to 4.99×10^{-13} at 100°C.

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If $[H_3O^+] > [OH^−]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^−]$, the solution is basic. For an aqueous solution, the H_3O^+ concentration is a quantitative measure of acidity: the higher the H_3O^+ concentration, the more acidic the solution. Conversely, the higher the $OH^−$ concentration, the more basic the solution. In most situations that you will encounter, the H_3O^+ and $OH^−$ concentrations from the dissociation of water are so small (1.003×10^{-7} M) that they can be ignored in calculating the H_3O^+ or $OH^−$ concentrations of solutions of acids and bases, but this is not always the case.

The Relationship among pH, pOH, and pK_w

The *pH scale* is a concise way of describing the H_3O^+ concentration and hence the acidity or basicity of a solution. Recall from Chapter 8 that pH and the H^+ (H_3O^+) concentration are related as follows:

$$pH = -log_{10}[H^+(aq)] \tag{16.1.9}$$

$$[H^+(aq)] = 10^{-pH} \tag{16.1.10}$$

Because the scale is logarithmic, a pH difference of *1* between two solutions corresponds to a difference of a factor of *10* in their hydronium ion concentrations. (Refer to Essential Skills 3 in Section 8.11 , if you need to refresh your memory about how to use logarithms.) Recall also that the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7}$ M), whereas acidic solutions have pH < 7.00 (corresponding to $[H_3O^+] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[H_3O^+] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous *pOH scale* to describe the hydroxide ion concentration of a solution. The pOH and $[OH^−]$ are related as follows:

$$pOH = -log_{10}[OH^−(aq)] \tag{16.1.11}$$

$$[OH^−(aq)] = 10^{-pOH} \tag{16.1.12}$$

The constant K_w can also be expressed using this notation, where $pK_w = -\log K_w$.

Because a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25°C is 7.00 + 7.00 = 14.00. We can show that the sum of pH and pOH is equal to 14.00 for *any* aqueous solution at 25°C by taking the negative logarithm of both sides of Equation 16.7:

$$-logKw = -log([H_3O^+(aq)][OH-(aq)]) = (-log[H_3O^+(aq)]) + (-log[OH^-(aq)]) = pH + pOH \tag{16.1.13}$$

Thus at any temperature, pH + pOH = pK_w, so at 25°C, where $K_w = 1.0 \times 10^{-14}$, pH + pOH = 14.00. More generally, the pH of any neutral solution is half of the pK_w at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in Figure 16.1.1 over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

Note the Pattern

For any neutral solution, pH + pOH = 14.00 (at 25°C) and and pH=12pKw.

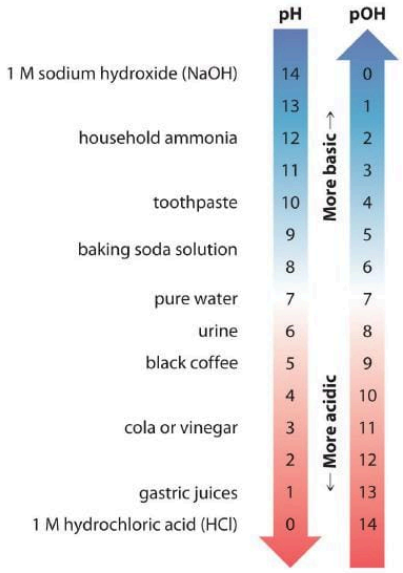


Figure 16.1.1 The Inverse Relationship between the pH and pOH **Scales**As pH decreases, $[H^+]$ and the acidity increase. As pOH increases, $[OH^-]$ and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic.

Example 16.1.1

The K_w for water at 100°C is 4.99×10^{-13}. Calculate pK_w for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100°C. Report pH and pOH values to two decimal places.

Given: K_w

Asked for: pK_w, pH, and pOH

Strategy:

A Calculate pK_w by taking the negative logarithm of K_w.

B For a neutral aqueous solution, $[H_3O^+] = [OH^-]$. Use this relationship and Equation 16.7 to calculate $[H_3O^+]$ and $[OH^-]$. Then determine the pH and the pOH for the solution.

Solution:

A Because pK_w is the negative logarithm of K_w, we can write

$$pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$$

The answer is reasonable: K_w is between 10^{-13} and 10^{-12}, so pK_w must be between 12 and 13.

B Equation 16.1.7 shows that $K_w = [H_3O^+][OH^-]$. Because $[H_3O^+] = [OH^-]$ in a neutral solution, we can let $x = [H_3O^+] = [OH^-]$:

$$K_w = [H_3O^+][OH^-] = (x)(x) = x^2$$

$$x = \sqrt{K_w} = \sqrt{4.99 \times 10^{-13}} = 7.06 \times 10^{-7}\ M$$

Because x is equal to both $[H_3O^+]$ and $[OH^-]$,

$$\text{pH} = \text{pOH} = -\log(7.06 \times 10^{-7}) = 6.15 \text{ (to two decimal places)}$$

We could obtain the same answer more easily (without using logarithms) by using the pK_w. In this case, we know that pK_w = 12.302, and from Equation 16.13, we know that pK_w = pH + pOH. Because pH = pOH in a neutral solution, we can use Equation 16.13 directly, setting pH = pOH = y. Solving to two decimal places we obtain the following:

$$pK_w pH + pOH = y + y = 2y$$

$$y = \frac{pK_w}{2} = \frac{12.302}{2} = 6.15 = pH = pOH$$

Exercise

Humans maintain an internal temperature of about 37°C. At this temperature, $K_w = 3.55 \times 10^{-14}$. Calculate p$K_w$ and the pH and the pOH of a neutral solution at 37°C. Report pH and pOH values to two decimal places.

Answer: pK_w = 13.45 pH = pOH = 6.73

Summary

Water is **amphiprotic**: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion (H_3O^+). The *autoionization* of liquid water produces OH^- and H_3O^+ ions. The equilibrium constant for this reaction is called the **ion-product constant of liquid water (K_w)** and is defined as $K_w = [H_3O^+][OH^-]$. At 25°C, K_w is 1.01×10^{-14}; hence pH + pOH = pK_w = 14.00.

Key Takeaway

- For any neutral solution, pH + pOH = 14.00 (at 25°C) and pH = 1/2 pK_w.

Key Equations

Ion-product constant of liquid water

Equation 16.1.7: $K_w = [H_3O^+][OH^-]$

Definition of pH

Equation 16.1.9: $\text{pH} = -\log_{10}[H^+]$

Equation 16.1.10: $[H^+] = 10^{-\text{pH}}$

Definition of pOH

Equation 16.1.11: $pOH = -\log_{10}[OH^+]$

Equation 16.1.12: $[OH^-] = 10^{-pOH}$

Relationship among pH, pOH, and p K_w

Equation 16.1.13: $pK_w = pH + pOH$

Conceptual Problems

1. What is the relationship between the value of the equilibrium constant for the autoionization of liquid water and the tabulated value of the ion-product constant of liquid water (K_w)?
2. The density of liquid water decreases as the temperature increases from 25°C to 50°C. Will this effect cause K_w to increase or decrease? Why?
3. Show that water is amphiprotic by writing balanced chemical equations for the reactions of water with HNO_3 and NH_3. In which reaction does water act as the acid? In which does it act as the base?
4. Write a chemical equation for each of the following.
    1. Nitric acid is added to water.
    2. Potassium hydroxide is added to water.
    3. Calcium hydroxide is added to water.
    4. Sulfuric acid is added to water.
5. Show that K for the sum of the following reactions is equal to K_w.
    1. $$HMnO_{4(aq)} \rightleftharpoons H^+_{(aq)} + MnO^-_{4(aq)}$$
    2.

Answers

1. $$K_{auto} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

    $$K_w = [H_3O^+][OH^-] = K_{auto}[H_2O]^2$$
2.
3. water is the base:

    $$H_2O_{(l)} + HNO_{3(g)} \rightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$$

    water is the acid:

    $$H_2O_{(l)} + NH_{3(g)} \rightarrow OH^-_{(aq)} + NH^-_{4(aq)}$$
4.
5.

Numerical Problems

1. The autoionization of sulfuric acid can be described by the following chemical equation:

    $$H_2SO_{4(l)} + H_2SO_{4(l)} \rightleftharpoons H_3SO^+_{4(soln)} + H_SO^-_{4(soln)}$$

At 25°C, $K = 3 \times 10^{-4}$. Write an equilibrium constant expression for K(H_2SO_4) that is analogous to K_w. The density of H_2SO_4 is 1.8 g/cm^3 at 25°C. What is the concentration of $H_3SO_4^+$? What fraction of H_2SO_4 is ionized?

2. An aqueous solution of a substance is found to have $[H_3O]^+ = 2.48 \times 10^{-8}$ M. Is the solution acidic, neutral, or basic?

3. The pH of a solution is 5.63. What is its pOH? What is the $[OH^-]$? Is the solution acidic or basic?

4. State whether each solution is acidic, neutral, or basic.

    1. $[H_3O^+] = 8.6 \times 10^{-3}$ M
    2. $[H_3O^+] = 3.7 \times 10^{-9}$ M
    3. $[H_3O^+] = 2.1 \times 10^{-7}$ M
    4. $[H_3O^+] = 1.4 \times 10^{-6}$ M

5. Calculate the pH and the pOH of each solution.

    1. 0.15 M HBr
    2. 0.03 M KOH
    3. 2.3×10^{-3} M HNO_3
    4. 9.78×10^{-2} M NaOH
    5. 0.00017 M HCl
    6. 5.78 M HI

6. Calculate the pH and the pOH of each solution.

    1. 25.0 mL of 2.3×10^{-2} M HCl, diluted to 100 mL
    2. 5.0 mL of 1.87 M NaOH, diluted to 125 mL
    3. 5.0 mL of 5.98 M HCl added to 100 mL of water
    4. 25.0 mL of 3.7 M HNO_3 added to 250 mL of water
    5. 35.0 mL of 0.046 M HI added to 500 mL of water
    6. 15.0 mL of 0.0087 M KOH added to 250 mL of water.

7. The pH of stomach acid is approximately 1.5. What is the $[H^+]$?

8. Given the pH values in parentheses, what is the $[H^+]$ of each solution?

    1. household bleach (11.4)
    2. milk (6.5)
    3. orange juice (3.5)
    4. seawater (8.5)
    5. tomato juice (4.2)

9. A reaction requires the addition of 250.0 mL of a solution with a pH of 3.50. What mass of HCl (in milligrams) must be dissolved in 250 mL of water to produce a solution with this pH?

10. If you require 333 mL of a pH 12.50 solution, how would you prepare it using a 0.500 M sodium hydroxide stock solution?

Answers

1. $$K_{H_2SO_4} = [H_3SO_4^+][HSO_4^-] = K[H_2SO_4]_2$$

$$[H_3SO_4^+] = 0.3M$$

$[H_3SO_4^+]$ = 0.3 M; the fraction ionized is 0.02.

2.

3. pOH = 8.37; $[OH^-] = 4.3 \times 10^{-9}$ M; acidic

4.
5. 1. pH = 0.82; pOH = 13.18
   2. pH = 12.5; pOH = 1.5
   3. pH = 2.64; pOH = 11.36
   4. pH = 12.990; pOH = 1.010
   5. pH = 3.77; pOH = 10.23
   6. pH = −0.762; pOH = 14.762
6.
7.
8.

9. 2.9 mg HCl

10.

Contributors

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Modified by Joshua B. Halpern

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11.5: Equilibria and pH of Weak Acid and Salt Solutions

Learning Objectives

At the end of this section, you will have background information that will help you to be able to:

- Determine the pH and pOH of a solution containing a single acid, base, or salt.

This section presents a quantitative approach to analyzing acid–base equilibriums. You will learn how to determine the values of K_a and K_b, how to use K_a or K_b to calculate the percent ionization and the pH of an aqueous solution of an acid or a base, and how to calculate the equilibrium constant for the reaction of an acid with a base from the K_a and K_b of the reactants.

Determining K_a and K_b

The ionization constants K_a and K_b are equilibrium constants that are calculated from experimentally measured concentrations, just like any other equilibrium constant. Before proceeding further, it is important to understand exactly what is meant when we describe the concentration of an aqueous solution of a weak acid or a weak base. Suppose, for example, we have a bottle labeled 1.0 M acetic acid or 1.0 M ammonia. Such a solution is usually prepared by dissolving 1.0 mol of acetic acid or ammonia in water and adding enough water to give a final volume of exactly 1.0 L. If, however, we were to list the actual concentrations of all the species present in either solution, we would find that *none* of the values is exactly 1.0 M because a weak acid such as acetic acid or a weak base such as ammonia always reacts with water to some extent. The extent of the reaction depends on the K_a or the K_b, the concentration of the acid or the base, and the temperature. Consequently, only the *total concentration* of both the ionized and unionized species is equal to 1.0 M.

The *analytical concentration* (C) is defined as the *total* concentration of all forms of an acid or a base that are present in solution, regardless of their state of protonation. Thus a "1.0 M" solution of acetic acid has an analytical concentration of 1.0 M, which is the sum of the *actual* concentrations of unionized acetic acid (CH_3CO_2H) and the ionized form ($CH_3CO_2^-$):

$$C_{CH_3CO_2H} = [CH_3CO_2H] + [CH_3CO_2^-] \tag{16.4.1}$$

As we shall see shortly, if we know the analytical concentration and the K_a, we can calculate the actual values of $[CH_3CO_2H]$ and $[CH_3CO_2^-]$.

The equilibrium equations for the reaction of acetic acid and ammonia with water are as follows:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} \tag{16.4.2}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{16.4.3}$$

where K_a and K_b are the ionization constants for acetic acid and ammonia, respectively. In addition to the analytical concentration of the acid (or the base), we must have a way to measure the concentration of at least *one* of the species in the equilibrium constant expression to determine the K_a (or the K_b). There are two common ways to obtain the concentrations: (1) measure the electrical conductivity of the solution, which is related to the total concentration of ions present, and (2) measure the pH of the solution, which gives $[H^+]$ or $[OH^-]$.

Example 6 and Example 7 illustrate the procedure for determining K_a for a weak acid and K_b for a weak base. In both cases, we will follow the procedure developed in Chapter 15: the analytical concentration of the acid or the base is the *initial* concentration, and the stoichiometry of the reaction with water determines the *change* in concentrations. The *final* concentrations of all species are calculated from the initial concentrations and the changes in the concentrations. Inserting the final concentrations into the

equilibrium constant expression enables us to calculate the K_a or the K_b.

Example 16.4.1

Electrical conductivity measurements indicate that 0.42% of the acetic acid molecules in a 1.00 M solution are ionized at 25°C. Calculate K_a and pK_a for acetic acid at this temperature.

Given: analytical concentration and percent ionization

Asked for: K_a and pK_a

Strategy:

A Write the balanced equilibrium equation for the reaction and derive the equilibrium constant expression.

B Use the data given and the stoichiometry of the reaction to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations for all species in the equilibrium constant expression.

C Substitute the final concentrations into the equilibrium constant expression and calculate the K_a. Take the negative logarithm of K_a to obtain the pK_a.

Solution:

A The balanced equilibrium equation for the dissociation of acetic acid is as follows:

$$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH3CO^-_{2(aq)} \tag{11.5.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} \tag{11.5.2}$$

B To calculate the K_a, we need to know the equilibrium concentrations of CH_3CO_2H, $CH_3CO_2^-$, and H^+. The most direct way to do this is to construct a table that lists the initial concentrations and the changes in concentrations that occur during the reaction to give the final concentrations, using the procedure introduced in Chapter 15. The initial concentration of unionized acetic acid ($[CH_3CO_2H]_i$) is the analytical concentration, 1.00 M, and the initial acetate concentration ($[CH_3CO_2^-]_i$) is zero. The initial concentration of H^+ is not zero, however; $[H^+]_i$ is 1.00×10^{-7} M due to the autoionization of water. The measured percent ionization tells us that 0.42% of the acetic acid molecules are ionized at equilibrium. Consequently, the change in the concentration of acetic acid is $\Delta[CH_3CO_2H] = -(4.2 \times 10^{-3})(1.00\ M) = -0.0042$ M. Conversely, the change in the acetate concentration is $\Delta[CH_3CO_2^-] = +0.0042$ M because every 1 mol of acetic acid that ionizes gives 1 mol of acetate. Because one proton is produced for each acetate ion formed, $\Delta[H^+] = +0.0042$ M as well. These results are summarized in the following table.

$$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CO^-_{2(aq)} \tag{11.5.3}$$

	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	1.00	1.00×10^{-7}	0
change	−0.0042	+0.0042	+0.0042
final			

The final concentrations of all species are therefore as follows:

- $[CH_3CO_2H]_f = [CH_3CO_2H]_i + \Delta[CH_3CO_2H] = 1.00\ M + (-0.0042\ M) = 1.00\ M$
- $[CH_3CO_2^-]_f = [CH_3CO_2^-]_i + \Delta[CH_3CO_2^-] = 0\ M + (+0.0042\ M) = 0.0042\ M$

- $[H^+]_f = [H^+]_i + \Delta[H^+] = 1.00 \times 10^{-7} M + (+0.0042\ \ M) = 0.0042\ \ M$

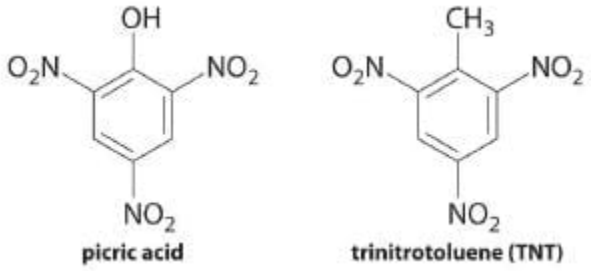
C We can now calculate K_a by inserting the final concentrations into the equilibrium constant expression:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(0.0042)(0.0042)}{1.00} = 1.8 \times 10^{-5} \tag{11.5.4}$$

The pK_a is the negative logarithm of K_a: pK_a = –log K_a = –log(1.8 × 10^{-5}) = 4.74.

Exercise

Picric acid is the common name for 2,4,6-trinitrophenol, a derivative of phenol (C_6H_5OH) in which three H atoms are replaced by nitro (–NO_2) groups. The presence of the nitro groups removes electron density from the phenyl ring, making picric acid a much stronger acid than phenol (pK_a = 9.99). The nitro groups also make picric acid potentially explosive, as you might expect based on its chemical similarity to 2,4,6-trinitrotoluene, better known as TNT. A 0.20 M solution of picric acid is 73% ionized at 25°C. Calculate K_a and pK_a for picric acid.



Answer: K_a = 0.39; pK_a = 0.41

Example 16.4.2

A 1.0 M aqueous solution of ammonia has a pH of 11.63 at 25°C. Calculate K_b and pK_b for ammonia.

Given: analytical concentration and pH

Asked for: K_b and pK_b

Strategy:

A Write the balanced equilibrium equation for the reaction and derive the equilibrium constant expression.

B Use the data given and the stoichiometry of the reaction to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations for all species in the equilibrium constant expression.

C Substitute the final concentrations into the equilibrium constant expression and calculate the K_b. Take the negative logarithm of K_b to obtain the pK_b.

Solution:

A The balanced equilibrium equation for the reaction of ammonia with water is as follows:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^-$$

and the equilibrium constant expression is as follows:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Remember that water does not appear in the equilibrium constant expression for K_b.

B To calculate K_b, we need to know the equilibrium concentrations of NH_3, NH_4^+, and OH^-. The initial concentration of NH_3 is the analytical concentration, 1.0 M, and the initial concentrations of NH_4^+ and OH^- are 0 M and 1.00×10^{-7} M, respectively. In this case, we are given the pH of the solution, which allows us to calculate the final concentration of one species (OH^-) directly, rather than the change in concentration. Recall that pK_w = pH + pOH = 14.00 at 25°C. Thus pOH = 14.00 − pH = 14.00 − 11.63 = 2.37, and $[OH^-]_f = 10^{-2.37} = 4.3 \times 10^{-3}$ M. Our data thus far are listed in the following table.

$$NH_{3(aq)} \rightleftharpoons NH_{4(aq)}^{+} + OH_{(aq)}^{-} \tag{11.5.5}$$

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	1.0	0	1.00×10^{-7}
change			
final			4.3×10^{-3}

The final $[OH^-]$ is much greater than the initial $[H^+]$, so the change in $[OH^-]$ is as follows:

$\Delta[OH^-] = (4.3 \times 10^{-3}\ M) - (1.00 \times 10^{-7}\ M) \approx 4.3 \times 10^{-3}\ M$

The stoichiometry of the reaction tells us that 1 mol of NH_3 is converted to NH_4^+ for each 1 mol of OH^- formed, so

$\Delta[NH_4^+] = +4.3 \times 10^{-3}$ M and $\Delta[NH_3] = -4.3 \times 10^{-3}$ M

We can now insert these values for the changes in concentrations into the table, which enables us to complete the table.

$$H_2O_{(l)} + NH3_{(aq)} \rightleftharpoons NH_{4(aq)}^{+} + OH_{(aq)}^{-} \tag{11.5.6}$$

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	1.0	0	1.00×10^{-7}
change	-4.3×10^{-3}	$+4.3 \times 10^{-3}$	$+4.3 \times 10^{-3}$
final	1.0	4.3×10^{-3}	4.3×10^{-3}

C Inserting the final concentrations into the equilibrium constant expression gives K_b:

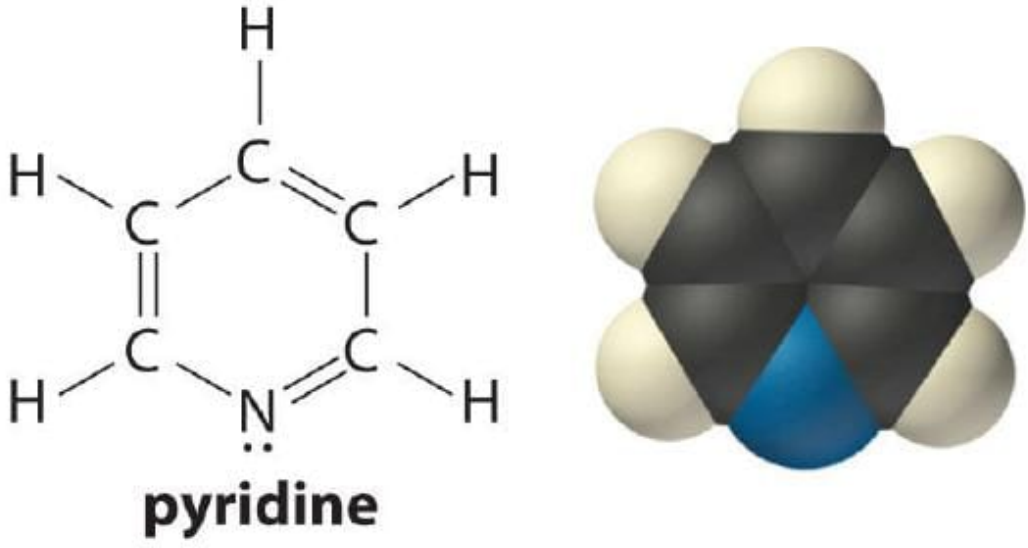
$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(4.3 \times 10^{-3})^2}{1.0} = 1.8 \times 10^{-5}$$

and $pK_b = -\log K_b = 4.74$.

The K_b and the pK_b for ammonia are almost exactly the same as the K_a and the pK_a for acetic acid at 25°C. In other words, ammonia is almost exactly as strong a base as acetic acid is an acid. Consequently, the extent of the ionization reaction in an aqueous solution of ammonia at a given concentration is the same as in an aqueous solution of acetic acid at the same concentration.

Exercise

The pH of a 0.050 M solution of pyridine (C_6H_5N) is 8.96 at 25°C. Calculate K_b and pK_b for pyridine.



Answer: $K_b = 1.7 \times 10^{-9}$; $pK_b = 8.77$

Calculating Percent Ionization from K_a or K_b

When carrying out a laboratory analysis, chemists frequently need to know the concentrations of all species in solution. Because the reactivity of a weak acid or a weak base is usually very different from the reactivity of its conjugate base or acid, we often need to know the percent ionization of a solution of an acid or a base to understand a chemical reaction. The percent ionization is defined as follows:

$$\text{percent ionization of acid} = \frac{[H^+]}{C_{HA}} \times 100 \tag{16.4.4}$$

$$\text{percent ionization of base} = \frac{[OH^-]}{C_B} \times 100 \tag{16.4.5}$$

One way to determine the concentrations of species in solutions of weak acids and bases is a variation of the tabular method we used previously to determine K_a and K_b values. As a demonstration, we will calculate the concentrations of all species and the percent ionization in a 0.150 M solution of formic acid at 25°C. The data in Table E1 show that formic acid ($K_a = 1.8 \times 10^{-4}$ at 25°C) is a slightly stronger acid than acetic acid. The equilibrium equation for the ionization of formic acid in water is as follows:

$$HCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{2(aq)} \tag{16.4.6}$$

and the equilibrium constant expression for this reaction is as follows:

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} \tag{16.4.7}$$

We set the initial concentration of HCO_2H equal to 0.150 M, and that of HCO_2^- is 0 M. The initial concentration of H^+ is 1.00×10^{-7} M due to the autoionization of water. Because the equilibrium constant for the ionization reaction is small, the equilibrium will lie to the left, favoring the unionized form of the acid. Hence we can define x as the amount of formic acid that dissociates.

If the change in $[HCO_2H]$ is $-x$, then the change in $[H^+]$ and $[HCO_2^-]$ is $+x$. The final concentration of each species is the sum of its initial concentration and the change in concentration, as summarized in the following table.

$$HCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{2(aq)} \tag{11.5.7}$$

	[HCO_2H]	[H^+]	[HCO_2^-]
initial	0.150	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.150 - x)$	$(1.00 \times 10^{-7} + x)$	x

We can calculate x by substituting the final concentrations from the table into the equilibrium constant expression:

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(1.00 \times 10^{-7} + x)x}{0.150 - x} \tag{11.5.8}$$

Because the ionization constant K_a is small, x is likely to be small compared with the initial concentration of formic acid: $(0.150 - x)$ M ≈ 0.150 M. Moreover, [H^+] due to the autoionization of water (1.00×10^{-7} M) is likely to be negligible compared with [H^+] due to the dissociation of formic acid: $(1.00 \times 10^{-7} + x)$ M ≈ x M. Inserting these values into the equilibrium constant expression and solving for x,

$$K_a = \frac{x^2}{0.150} = 1.8 \times 10^{-4} \tag{11.5.9}$$

$$x = 5.2 \times 10^{-3} \tag{11.5.10}$$

We can now calculate the concentrations of the species present in a 0.150 M formic acid solution by inserting this value of x into the expressions in the last line of the table:

$$[HCO_2H] = (0.150 - x)\ M = 0.145\ M \tag{11.5.11}$$

$$[HCO_2] = x = 5.2 \times 10^{-3}\ M \tag{11.5.12}$$

$$[H^+] = (1.00 \times 10 - 7 + x)M = 5.2 \times 10^{-3}M \tag{11.5.13}$$

Thus the pH of the solution is $-\log(5.2 \times 10^{-3}) = 2.28$. We can also use these concentrations to calculate the fraction of the original acid that is ionized. In this case, the percent ionization is the ratio of [H^+] (or [HCO_2^-]) to the analytical concentration, multiplied by 100 to give a percentage:

$$\text{percent ionization} = \frac{[H^+]}{C_{HA}} \times 100 = \frac{5.2 \times 10^{-3}\ M}{0.150} \times 100 = 3.5\% \tag{11.5.14}$$

Always check to make sure that any simplifying assumption was valid. As a general rule of thumb, approximations such as those used here are valid *only* if the quantity being neglected is no more than about 5% of the quantity to which it is being added or from which it is being subtracted. If the quantity that was neglected is much greater than about 5%, then the approximation is probably not valid, and you should go back and solve the problem using the quadratic formula. In the previous demonstration, both simplifying assumptions were justified: the percent ionization is only 3.5%, which is well below the approximately 5% limit, and the 1.00×10^{-7} M [H^+] due to the autoionization of water is much, much less than the 5.2×10^{-3} M [H^+] due to the ionization of formic acid.

As a general rule, the [H^+] contribution due to the autoionization of water can be ignored as long as the product of the acid or the base ionization constant and the analytical concentration of the acid or the base is at least 10 times greater than the [H^+] or [OH^-] from the autoionization of water—that is, if

$$K_aC_{HA} \geq 10(1.00 \times 10^{-7}) = 1.0 \times 10^{-6} \tag{16.4.8}$$

or

$$K_bC_B \geq 10(1.00 \times 10^{-7}) = 1.0 \times 10^{-6} \tag{16.4.9}$$

By substituting the appropriate values for the formic acid solution into Equation 16.45, we see that the simplifying assumption is valid in this case:

$$K_aC_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5} > 1.0 \times 10^{-6} \tag{16.4.10}$$

Doing this simple calculation before solving this type of problem saves time and allows you to write simplified expressions for the final concentrations of the species present. In practice, it is necessary to include the $[H^+]$ contribution due to the autoionization of water only for extremely dilute solutions of very weak acids or bases.

Example 8 illustrates how the procedure outlined previously can be used to calculate the pH of a solution of a weak base.

Example 16.4.3

Calculate the pH and percent ionization of a 0.225 M solution of ethylamine ($CH_3CH_2NH_2$), which is used in the synthesis of some dyes and medicines. The pK_b of ethylamine is 3.19 at 20°C.

Given: concentration and pK_b

Asked for: pH and percent ionization

Strategy:

A Write the balanced equilibrium equation for the reaction and the equilibrium constant expression. Calculate K_b from pK_b.

B Use Equation 16.4.8 to see whether you can ignore $[H^+]$ due to the autoionization of water. Then use a tabular format to write expressions for the final concentrations of all species in solution. Substitute these values into the equilibrium equation and solve for $[OH^-]$. Use Equation 16.4.5 to calculate the percent ionization.

C Use the relationship $K_w = [OH^-][H^+]$ to obtain $[H^+]$. Then calculate the pH of the solution.

Solution:

A We begin by writing the balanced equilibrium equation for the reaction:

$$CH_3CH_2NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CH_2NH^+_{3(aq)} + OH^-_{(aq)}$$

The corresponding equilibrium constant expression is as follows:

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2}]$$

From the pK_b, we have $K_b = 10 - 3.19 = 6.5 \times 10^{-4}$.

B To calculate the pH, we need to determine the H^+ concentration. Unfortunately, H^+ does not appear in either the chemical equation or the equilibrium constant expression. However, $[H^+]$ and $[OH^-]$ in an aqueous solution are related by $K_w = [H^+][OH^-]$. Hence if we can determine $[OH^-]$, we can calculate $[H^+]$ and then the pH. The initial concentration of $CH_3CH_2NH_2$ is 0.225 M, and the initial $[OH^-]$ is 1.00×10^{-7} M. Because ethylamine is a weak base, the extent of the reaction will be small, and it makes sense to let x equal the amount of $CH_3CH_2NH_2$ that reacts with water. The change in $[CH_3CH_2NH_2]$ is therefore $–x$, and the change in both $[CH_3CH_2NH_3^+]$ and $[OH^-]$ is $+x$. To see whether the autoionization of water can safely be ignored, we substitute K_b and C_B into Equation 16.4.10:

$$K_bC_B = (6.5 \times 10^{-4})(0.225) = 1.5 \times 10^{-4} > 1.0 \times 10^{-6}$$

Thus the simplifying assumption is valid, and we will not include $[OH^-]$ due to the autoionization of water in our calculations.

$$H_2O_{(l)} + CH_3CH_2NH_{2(aq)} \rightleftharpoons CH_3CH_2NH^+_{3(aq)} + OH^-_{(aq)} \quad (11.5.15)$$

	$[CH_3CH_2NH_2]$	$[CH_3CH_2NH_3^+]$	$[OH^-]$
initial	0.225	0	1.00×10^{-7}
change	$-x$	$+x$	$+x$
final	$(0.225 - x)$	x	x

Substituting the quantities from the last line of the table into the equilibrium constant expression,

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]} = \frac{(x)(x)}{0.225 - x} = 6.5 \times 10^{-4}$$

As before, we assume the amount of $CH_3CH_2NH_2$ that ionizes is small compared with the initial concentration, so $[CH_3CH_2NH_2]_f = 0.225 - x \approx 0.225$. With this assumption, we can simplify the equilibrium equation and solve for x:

$$K_b = \frac{x^2}{0.225} = 6.5 \times 10^{-4}$$

$$x = 0.012 = [CH_3CH_2NH_3^+]_f = [OH^-]_f$$

The percent ionization is therefore

$$\text{percent ionization} = \frac{[OH^-]}{C_B} \times 100 = \frac{0.012\ M}{0.225\ M} \times 100 = 5.4\% \quad (11.5.16)$$

which is at the upper limit of the approximately 5% range that can be ignored. The final hydroxide concentration is thus 0.012 M.

C We can now determine the $[H^+]$ using the expression for K_w:

$$K_w = [OH^-][H^+]$$

$$1.01 \times 10^{-14} = (0.012\ M)[H^+]$$

$$8.4 \times 10^{-13}\ M = [H^+]$$

The pH of the solution is $-\log(8.4 \times 10^{-13}) = 12.08$. Alternatively, we could have calculated pOH as $-\log(0.012) = 1.92$ and determined the pH as follows:

$$pH + pOH = pKw = 14.00$$

$$pH = 14.00 - 1.92 = 12.08$$

The two methods are equivalent.

Exercise

Aromatic amines, in which the nitrogen atom is bonded directly to a phenyl ring ($-C_6H_5$) tend to be much weaker bases than simple alkylamines. For example, aniline ($C_6H_5NH_2$) has a pK_b of 9.13 at 25°C. What is the pH of a 0.050 M solution of aniline?

Answer: 8.78

The previous examples illustrate a key difference between solutions of strong acids and bases and solutions of weak acids and bases. Because strong acids and bases ionize essentially completely in water, the percent ionization is always approximately 100%, regardless of the concentration. In contrast, the percent ionization in solutions of weak acids and bases is small and depends on the analytical concentration of the weak acid or base. As illustrated for benzoic acid in Figure 16.4.1, the percent ionization of a weak acid or a weak base actually *increases* as its analytical concentration decreases. The percent ionization also increases as the magnitude of K_a and K_b increases.

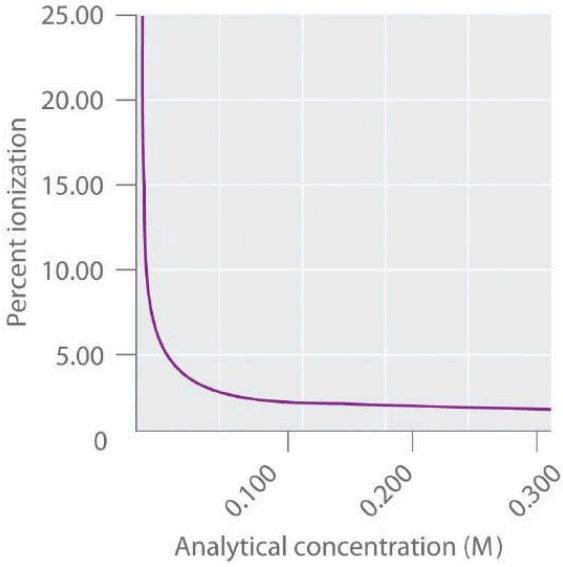


Figure 16.4.1 The Relationship between the Analytical Concentration of a Weak Acid and Percent **Ionization** As shown here for benzoic acid ($C_6H_5CO_2H$), the percent ionization decreases as the analytical concentration of a weak acid increases.

Unlike the K_a or the K_b, the percent ionization is not a constant for weak acids and bases but depends on *both* the K_a or the K_b *and* the analytical concentration. Consequently, the procedure in Example 8 must be used to calculate the percent ionization and pH for solutions of weak acids and bases. Example 9 and its corresponding exercise demonstrate that the combination of a dilute solution and a relatively large K_a or K_b can give a percent ionization much greater than 5%, making it necessary to use the quadratic equation to determine the concentrations of species in solution.

Note the Pattern

The percent ionization in a solution of a weak acid or a weak base *increases* as the analytical concentration *decreases* and as the K_a or the K_b *increases*.

Example 16.4.4

Benzoic acid ($C_6H_5CO_2H$) is used in the food industry as a preservative and medically as an antifungal agent. Its pK_a at 25°C is 4.20, making it a somewhat stronger acid than acetic acid. Calculate the percentage of benzoic acid molecules that are ionized in each solution.

1. a 0.0500 M solution
2. a 0.00500 M solution

Given: concentrations and pK_a

Asked for: percent ionization

Strategy:

A Write both the balanced equilibrium equation for the ionization reaction and the equilibrium equation (Equation 16.2.2). Use Equation 16.2.13 to calculate the K_a from the pK_a.

B For both the concentrated solution and the dilute solution, use a tabular format to write expressions for the final concentrations of all species in solution. Substitute these values into the equilibrium equation and solve for $[C_6H_5CO_2^-]_f$ for each solution.

C Use the values of $[C_6H_5CO_2^-]_f$ and Equation 16.4.4 to calculate the percent ionization.

Solution:

A If we abbreviate benzoic acid as $PhCO_2H$ where Ph = $-C_6H_5$, the balanced equilibrium equation for the ionization reaction and the equilibrium equation can be written as follows:

$$PhCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + PhCO^-_{2(aq)}$$

$$K_a = \frac{[H^+][PhCO_2^-]}{[PhCO_2H]}$$

From the pK_a, we have $K_a = 10^{-4.20} = 6.3 \times 10^{-5}$.

1. **B** For the more concentrated solution, we set up our table of initial concentrations, changes in concentrations, and final concentrations:

$$PhCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + PhCO^-_{2(aq)} \quad (11.5.17)$$

	[$PhCO_2H$]	[H^+]	[$PhCO_2^-$]
initial	0.0500	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.0500 - x)$	$(1.00 \times 10^{-7} + x)$	x

Inserting the expressions for the final concentrations into the equilibrium equation and making our usual assumptions, that [$PhCO_2^-$] and [H^+] are negligible due to the autoionization of water,

$$K_a = \frac{[H^+][PhCO_2^-]}{[PhCO_2H]} = \frac{(x)(x)}{0.0500 - x} = \frac{x^2}{0.0500} = 6.3 \times 10^{-5}$$

$$1.8 \times 10^{-3} = x$$

This value is less than 5% of 0.0500, so our simplifying assumption is justified, and [$PhCO_2^-$] at equilibrium is 1.8×10^{-3} M. We reach the same conclusion using C_{HA}: $K_aC_{HA} = (6.3 \times 10^{-5})(0.0500) = 3.2 \times 10^{-6} > 1.0 \times 10^{-6}$.

C The percent ionized is the ratio of the concentration of $PhCO_2^-$ to the analytical concentration, multiplied by 100:

$$\text{percent ionized} = \frac{[PhCO_2^-]}{C_{PhCO_2H}} \times 100 = \frac{1.8 \times 10^{-30}}{0.0500} \times 100 = 3.6\%$$

Because only 3.6% of the benzoic acid molecules are ionized in a 0.0500 M solution, our simplifying assumptions are confirmed.

2. **B** For the more dilute solution, we proceed in exactly the same manner. Our table of concentrations is therefore as follows:

$$PhCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + PhCO^-_{2(aq)} \quad (11.5.18)$$

	[$PhCO_2H$]	[H^+]	[$PhCO_2^-$]
initial	0.00500	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.00500 - x)$	$(1.00 \times 10^{-7} + x)$	x

Inserting the expressions for the final concentrations into the equilibrium equation and making our usual simplifying assumptions,

$$K_a = \frac{[H^+][PhCO_2^-]}{[PhCO_2H]} = \frac{(x)(x)}{0.00500 - x} = \frac{x^2}{0.00500} = 6.3 \times 10^{-5}$$

$$5.6 \times 10^{-4} = x$$

Unfortunately, this number is greater than 10% of 0.00500, so our assumption that the fraction of benzoic acid that is ionized in this solution could be neglected and that (0.00500 – x) ≈ x is not valid. Furthermore, we see that K_aC_{HA} = (6.3 × 10^{-5})(0.00500) = 3.2 × 10^{-7} < 1.0 × 10^{-6}. Thus the relevant equation is as follows:

$$\frac{x^2}{0.00500 - x} = 6.3 \times 10^{-5}$$

which must be solved using the quadratic formula. Multiplying out the quantities,

x^2 = (6.3 × 10^{-5})(0.00500 – x) = (3.2 × 10^{-7}) – (6.3 × 10^{-5})x

Rearranging the equation to fit the standard quadratic equation format,

x^2 + (6.3 × 10^{-5})x – (3.2 × 10^{-7}) = 0

This equation can be solved by using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(6.3 \times 10^{-5}) \pm \sqrt{(6.3 \times 10^{-5})^2 - 4(1)(-3.2 \times 10^{-7})}}{2(1)}$$

$$x = \frac{-(6.3 \times 10^{-5}) \pm (1.1 \times 10^{-3})}{2} = 5.3 \times 10^{-4}$$

or

$$x = -5.9 \times 10^{-4}$$

Because a negative x value corresponds to a negative [$PhCO_2^-$], which is not physically meaningful, we use the positive solution: x = 5.3 × 10^{-4}. Thus [$PhCO_2^-$] = 5.3 × 10^{-4} M.

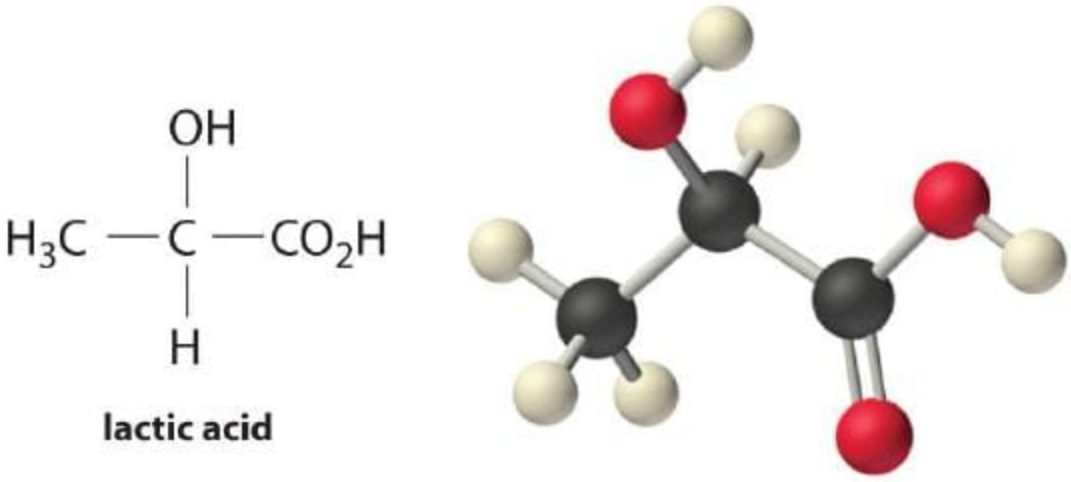
C The percent ionized is therefore

$$\text{percent ionized} = \frac{[PhCO_2^-]C_{PhCO_2H}}{\times}100 = \frac{5.3 \times 10^{-4}}{0.00500} \times 100 = 11\%$$

In the more dilute solution (C = 0.00500 M), 11% of the benzoic acid molecules are ionized versus only 3.6% in the more concentrated solution (C = 0.0500 M). Decreasing the analytical concentration by a factor of 10 results in an approximately threefold increase in the percentage of benzoic acid molecules that are ionized.

Exercise

Lactic acid ($CH_3CH(OH)CO_2H$) is a weak acid with a pK_a of 3.86 at 25°C. What percentage of the lactic acid is ionized in each solution?



1. a 0.10 M solution
2. a 0.0020 M solution

Answer

1. 3.7%
2. 23%

Determining K_{eq} of a neutralization reaction from K_a and K_b

In Section 16.2 , you learned how to use K_a and K_b values to qualitatively predict whether reactants or products are favored in an acid–base reaction. Tabulated values of K_a (or pK_a) and K_b (or pK_b), plus the K_w, enable us to quantitatively determine the direction and extent of reaction for a weak acid and a weak base by calculating K for the reaction. To illustrate how to do this, we begin by writing the dissociation equilibriums for a weak acid and a weak base and then summing them:

$$acid: \quad HA \rightleftharpoons H^+ + A^- \quad K_a \tag{16.4.11a}$$

$$base: \quad B + H_2O \rightleftharpoons HB^+ + OH^- \quad K_b \tag{16.4.11b}$$

$$sum: \quad HA + B + H_2O \rightleftharpoons H^+ + A^- + HB^+ + OH^- \quad K_{sum} = K_aK_b \tag{16.4.11c}$$

The overall reaction has H_2O on the left and H^+ and OH^- on the right, which means it involves the autoionization of water ($H_2O \rightleftharpoons H^+ + OH^-$) in addition to the acid–base equilibrium in which we are interested. We can obtain an equation that includes only the acid–base equilibrium by simply adding the equation for the reverse of the autoionization of water ($H^+ + OH^- \rightleftharpoons H_2O$), for which $K = 1/K_w$, to the overall equilibrium in Equation 16.4.11 and canceling:

$$HA + B + \cancel{H_2O} \rightleftharpoons \cancel{H^+} + A^- + HB^+ + \cancel{OH^-} \quad K_{sum} = K_aK_b \tag{16.4.12a}$$

$$\cancel{H^+} + \cancel{OH^-} \rightleftharpoons \cancel{H_2O} \quad 1/K_w \tag{16.4.12b}$$

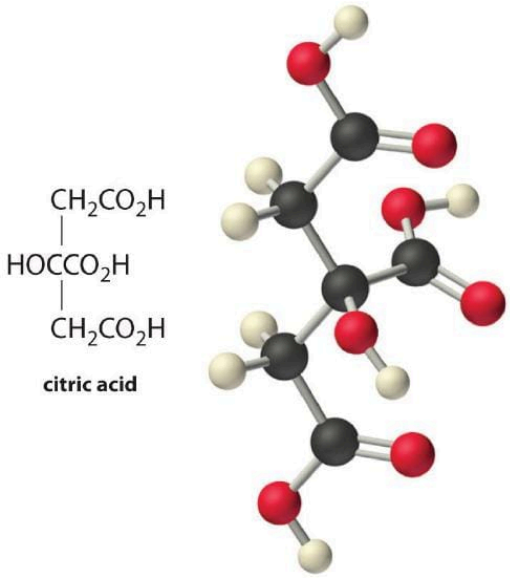
$$HA + B \rightleftharpoons A^- + HB^+ \quad K = (K_aK_b)/K_w \tag{16.4.12c}$$

Thus the equilibrium constant for the reaction of a weak acid with a weak base is the product of the ionization constants of the acid and the base divided by K_w. Example 10 illustrates how to calculate the equilibrium constant for the reaction of a weak acid with a weak base.

Example 16.4.5

Fish tend to spoil rapidly, even when refrigerated. The cause of the resulting “fishy” odor is a mixture of amines, particularly

methylamine (CH_3NH_2), a volatile weak base (pK_b = 3.34). Fish is often served with a wedge of lemon because lemon juice contains citric acid, a triprotic acid with pK_a values of 3.13, 4.76, and 6.40 that can neutralize amines. Calculate the equilibrium constant for the reaction of excess citric acid with methylamine, assuming that only the first dissociation constant of citric acid is important.



Given: pK_b for base and pK_a for acid

Asked for: *K*

Strategy:

A Write the balanced equilibrium equation and the equilibrium constant expression for the reaction.

B Convert pK_a and pK_b to K_a and K_b and then use Equation 16.4.12 to calculate *K*.

Solution:

A If we abbreviate citric acid as H_3citrate, the equilibrium equation for its reaction with methylamine is as follows:

$$CH_3NH_{2(aq)} + H_3citrate_{(aq)} \rightleftharpoons CH_3NH^+_{3(aq)} + H_2citrate^-_{(aq)}$$

The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CH_3NH_3^+][H_2citrate^-]}{[CH_3NH_2][H_3citrate]}$$

B Equation 16.49 is $K = (K_aK_b)/K_w$. Converting pK_a and pK_b to K_a and K_b gives $K_a = 10^{-3.13} = 7.4 \times 10^{-4}$ for citric acid and $K_b = 10^{-3.34} = 4.6 \times 10^{-4}$ for methylamine. Substituting these values into the equilibrium equation,

$$K = \frac{K_aK_b}{K_w} = \frac{(7.4 \times 10^{-4})(4.6 \times 10^{-4})}{1.01 \times 10^{-14}} = 3.4 \times 10^7$$

The value of *pK* can also be calculated directly by taking the negative logarithm of both sides of Equation 16.49, which gives

\(pK = pK_a + pK_b – pK_w = 3.13 + 3.34 – 14.00 = –7.53 \notag \]

Thus $K = 10^{-(-7.53)} = 3.4 \times 10^7$, in agreement with the earlier value. In either case, the *K* values show that the reaction of citric acid with the volatile, foul-smelling methylamine lies very far to the right, favoring the formation of a much less volatile salt with no odor. This is one reason a little lemon juice helps make less-than-fresh fish more appetizing.

Exercise

Dilute aqueous ammonia solution, often used as a cleaning agent, is also effective as a deodorizing agent. To see why, calculate the equilibrium constant for the reaction of aqueous ammonia with butyric acid ($CH_3CH_2CH_2CO_2H$), a particularly foul-smelling substance associated with the odor of rancid butter and smelly socks. The pK_b of ammonia is 4.75, and the pK_a of butyric acid is 4.83.

Answer: 2.6×10^4

pH of a Salt Solution

A *salt* is the ionic product of an acid-base neutralization reaction. The cation of the salt is the conjugate of the base in the neutralization reaction, while the anion of the salt is the conjugate of the acid. Once you identify the origin of the cation and anion, you can treat it accordingly. Table 11.5.1 will help you to classify.

Table 11.5.1. Acid and Base Properties of Salt Solutions

Cation is conjugate of:	Anion is conjugate of:	pH of salt solution will be:	Examples	How to find pH
strong base	strong acid	neutral (=7)	KCl, $LiNO_3$, Na_2SO_4	n/a - it's neutral
strong base	weak acid	acidic (< 7)	NH_4Cl, CH_3NH_3I	find K_a of the cation and make an ICE chart
weak base	strong acid	basic (>7)	$NaC_2H_3O_2$, $Mg(ClO_3)_2$	find K_b of the anion and make an ICE chart
weak base	weak acid	uncertain - it depends on the individual K_a and K_b values		You *can* do it, but we *won't* in this class

Summary

If the concentration of one or more of the species in a solution of an acid or a base is determined experimentally, K_a and K_b can be calculated, and K_a, pK_a, K_b, and pK_b can be used to quantitatively describe the composition of solutions of acids and bases. The concentrations of all species present in solution can be determined, as can the pH of the solution and the percentage of the acid or base that is ionized. The equilibrium constant for the reaction of a weak acid with a weak base can be calculated from K_a (or pK_a), K_b (or pK_b), and K_w.

Key Takeaway

- For a solution of a weak acid or a weak base, the percent ionization increases as the K_a or the K_b increases and as the analytical concentration decreases.

Key Equations

Percent ionization of acid

Equation 16.4.4: $= \frac{[H^+]}{C_{HA}} \times 100$

Percent ionization of base

Equation 16.4.5: $= \frac{[OH^-]}{C_B} \times 100$

Equilibrium constant for reaction of a weak acid with a weak base

Equation 16.4.12: $K = \frac{K_a K_b}{K_w}$

Conceptual Problems

1. Explain why the analytical concentration (C) of H_2SO_4 is equal to [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}].
2. Write an expression for the analytical concentration (C) of H_3PO_4 in terms of the concentrations of the species actually present in solution.
3. For relatively dilute solutions of a weak acid such as acetic acid (CH_3CO_2H), the concentration of undissociated acetic acid in solution is often assumed to be the same as the analytical concentration. Explain why this is a valid practice.
4. How does dilution affect the percent ionization of a weak acid or a weak base?
5. What is the relationship between the K_a of a weak acid and its percent ionization? Does a compound with a large pK_a value have a higher or a lower percent ionization than a compound with a small pK_a value (assuming the same analytical concentration in both cases)? Explain.
6. For a dilute solution of a weak acid (HA), show that the pH of the solution can be approximated using the following equation (where C_{HA} is the analytical concentration of the weak acid):

$$pH = -\log \sqrt{K_a C_{HA}} \tag{11.5.19}$$

Under what conditions is this approximation valid?

Numerical Problems

1. The pK_a of NH_3 is estimated to be 35. Its conjugate base, the amide ion (NH_2^-), can be isolated as an alkali metal salt, such as sodium amide ($NaNH_2$). Calculate the pH of a solution prepared by adding 0.100 mol of sodium amide to 1.00 L of water. Does the pH differ appreciably from the pH of a NaOH solution of the same concentration? Why or why not?
2. Phenol is a topical anesthetic that has been used in throat lozenges to relieve sore throat pain. Describe in detail how you would prepare a 2.00 M solution of phenol (C_6H_5OH) in water; then write equations to show all the species present in the solution. What is the equilibrium constant expression for the reaction of phenol with water? Use the information in Table E1 and Table E2 to calculate the pH of the phenol solution.
3. Describe in detail how you would prepare a 1.50 M solution of methylamine in water; then write equations to show all the species present in the solution. What is the equilibrium constant expression for the reaction of methylamine with water? Use the information in Table E1 and Table E2 to calculate the pH of the solution.
4. A 0.200 M solution of diethylamine, a substance used in insecticides and fungicides, is only 3.9% ionized at 25°C. Write an equation showing the equilibrium reaction and then calculate the pK_b of diethylamine. What is the pK_a of its conjugate acid, the diethylammonium ion? What is the equilibrium constant expression for the reaction of diethylammonium chloride with water?
5. A 1.00 M solution of fluoroacetic acid (FCH_2CO_2H) is 5% dissociated in water. What is the equilibrium constant expression for the dissociation reaction? Calculate the concentration of each species in solution and then calculate the pK_a of FCH_2CO_2H.
6. The pK_a of 3-chlorobutanoic acid ($CH_3CHClCH_2CO_2H$) is 4.05. What percentage is dissociated in a 1.0 M solution? Do you expect the pK_a of butanoic acid to be greater than or less than the pK_a of 3-chlorobutanoic acid? Why?
7. The pK_a of the ethylammonium ion ($C_2H_5NH_3^+$) is 10.64. What percentage of ethylamine is ionized in a 1.00 M solution of ethylamine?

8. The pK_a of Cl_3CCO_2H is 0.64. What is the pH of a 0.580 M solution? What percentage of the Cl_3CCO_2H is dissociated?

9. The pH of a 0.150 M solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) is 2.70. What is the pK_b of the conjugate base, aniline ($C_6H_5NH_2$)? Do you expect the pK_b of $(CH_3)_2CHNH_2$ to be greater than or less than the pK_b of $C_6H_5NH_2$? Why?

10. What is the pH of a 0.620 M solution of $CH_3NH_3^+Br^-$ if the pK_b of CH_3NH_2 is 10.62?

11. The pK_b of 4-hydroxypyridine is 10.80 at 25°C. What is the pH of a 0.0250 M solution?



12. The pK_a values of formic acid and the methylammonium ion are 3.75 and 10.62, respectively. Calculate *K* for the following reaction:

$$HCO^-_{2(aq)} + CH_3NH^+_{3(aq)} \rightleftharpoons HCO_2H_{(aq)} + CH_3NH_{2(aq)} \tag{11.5.20}$$

13. The pK_a values of butanoic acid and the ammonium ion are 4.82 and 9.24, respectively. Calculate *K* for the following reaction:

$$CH_3CH_2CH_2CO^-_{2(aq)} + NH^+_{4(aq)} \rightleftharpoons CH_3CH_2CH_2CO_2H_{(aq)} + NH_{3(aq)} \tag{11.5.21}$$

14. Use the information in Tables E1 and E2 to calculate the pH of a 0.0968 M solution of calcium formate.

15. Calculate the pH of a 0.24 M solution of sodium lactate. The pK_a of lactic acid is 3.86.

16. Use the information in Tables E1 and E2 to determine the pH of a solution prepared by dissolving 750.0 mg of methylammonium chloride ($CH_3NH_3^+Cl^-$) in enough water to make 150.0 mL of solution.

17. Use the information in Tables E1 and E2 to determine the pH of a solution prepared by dissolving 855 mg of sodium nitrite ($NaNO_2$) in enough water to make 100.0 mL of solution.

Answers

1.
2.
3.
4.
5.
6.
7.
8.

9. pK_b = 9.43; $(CH_3)_2CHNH_2$ will be a stronger base and have a lower pK_b; aniline is a weaker base because the lone pair on the nitrogen atom can be delocalized on the aromatic ring.

10.
11.
12.

13. 3.8×10^{-5}
14.
15.
16.
17. 8.18

Contributors

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Modified by Joshua B. Halpern

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11.6: Buffers

Learning Objectives

By the end of this chapter, you will have background information that will help you to be able to:

- Identify buffer solutions and calculate their pH

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or "buffer," other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of H^+). Le Chatelier's principle can be used to predict the effect on the equilibrium position of the solution.

A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. Recall that the dissociation reaction of acetic acid is as follows:

$$CH_3CO_2H_{(aq)} \leftrightharpoons CH_3CO^-_{(aq)} + H^+_{(aq)} \tag{16.6.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3CO_2]}{[CH_3CO_2H]} \tag{16.6.2}$$

Sodium acetate (CH_3CO_2Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na^+ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier's principle predicts that the equilibrium in Equation 16.6.1 will shift to the left, consuming some of the added $CH_3CO_2^-$ and some of the H^+ ions originally present in solution:

Because Na^+ is a spectator ion, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[H^+]$ is less than the initial value. Because $[H^+]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding *any* base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess H^+ ions react with the conjugate base ($CH_3CO_2^-$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $[CH_3CO_2^-]$ than before. In both cases, *only the equilibrium composition has changed; the ionization constant K_a for acetic acid remains the same*. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $CH_3CO_2^-$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is called the common ion effectThe shift in equilibrium that results when a strong electrolyte containing one ion in common with a reaction system that is at equilibrium is added to the system..

Note the Pattern

Adding a common ion to a system at equilibrium affects the equilibrium composition but not the ionization constant.

Example 16.6.1

In Section 16.4, we calculated that a 0.150 M solution of formic acid at 25°C (pK_a = 3.75) has a pH of 2.28 and is 3.5% ionized.

1. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
2. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a, and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.

B Substitute the expressions for the final concentrations into the expression for K_a. Calculate [H^+] and the pH of the solution.

C Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

1. **A** Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:

$$HCO_2H_{(aq)} \leftrightharpoons HCO^-_{2(aq)} + H^+_{(aq)}$$

The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

$$HCO_2H_{(aq)} \leftrightharpoons HCO^-_{2(aq)} + H^+_{(aq)} \quad (11.6.1)$$

	[HCO_2H]	[H^+]	[HCO_2^-]
initial	0.150	1.00×10^{-7}	0.100
change	$-x$	$+x$	$+x$
final	$(0.150 - x)$	x	$(0.100 + x)$

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(x)\,(0.100 + x)}{0.150 + x} \approx \frac{x(0.100)}{0.150} = 10^{-3.75} = 1.8 \times 10^{-4}$$

Rearranging and solving for x,

$$x = (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M} = 1.35 \times 10^{-4} = [HCO_2^-]$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover, K_aC_{HA} = $(1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$, which is greater than 1.0×10^{-6}, so again, our assumption is justified. The final pH is $-\log(2.7 \times 10^{-4})$ = 3.57, compared with the initial value of 2.29. Thus adding a salt containing the conjugate base

of the acid has increased the pH of the solution, as we expect based on Le Chatelier's principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

2. **C** Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$$HCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{2(aq)} \tag{11.6.2}$$

	[HCO_2H]	[H^+]	[HCO_2^-]
initial	0.150	0.200	0
change	$-x$	$+x$	$+x$
final	$(0.150 - x)$	$(0.200 + x)$	x

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final [HCO_2^-]. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$Ka = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(0.200 + x)(x)}{0.150 - x} \approx \frac{x(0.200)}{0.150} = 1.80 \times 10^{-4}$$

Rearranging and solving for x,

$$x = (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M} = 1.35 \times 10^{-4} = [HCO_2^-]$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4}\ M}{0.150\ M} \times 100$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding H^+ ions drives the dissociation equlibrium to the left.

Exercise

As you learned in Example 8, a 0.225 M solution of ethylamine ($CH_3CH_2NH_2$, pK_b = 3.19) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

1. the pH of the solution if enough solid ethylamine hydrochloride ($EtNH_3Cl$) is added to make the solution 0.100 M in $EtNH_3^+$
2. the percentage of ethylamine that is ionized if enough solid NaOH is added to the original solution to give a final concentration of 0.050 M NaOH

Answer

1. 11.16
2. 1.3%

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{16.6.3}$$

If the equilibrium constant for the reaction as written in Equation 16.6.3 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = 1/K_b = 10^5$. Adding a strong base such as OH^- to the solution therefore causes

the equilibrium in Equation 16.6.3 to shift to the left, consuming the added OH^-. As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier's principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.0, the pK_a of its conjugate acid is $pK_a = pK_w - pK_b = 14.0 - 5.0 = 9.0$. Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

$$BH^+_{(aq)} + H_2O_{(l)} \rightleftharpoons B_{(aq)} + H_3O^+_{(aq)} \tag{16.6.4}$$

Again, the equilibrium constant for the reverse of this reaction is very large: $K = 1/K_a = 10^9$. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 16.6.4 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the *pH range* over which they can maintain a more or less constant pH and by their buffer capacityThe amount of strong acid or strong base that a buffer solution can absorb before the pH changes dramatically., the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 16.6.1, when NaOH is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

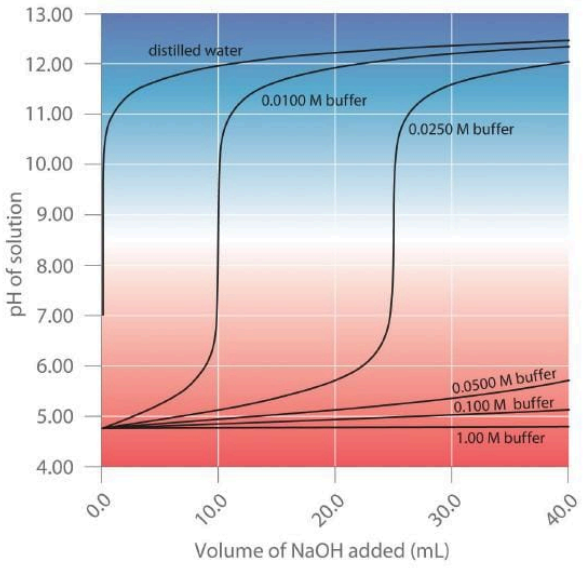


Figure 16.6.1 Effect of Buffer Concentration on the Capacity of a Buffer A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M NaOH to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of NaOH solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the NaOH solution results in only a relatively small change in pH.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 14 to calculate the pH of a solution containing known concentrations of formic acid and

formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is HA ⇌ H^+ + A^- for which the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{16.6.5}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{16.6.6}$$

Taking the logarithm of both sides and multiplying both sides by –1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) = -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{16.6.7}$$

Replacing the negative logarithms in Equation 16.60,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{16.6.8}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{16.6.9}$$

Equation 16.6.8 and Equation 16.6.9 are both forms of the Henderson-Hasselbalch equationA rearranged version of the equilibrium constant expression that provides a direct way to calculate the pH of a buffer solution: pH = pK_a + log([base]/[acid])., named after the two early-20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch equation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch equation is easily interpreted without the need for calculations:

1. **[base] = [acid].** Under these conditions, [base]/[acid] = 1 in Equation 16.6.9. Because log 1 = 0, pH = pK_a, *regardless of the actual concentrations of the acid and base*. Recall from Section 16.5 that this corresponds to the midpoint in the titration of a weak acid or a weak base.
2. **[base]/[acid] = 10.** In Equation 16.6.9, because log 10 = 1, pH = pK_a + 1.
3. **[base]/[acid] = 100.** In Equation 16.6.9, because log 100 = 2, pH = pK_a + 2.

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = pK_a – 1. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

Note the Pattern

If [base] = [acid] for a buffer, then pH = pK_a. Changing this ratio by a factor of 10 either way changes the pH by ±1 unit.

Example 16.6.2

What is the pH of a solution that contains

1. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)
2. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?
3. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch equation (Equation 16.61 or Equation 16.62) to calculate the pH.

Solution:

1. According to the Henderson-Hasselbalch equation, the pH of a solution that contains both a weak acid and its conjugate base is pH = pK_a + log([A^-]/[HA]). Inserting the given values into the equation,

$$pH = 3.75 + \log\left(\frac{0.215}{0.135}\right) = 3.75 + \log 1.593 = 3.95$$

   This result makes sense because the [A^-]/[HA] ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and pK_a + 1, or 4.75.

2. This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch equation,

$$pH = 3.75 + \log\left(\frac{0.0215}{0.0135}\right) = 3.75 + \log 1.593 = 3.95$$

   This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends *only* on the *ratio* of the concentrations of the conjugate base and the acid, *not* on the magnitude of the concentrations. Because the [A^-]/[HA] ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

3. In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Equation 16.62, the more general form of the Henderson-Hasselbalch equation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and [acid] = [HPy^+] = 0.234 M. We also are given pK_b = 8.77 for pyridine, but we need pK_a for the pyridinium ion. Recall from Equation 16.2.10 that the pK_b of a weak base and the pK_a of its conjugate acid are related: pK_a + pK_b = pK_w. Thus pK_a for the pyridinium ion is pK_w – pK_b = 14.00 – 8.77 = 5.23. Substituting this pK_a value into the Henderson-Hasselbalch equation,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) = 5.23 + \log\left(\frac{0.119}{0.234}\right) = 5.23 - 0.294 = 4.94$$

   Once again, this result makes sense: the [B]/[BH^+] ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and pK_a – 1, or 4.23.

Exercise

What is the pH of a solution that contains

1. 0.333 M benzoic acid and 0.252 M sodium benzoate?
2. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer

1. 4.08
2. 9.68

The Henderson-Hasselbalch equation can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 16.

Example 16.6.3

The buffer solution in Example 15 contained 0.135 M HCO_2H and 0.215 M HCO_2Na and had a pH of 3.95.

1. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?
2. What is the final pH if 5.00 mL of 1.00 M NaOH are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example 14. Then calculate the amount of acid or base added.

B Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch equation (Equation 16.6.9) to obtain the pH.

Solution:

The added HCl (a strong acid) or NaOH (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

1. **A** We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100 \cancel{mL}\left(\frac{0.135\ mmol\ HCO_2H}{\cancel{mL}}\right) = 13.5\ mmol\ HCO_2H$$

$$100 \cancel{mL}\left(\frac{0.215\ mmol\ HCO_2^-}{\cancel{mL}}\right) = 21.5\ mmol\ HCO_2^-$$

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00 \cancel{mL}\left(\frac{1.00\ mmol\ H^+}{\cancel{mL}}\right) = 5.00\ mmol\ H^+$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$HCO_{2(aq)}^{2-} + H_{(aq)}^+ \rightarrow HCO_2H_{(aq)}$$

$HCO_2^-(aq) + H^+(aq) \rightarrow HCO_2H(aq)$			
	$[HCO_2^-]$	$[H^+]$	$[HCO_2H]$
initial	21.5 mmol	5.00 mmol	13.5 mmol
change	−5.00 mmol	−5.00 mmol	+5.00 mmol
final	16.5 mmol	~0 mmol	18.5 mmol

The final amount of H^+ in solution is given as "~0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 14 or the Henderson–Hasselbach equation. Because we have performed *many* equilibrium calculations in this chapter, we'll take the latter approach. The Henderson-Hasselbalch equation requires the concentrations of HCO_2^- and HCO_2H, which can be calculated using the number of millimoles (n) of each

and the total volume (V_T). Substituting these values into the Henderson-Hasselbalch equation,

$$pH = pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) = pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right)$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$pH = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) = 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right) = 3.75\ - 0.050 = 3.70$$

Once again, this result makes sense on two levels. First, the addition of HCl has decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the pK_a and pK_a – 1.

1. **A** The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^-. The number of millimoles of OH^- in 5.00 mL of 1.00 M NaOH is as follows:

$$5.00\ \cancel{mL}\left(\frac{1.00\ mmol\ H^+}{\cancel{mL}}\right) = 5.00\ mmol\ H^+$$

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.

$HCO_2H(aq) + OH^-(aq) \rightarrow HCO_2^-(aq) + H_2O(l)$			
	$[HCO_2H]$	$[OH^-]$	$[HCO_2^-]$
initial	13.5 mmol	5.00 mmol	21.5 mmol
change	–5.00 mmol	–5.00 mmol	+5.00 mmol
final	8.5 mmol	~0 mmol	26.5 mmol

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$pH = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) = 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right) = 3.75 + 0.494 = 4.24$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO_2^-/HCO_2H ratio between 1 and 10.

Exercise

The buffer solution from Example 15 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

1. What is the final pH if 12.0 mL of 1.5 M NaOH are added to 250 mL of this solution?
2. What is the final pH if 12.0 mL of 1.5 M HCl are added?

Answer

1. 5.30
2. 4.42

Note the Pattern

Only the *amounts* (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-

Hasselbalch equation, *not* their concentrations.

Note the Pattern

The most effective buffers contain equal concentrations of an acid and its conjugate base.

The results obtained in Example 16 and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or NaOH solution to 100 mL of an *un*buffered solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M NaOH would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure 16.6.2 for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to CH_3CO_2H from 1:1 reduces the buffer capacity of the solution.

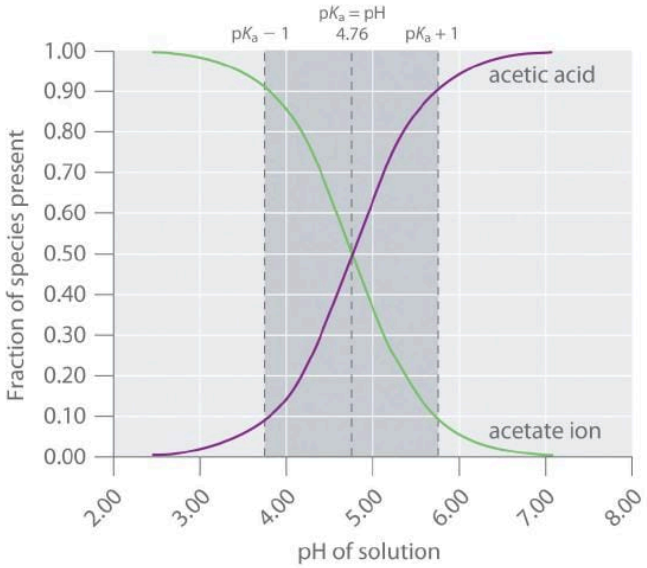


Figure 16.6.2 Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to pH = $pK_a \pm 1$).

The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5. Consider the schematic titration curve of a weak acid with a strong base shown in Figure 16.6.3. As indicated by the labels, the region around pK_a corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat portion of the curve extends only from approximately a pH value of 1 unit less than the pK_a to approximately a pH value of 1 unit greater than the pK_a, which is why buffer solutions usually have a pH that is within ±1 pH units of the pK_a of the acid component of the buffer.

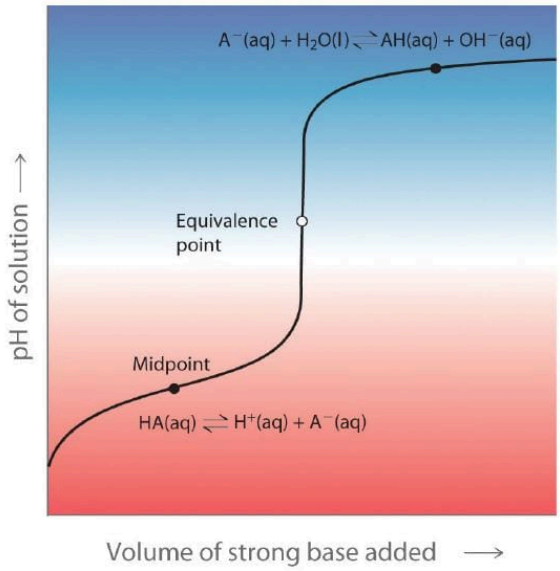


Figure 16.6.3 The Relationship between Titration Curves and **Buffers**This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

In the region of the titration curve at the lower left, before the midpoint, the acid–base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to K_a. In the region of the titration curve at the upper right, after the midpoint, the acid–base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the weak acid with water, corresponding to K_b. However, we can calculate either K_a or K_b from the other because they are related by K_w.

Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

The acid–base equilibrium in the CO_2/HCO_3^- buffer system is usually written as follows:

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)} \tag{16.6.10}$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 16.6.10 is a grossly oversimplified version of the CO_2/HCO_3^- system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3. Thus Equation 16.6.10 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C. As shown in Equation 16.6.11, CO_2 is in equilibrium with H_2CO_3, but the equilibrium lies far to the left, with an H_2CO_3/CO_2 ratio less than 0.01 under most conditions:

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \tag{16.6.11}$$

with $K' = 4.0 \times 10^{-3}$ at 37°C. The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4}, which makes it a much stronger acid than Equation 16.6.10 suggests. Adding Equation 16.6.10 and Equation 16.6.11 and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

$$CO_{2(aq)} + H_2O_{(l)} \leftrightharpoons H_2CO_{3(aq)} \tag{16.6.12a}$$

with $K' = 4.0 \times 10^{-3} (37\ ^\circ C)$

$$H_2CO_{3(aq)} \leftrightharpoons H^+_{(aq)} + HCO^-_{3(aq)} \tag{16.6.12b}$$

with $K_a = 2.0 \times 10^{-4} (37\ ^\circ C)$

$$CO_{2(aq)} + H_2O_{(l)} \leftrightharpoons H^+_{(aq)} + HCO^-_{3(aq)} \tag{16.6.12c}$$

with $K = 8.0 \times 10^{-7} (37\ ^\circ C)$

The *K* value for the reaction in Equation 16.6.12 is the product of the *true* ionization constant for carbonic acid (K_a) and the equilibrium constant (*K*) for the reaction of CO_2(aq) with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

$$K = \frac{[H^+][HCO_3^-]}{[CO_2]} = 8.0 \times 10^{-7} \tag{16.6.13}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to Henry's law, $[CO_2] = kP(CO_2)$ where *k* is the Henry's law constant for CO_2, which is 3.0×10^{-5} M/mmHg at 37°C. (For more information about Henry's law, see Section 13.4 .) Substituting this expression for $[CO_2]$ in Equation 16.6.13,

$$K = \frac{[H^+][HCO_3^-]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{CO_2})} \tag{16.6.14}$$

where $P(CO_2)$ is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[HCO_3^-]}{(3.0 \times 10^{-5} M/mm\ Hg)\ (P_{CO_2})}\right) \tag{16.6.15}$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 16.6.4 plots the relationship between pH and $[HCO_3^-]$ under physiological conditions for several different values of $P(CO_2)$ with normal pH and $[HCO_3^-]$ values indicated by the dashed lines.

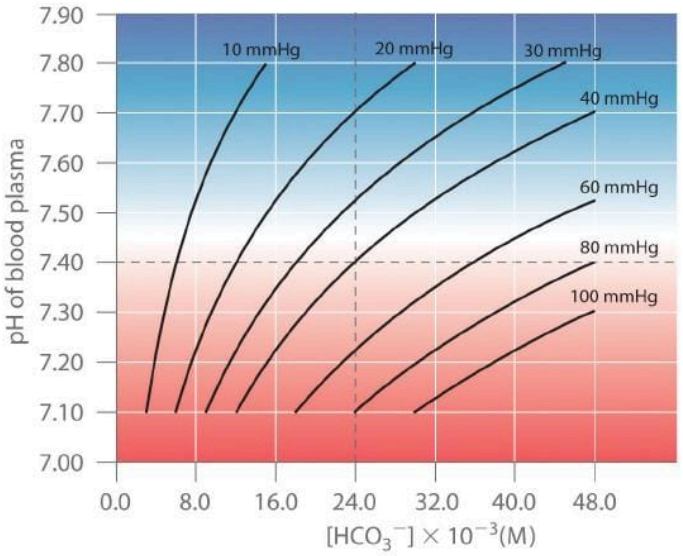


Figure 16.6.4 Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of $P(CO_2)$Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of $P(CO_2)$ indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines.

According to Equation 16.6.12, adding a strong acid to the CO_2/HCO_3^- system causes $[HCO_3^-]$ to decrease as HCO_3^- is converted to CO_2. Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in $P(CO_2)$. Because the change in $[HCO_3^-]/P(CO_2)$ is small, Equation 16.6.15 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO_2 to form $[HCO_3^-]$, but CO_2 is replenished by the body, again limiting the change in both $[HCO_3^-]/P(CO_2)$ and pH. The CO_2/HCO_3^- buffer system is an example of an *open* system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower $P(CO_2)$ at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[HCO_3^-]$. The increase in pH and decrease in $[HCO_3^-]$ in response to the decrease in $P(CO_2)$ are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the **common ion effect**. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its **buffer capacity** depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the **Henderson-Hasselbalch equation**, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

Key Equations

Henderson-Hasselbalch equation

Equation 16.6.8:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Equation 16.6.9:

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

Key Takeaway

- The common ion effect allows solutions to act as buffers, whose pH can be calculated using the Henderson-Hasselbalch equation.

Conceptual Problems

1. Explain why buffers are crucial for the proper functioning of biological systems.
2. What is the role of a buffer in chemistry and biology? Is it correct to say that buffers prevent a change in $[H_3O^+]$? Explain your reasoning.
3. Explain why the most effective buffers are those that contain approximately equal amounts of the weak acid and its conjugate base.

4. Which region of the titration curve of a weak acid or a weak base corresponds to the region of the smallest change in pH per amount of added strong acid or strong base?

5. If you were given a solution of sodium acetate, describe two ways you could convert the solution to a buffer.

6. Why are buffers usually used only within approximately one pH unit of the pK_a or pK_b of the parent weak acid or base?

7. The titration curve for a monoprotic acid can be divided into four regions: the starting point, the region around the midpoint of the titration, the equivalence point, and the region after the equivalence point. For which region would you use each approach to describe the behavior of the solution?

    1. a buffer
    2. a solution of a salt of a weak base
    3. a solution of a weak acid
    4. diluting a strong base

8. Which of the following will produce a buffer solution? Explain your reasoning in each case.

    1. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
    2. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
    3. mixing 100 mL of 0.1 M hydrofluoric acid and 100 mL of 0.1 M HCl
    4. mixing 100 mL of 0.1 M hydrofluoric acid and 50 mL of 0.1 M NaOH
    5. mixing 100 mL of 0.1 M sodium fluoride and 50 mL of 0.1 M NaOH.

9. Which of the following will produce a buffer solution? Explain your reasoning in each case.

    1. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
    2. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
    3. mixing 100 mL of 0.1 M acetic acid and 100 mL of 0.1 M NaOH
    4. mixing 100 mL of 0.1 M acetic acid and 50 mL of 0.1 M NaOH
    5. mixing 100 mL of 0.1 M sodium acetate and 50 mL of 0.1 M acetic acid

10. Use the definition of K_b for a weak base to derive the following expression, which is analogous to the Henderson-Hasselbalch equation but for a weak base (B) rather than a weak acid (HA):

$$pOH = pK_b - \log\left(\frac{[base]}{[acid]}\right) \tag{11.6.3}$$

11. Why do biological systems use overlapping buffer systems to maintain a constant pH?

12. The CO_2/HCO_3^- buffer system of blood has an effective pK_a of approximately 6.1, yet the normal pH of blood is 7.4. Why is CO_2/HCO_3^- an effective buffer when the pK_a is more than 1 unit below the pH of blood? What happens to the pH of blood when the CO_2 pressure increases? when the O_2 pressure increases?

13. Carbon dioxide produced during respiration is converted to carbonic acid (H_2CO_3). The pK_{a1} of carbonic acid is 6.35, and its pK_{a2} is 10.33. Write the equations corresponding to each pK value and predict the equilibrium position for each reaction.

Answer

1.
2.
3.
4.
5.
6.
7.
8.
9. 1. Not a buffer; the HCl completely neutralizes the sodium acetate to give acetic acid and NaCl(aq).

2. Buffer; the HCl neutralizes only half of the sodium acetate to give a solution containing equal amounts of acetic acid and sodium acetate.
3. Not a buffer; the NaOH completely neutralizes the acetic acid to give sodium acetate.
4. Buffer; the NaOH neutralizes only half of the acetic acid to give a solution containing equal amounts of acetic acid and sodium acetate.
5. Buffer; the solution will contain a 2:1 ratio of sodium acetate and acetic acid.

10.
11.
12.
13.

Numerical Problems

1. Benzenesulfonic acid (pK_a = 0.70) is synthesized by treating benzene with concentrated sulfuric acid. Calculate the following:

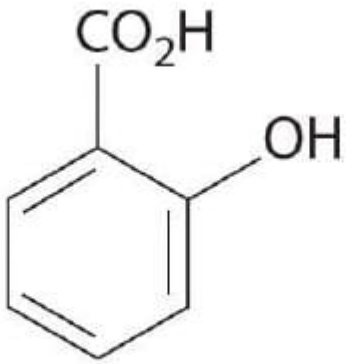
    1. the pH of a 0.286 M solution of benzenesulfonic acid
    2. the pH after adding enough sodium benzenesulfonate to give a final benzenesulfonate concentration of 0.100 M

2. Phenol has a pK_a of 9.99. Calculate the following:

    1. the pH of a 0.195 M solution
    2. the percent increase in the concentration of phenol after adding enough solid sodium phenoxide (the sodium salt of the conjugate base) to give a total phenoxide concentration of 0.100 M

3. Salicylic acid is used in the synthesis of acetylsalicylic acid, or aspirin. One gram dissolves in 460 mL of water to create a saturated solution with a pH of 2.40.

    1. What is the K_a of salicylic acid?
    2. What is the final pH of a saturated solution that is also 0.238 M in sodium salicylate?
    3. What is the final pH if 10.00 mL of 0.100 M HCl are added to 150.0 mL of the buffered solution?
    4. What is the final pH if 10.00 mL of 0.100 M NaOH are added to 150.0 mL of the buffered solution?



salicylic acid

4. An intermediate used in the synthesis of perfumes is valeric acid, also called pentanoic acid. The pK_a of pentanoic acid is 4.84 at 25°C.

    1. What is the pH of a 0.259 M solution of pentanoic acid?
    2. Sodium pentanoate is added to make a buffered solution. What is the pH of the solution if it is 0.210 M in sodium pentanoate?
    3. What is the final pH if 8.00 mL of 0.100 M HCl are added to 75.0 mL of the buffered solution?
    4. What is the final pH if 8.00 mL of 0.100 M NaOH are added to 75.0 mL of the buffered solution?

Answer

1.
2.
3.
    1. 1.35×10^{-3}
    2. 4.03
    3. 3.88
    4. 4.30
4.

Contributors

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Modified by Joshua B. Halpern

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11.7: Acid-Base Titrations

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- For any titration process, write the neutralization reaction and determine concentration, moles, or pH at the end of the titration.

In an acid–base titration, a buret is used to deliver measured volumes of an acid or a base solution of known concentration (the *titrant*) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the *unknown*). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a titration curve, which is a plot of the pH of the solution being titrated versus the amount of acid or base (of known concentration) added.. The shape of the curve provides important information about what is occurring in solution during the titration.

Titrations of Strong Acids and Bases

Part (a) of Figure 16.5.1 shows a plot of the pH as 0.20 M HCl is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as HCl is added. Eventually the pH becomes constant at 0.70—a point well beyond its value of 1.00 with the addition of 50.0 mL of HCl (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M NaOH is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of NaOH as shown in part (b) in Figure 16.5.1 . As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.

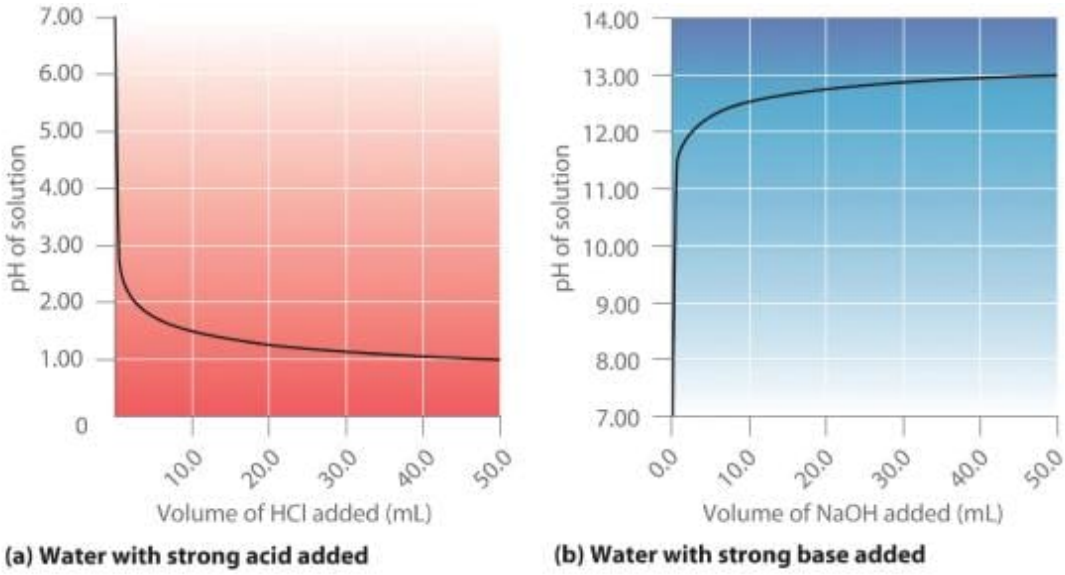


Figure 16.5.1 Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M NaOH.

Suppose that we now add 0.20 M NaOH to 50.0 mL of a 0.10 M solution of HCl. Because HCl is a strong acid that is completely ionized in water, the initial $[H^+]$ is 0.10 M, and the initial pH is 1.00. Adding NaOH decreases the concentration of H^+ because of the neutralization reaction: $OH^- + H^+ \rightarrow H_2O$ (in part (a) in Figure 16.5.2). Thus the pH of the solution increases gradually. Near

the equivalence pointThe point in a titration where a stoichiometric amount of the titrant has been added., however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution, the pH increases much more rapidly because most of the H^+ ions originally present have been consumed. (For more information on titrations and the equivalence point, see Section 8.9 .) For the titration of a monoprotic strong acid (HCl) with a *monobasic* strong base (NaOH), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

$$moles\ of\ base = (volume)_b(molarity)_b V_b M_b = moles\ of\ acid = (volume)_a(molarity)_a = V_a M_a \tag{16.5.1}$$

If 0.20 M NaOH is added to 50.0 mL of a 0.10 M solution of HCl, we solve for V_b:

$$V_b(0.20Me) = 0.025L = 25mL \tag{11.7.1}$$

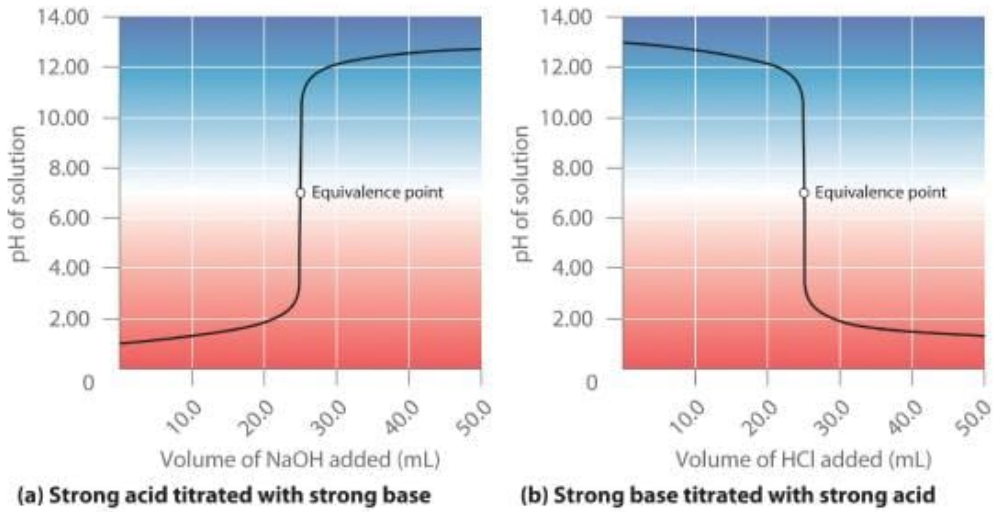


Figure 16.5.2 The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M NaOH is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M HCl is slowly added to 50.0 mL of 0.10 M NaOH, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more.

At the equivalence point (when 25.0 mL of NaOH solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more NaOH produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M NaOH.

As shown in part (b) in Figure 16.5.2, the titration of 50.0 mL of a 0.10 M solution of NaOH with 0.20 M HCl produces a titration curve that is nearly the mirror image of the titration curve in part (a) in Figure 16.5.2. The pH is initially 13.00, and it slowly decreases as HCl is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M HCl.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on *only* the concentrations of the acid and base, *not* their identities.

Note the Pattern

The shape of the titration curve involving a strong acid and a strong base depends only on their concentrations, not their identities.

Example 16.5.1

Calculate the pH of the solution after 24.90 mL of 0.200 M NaOH has been added to 50.00 mL of 0.100 M HCl.

Given: volumes and concentrations of strong base and acid

Asked for: pH

Strategy:

A Calculate the number of millimoles of H^+ and OH^- to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.

B Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

Solution:

A Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of H^+ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$50.00 \cancel{mL} \left(\frac{0.100\ mmol\ HCl}{\cancel{mL}} \right) = 5.00\ mmol\ HCl = 5.00\ mmol\ H^+$$

The number of millimoles of NaOH added is as follows:

$$24.90 \cancel{mL} \left(\frac{0.200\ mmol\ NaOH}{\cancel{mL}} \right) = 4.98\ mmol\ NaOH = 4.98\ mmol\ OH^-$$

Thus H^+ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of OH^- to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess H^+ is 5.00 mmol – 4.98 mmol = 0.02 mmol of H^+.

B The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of H^+ is as follows:

$$[H^+] = \frac{0.02\ mmol\ H^+}{74.90\ mL} = 3 \times 10^{=4}\ M$$

The pH is $-\log[H^+] = -\log(3 \times 10^{-4}) = 3.5$, which is significantly less than the pH of 7.00 for a neutral solution.

Exercise

Calculate the pH of a solution prepared by adding 40.00 mL of 0.237 M HCl to 75.00 mL of a 0.133 M solution of NaOH.

Answer: 11.6

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned in Section 16.4, $[H^+]$ of a solution of a weak acid (HA) is *not* equal to the concentration of the acid but depends on both its pK_a and its concentration. Because only a fraction of a weak acid dissociates, $[H^+]$ is less than [HA]. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration. Part (a) in Figure 16.5.3 shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M HCl shown in part (a) in Figure 16.5.2 . Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the HCl solution, and the pH changes more rapidly during the first part of the titration. Note also that the pH of the acetic acid solution at the equivalence point is greater than 7.00. That is, at the equivalence point, the solution is basic. In addition, the change in pH around the equivalence point is only about half as large as for the HCl titration; the magnitude of the pH change at the equivalence point depends on the pK_a of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess NaOH present, regardless of whether the acid is weak or strong.

Note the Pattern

The shape of the titration curve of a weak acid or weak base depends heavily on their identities and the K_a or K_b.

The titration curve in part (a) in Figure 16.5.3 was created by calculating the starting pH of the acetic acid solution before any NaOH is added and then calculating the pH of the solution after adding increasing volumes of NaOH. The procedure is illustrated in the following subsection and Example 12 for three points on the titration curve, using the pK_a of acetic acid (4.76 at 25°C; K_a = 1.7×10^{-5}).

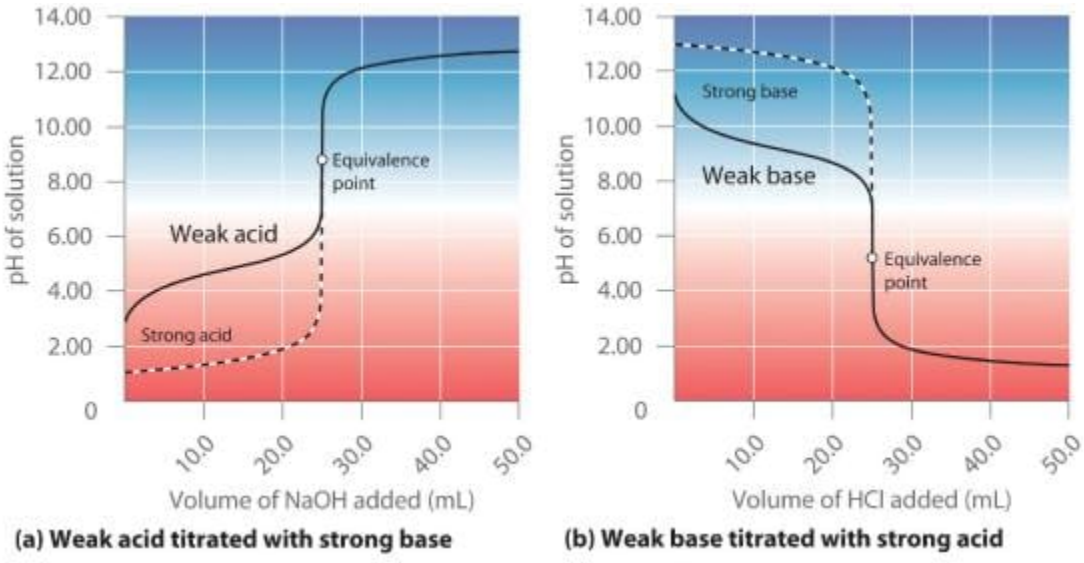


Figure 16.5.3 The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid(a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH is shown as a dashed line. (b) As 0.200 M HCl is slowly added to 50.0 mL of 0.100 M NH_3, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M NaOH with 0.200 M HCl is shown as a dashed line.

Calculating the pH of a Solution of a Weak Acid or a Weak Base

As explained Section 16.4, if we know K_a or K_b and the initial concentration of a weak acid or a weak base, we can calculate the pH of a solution of a weak acid or a weak base by setting up a table of initial concentrations, changes in concentrations, and final concentrations. In this situation, the initial concentration of acetic acid is 0.100 M. If we define x as $[H^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CO_2^- \tag{11.7.2}$$

	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	0.100	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.100 - x)$	x	x

In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.4.8 and Equation 16.4.9 to check that this assumption is justified.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(x)(x)}{0.100 - x} \approx \frac{x^2}{0.100} = 1.74 \times 10^{-5}$$

Solving this equation gives $x = [H^+] = 1.32 \times 10^{-3}\ M$. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$

Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we add 5.00 mL of 0.200 M NaOH to 50.00 mL of 0.100 M CH_3CO_2H (part (a) in Figure 16.5.4). Because the neutralization reaction proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{16.5.2}$$

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the *amounts* of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation (Equation 16.2.2) to determine $[H^+]$ of the resulting solution.

Step 1: To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of CH_3CO_2H in the original solution and the amount of OH^- in the NaOH solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL}\ (0.100\ \ mmol(CH_3CO_2H)/\cancel{mL}) = 5.00\ \ mmol(CH_3CO_2H)$$

The NaOH solution contained

5.00 mL=1.00 mmol (NaOH)

Comparing the amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:

5.00 mmol CH_3CO_2H – 1.00 mmol OH^- = 4.00 mmol CH_3CO_2H

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following table, which shows the numbers of moles of the various species, *not* their concentrations.

$$CH_3CO_2H(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l) \tag{11.7.3}$$

	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
initial	5.00 mmol	1.00 mmol	0 mmol
change	–1.00 mmol	–1.00 mmol	+1.00 mmol
final	4.00 mmol	0 mmol	1.00 mmol

This table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^-, but the amount of OH^- due to the autoionization of water is insignificant compared to the amount of OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium

until the second half of the problem.

Step 2: To calculate [H^+] at equilibrium following the addition of NaOH, we must first calculate [CH_3CO_2H] and [$CH_3CO_2^-$] using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M$$

$$[CH_3CO_2^-] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can use Equation 16.2.2 to calculate [H^+] at equilibrium:

$$K_a = \frac{[CH_3CO_2^-]\,[H^+]}{[CH_3CO_2H]}$$

$$[H^+] = \frac{K_a\,[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{\left(1.72 \times 10^{-5}\right)\left(7.27 \times 10^{-2}\ M\right)}{\left(1.82 \times 10^{-2}\right)} = 6.95 \times 10^{-5}\ M$$

Calculating $-\log[H^+]$ gives pH = $-\log(6.95 \times 10^{-5})$ = 4.158.

Comparing the titration curves for HCl and acetic acid in part (a) in Figure 16.5.3, we see that adding the same amount (5.00 mL) of 0.200 M NaOH to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for HCl (from 1.00 to 1.14) than for acetic acid (2.88 to 4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. In Example 16.5.2, we calculate another point for constructing the titration curve of acetic acid.

Example 16.5.2

What is the pH of the solution after 25.00 mL of 0.200 M NaOH is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of OH^- and CH_3CO_2H. Determine which species, if either, is present in excess.
B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.
C. If excess acetate is present after the reaction with OH^-, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.
D. Calculate K_b using the relationship $K_w = K_aK_b$ (Equation 16.2.10). Calculate [OH^-] and use this to calculate the pH of the solution.

Solution:

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

The initial numbers of millimoles of OH^- and CH_3CO_2H are as follows:

$$25.00\ \cancel{mL}\left(\frac{0.200\ mmol\ OH^-}{\cancel{mL}}\right) = 5.00\ mmol\ OH^-$$

$$50.00 \cancel{mL} \left(\frac{0.100\ mmol\ CH_3CO_2H}{\cancel{mL}} \right) = 5.00\ mmol\ CH_3CO_2H$$

The number of millimoles of OH^- equals the number of millimoles of CH_3CO_2H, so neither species is present in excess.

B Because the number of millimoles of OH^- added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)$			
	[CH_3CO_2H]	**[OH^-]**	**[$CH_3CO_2^-$]**
initial	5.00 mmol	5.00 mmol	0 mmol
final	0 mmol	0 mmol	5.00 mmol
change	−5.00 mmol	−5.00 mmol	+5.00 mmol

C Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base *with water* to calculate $[H^+]$ at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

$$[CH_3CO_2] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00 + 25.00)\ mL} = 6.67 \times 10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

$$CH_3CO^-_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant for this reaction is $K_b = K_w/K_a$, where K_a is the acid ionization constant of acetic acid. We therefore define x as $[OH^-]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$H_2O_{(l)} + CH_3CO^-_{2(aq)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)}$			
	[$CH_3CO_2^-$]	**[CH_3CO_2H]**	**[OH^-]**
initial	0.0667	0	1.00×10^{-7}
change	$-x$	$+x$	$+x$
final	$(0.0667 - x)$	x	x

D Substituting the expressions for the final values from this table into Equation 16.2.5,

$$K_b = \frac{[CH_3CO_2H]\,[OH^-]}{[CH_3CO_2^-]} \approx= \frac{x \cdot x}{0.0667 - x} = \frac{x^2}{0.0667}$$

We can obtain K_b by rearranging Equation 16.2.10 and substituting the known values:

$$K_b = \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.80 \times 10^{-10} = \frac{x^2}{0.0667}$$

which we can solve to get $x = 6.22 \times 10^{-6}$. Thus $[OH^-] = 6.22 \times 10^{-6}$ M, and the pH of the final solution is 8.794 (part (a) in Figure 16.5.4). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce OH^-.

Exercise

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of

ammonia. The pK_b of ammonia is 4.75 at 25°C.

Answer: 9.23

As shown in part (b) in Figure 16.5.3, the titration curve for NH_3, a weak base, is the reverse of the titration curve for acetic acid. In particular, the pH at the equivalence point in the titration of a weak base is *less* than 7.00 because the titration produces an acid.

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure 16.5.4 illustrates the shape of titration curves as a function of the pK_a or the pK_b. As the acid or the base being titrated becomes weaker (its pK_a or pK_b becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.

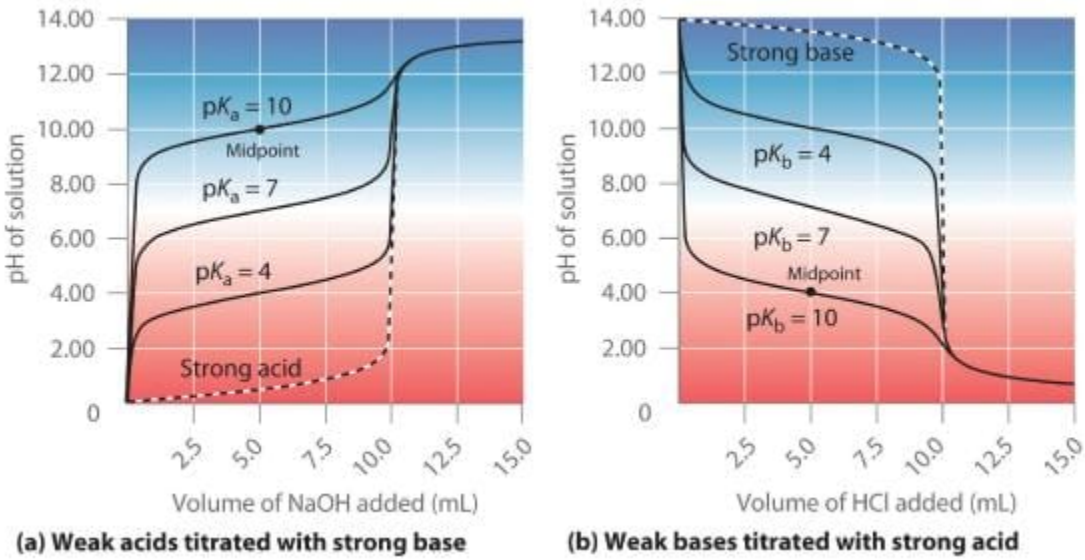


Figure 16.5.4 Effect of Acid or Base Strength on the Shape of Titration **Curves** Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added to 10.00 mL of 1.00 M solutions of weak acids with the indicated pK_a values. (b) Solution pH as a function of the volume of 1.00 M HCl added to 10.00 mL of 1.00 M solutions of weak bases with the indicated pK_b values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to pK_a = 10 and pK_b = 10.

One point in the titration of a weak acid or a weak base is particularly important: the midpoint of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in part (a) in Figure 16.5.5 and part (b) in Figure 16.5.5 for the two shallowest curves. By definition, at the midpoint of the titration of an acid, [HA] = [A^-]. Recall from Equation 16.2.2 that the ionization constant for a weak acid is as follows:

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

If [HA] = [A^-], this reduces to K_a = [H_3O^+]. Taking the negative logarithm of both sides,

$$log\ K_a = -log\,[H_3O^+]$$

From the definitions of pK_a and pH, we see that this is identical to

$$pK_a = pH$$

Thus *the pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid*, as indicated in part (a) in Figure 16.5.4 for the weakest acid where we see that the midpoint for pK_a = 10 occurs at pH = 10. Titration methods can therefore be used to determine both the concentration *and* the pK_a (or the pK_b) of a weak acid (or a weak base).

Note the Pattern

The pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid.

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group is titrated first, followed by the next most acidic, and so forth. If the pK_a values are separated by at least three pK_a units, then the overall titration curve shows well-resolved "steps" corresponding to the titration of each proton. A titration of the triprotic acid H_3PO_4 with NaOH is illustrated in Figure 16.5.5 and shows two well-defined steps: the first midpoint corresponds to pK_{a1}, and the second midpoint corresponds to pK_{a2}. Because HPO_4^{2-} is such a weak acid, pK_{a3} has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

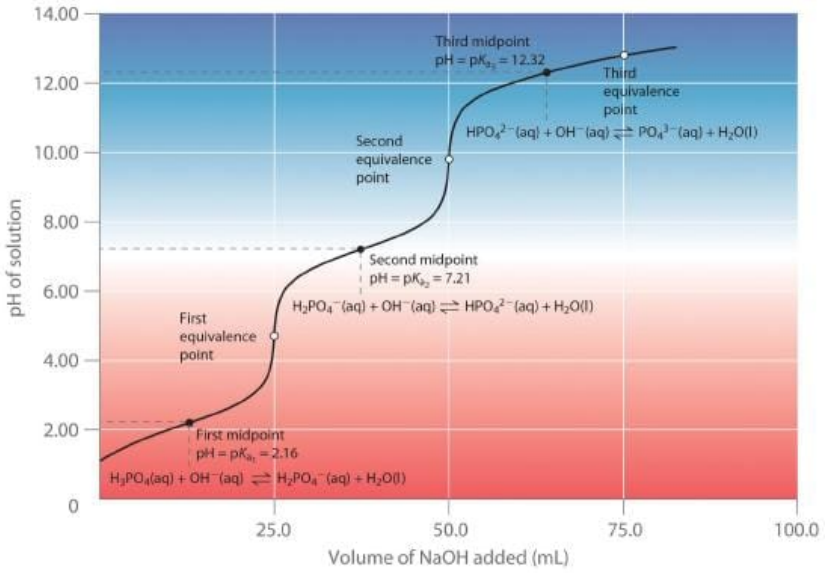
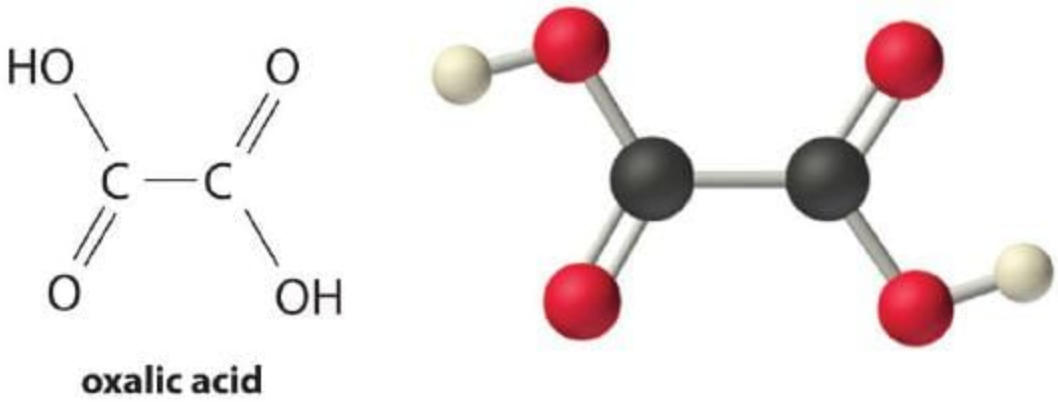


Figure 16.5.5 Titration Curve for Phosphoric Acid (H_3PO_4), a Typical Polyprotic **Acid**The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each K_a is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^{2-}$ at pH ≈ 9.8. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined.

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure 16.5.5 The initial pH is high, but as acid is added, the pH decreases in steps if the successive pK_b values are well separated. Table16.3.1 lists the ionization constants and pK_a values for some common polyprotic acids and bases.

Example 16.5.3

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M NaOH solution to 100.0 mL of a 0.0510 M solution of oxalic acid (HO_2CCO_2H), a diprotic acid (abbreviated as H_2ox). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($^-O_2CCO_2^-$, abbreviated ox^{2-}).Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as Ca^{2+} are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



Given: volume and concentration of acid and base

Asked for: pH

Strategy:

A Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.

B Calculate the concentrations of all the species in the final solution. Use Equation 16.2.3 to determine $[H^+]$ and convert this value to pH.

Solution:

A Table 16.3.1 gives the pK_a values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

$$100.00\ \cancel{mL}\left(\frac{0.510\ mmol\ H_2ox}{\cancel{mL}}\right) = 5.10\ mmol\ H_2ox$$

$$55.00\ \cancel{mL}\left(\frac{0.120\ mmol\ NaOH}{\cancel{mL}}\right) = 6.60\ mmol\ NaOH$$

The strongest acid (H_2ox) reacts with the base first. This leaves (6.60 – 5.10) = 1.50 mmol of OH^- to react with Hox^-, forming ox^{2-} and H_2O. The reactions can be written as follows:

$$\underset{5.10\ mmol}{H_2ox} + \underset{6.60\ mmol}{OH^-} \rightarrow \underset{5.10\ mmol}{Hox^-} + \underset{5.10\ mmol}{H_2O}$$

$$\underset{5.10\ mmol}{Hox^-} + \underset{1.50\ mmol}{OH^-} \rightarrow \underset{1.50\ mmol}{ox^{2-}} + \underset{1.50\ mmol}{H_2O}$$

In tabular form,

	H_2ox	OH^-	Hox^-	ox^{2-}
initial	5.10 mmol	6.60 mmol	0 mmol	0 mmol
change (step 1)	–5.10 mmol	–5.10 mmol	+5.10 mmol	0 mmol
final (step 1)	0 mmol	1.50 mmol	5.10 mmol	0 mmol
change (step 2)	—	–1.50 mmol	–1.50 mmol	+1.50 mmol
final	0 mmol	0 mmol	3.60 mmol	1.50 mmol

B The equilibrium between the weak acid (Hox^-) and its conjugate base (ox^{2-}) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}$. To calculate the pH of the solution, we need to know $[H^+]$, which is determined using exactly the same method as in the acetic acid titration in Example 12:

final volume of solution = 100.0 mL + 55.0 mL = 155.0 mL

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$[Hox^-] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$[ox^{2-}] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate $[H^+]$ at equilibrium using the following equation:

$$K_{a2} == \frac{[ox^{2-}]\,[H^+]}{[Hox^-]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$[H^+] = \frac{K_{a2}\,[Hox^-]}{[ox^{2-}]} = \frac{\left(1.6 \times 10^{-4}\right)\left(2.32 \times 10^{-2}\right)}{\left(9.68 \times 10^{-3}\right)} = 3.7 \times 10^{-4}\ M$$

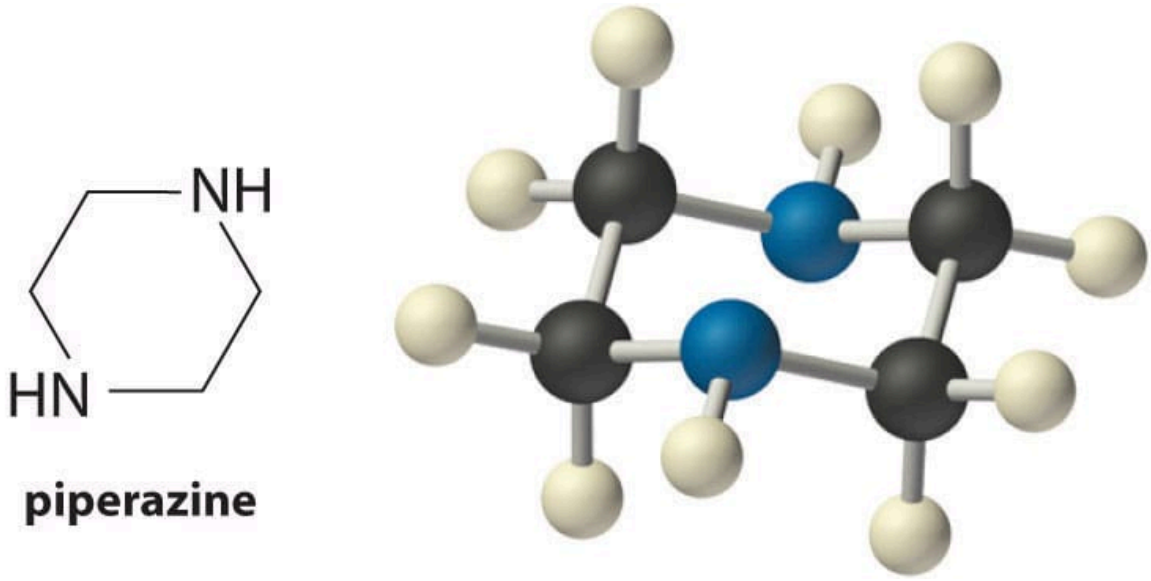
So

$$pH = -log\,[H^+] = -log\left(3.7 \times 10^{-4}\right) = 3.43$$

This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}), but we added only enough to titrate less than half of the second, less acidic proton, with pK_{a2}. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to pK_{a2}.

Exercise

Piperazine is a diprotic base used to control intestinal parasites (“worms”) in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (pK_{b1} = 4.27, pK_{b2} = 8.67). If the dog’s stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



Answer: 4.9 (Video Solution)

Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated (phenolphthalein, for example), which makes them particularly useful. The choice of indicator depends on the nature of the acid or base being titrated and is beyond the scope of this class.

Summary

The shape of a **titration curve**, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The **equivalence point** of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases, however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the **midpoint**, the point halfway on the titration curve to the equivalence point, is equal to the pK_a of the weak acid or the pK_b of the weak base. Thus titration methods can be used to determine both the concentration *and* the pK_a (or the pK_b) of a weak acid (or a weak base). **Acid–base indicators** are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

Key Takeaway

- Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the pK_a, and the pK_b of the system.

Conceptual Problems

1. Why is the portion of the titration curve that lies below the equivalence point of a solution of a weak acid displaced upward relative to the titration curve of a strong acid? How are the slopes of the curves different at the equivalence point? Why?

2. Predict whether each solution will be neutral, basic, or acidic at the equivalence point of each titration.

    1. An aqueous solution of NaOH is titrated with 0.100 M HCl.
    2. An aqueous solution of ethylamine ($CH_3CH_2NH_2$) is titrated with 0.150 M HNO_3
    3. An aqueous solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) is titrated with 0.050 M KOH.

3. The pK_a values of phenol red, bromophenol blue, and phenolphthalein are 7.4, 4.1, and 9.5, respectively. Which indicator is best suited for each acid–base titration?

    1. titrating a solution of $Ba(OH)_2$ with 0.100 M HCl
    2. titrating a solution of trimethylamine (Me_3N) with 0.150 M HNO_3
    3. titrating a solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) with 0.050 M KOH

4. For the titration of any strong acid with any strong base, the pH at the equivalence point is 7.0. Why is this not usually the case in titrations of weak acids or weak bases?

5. Why are the titration curves for a strong acid with a strong base and a weak acid with a strong base identical in shape above the equivalence points but not below?

6. Describe what is occurring on a molecular level during the titration of a weak acid, such as acetic acid, with a strong base, such as NaOH, at the following points along the titration curve. Which of these points corresponds to pH = pK_a?

    1. at the beginning of the titration
    2. at the midpoint of the titration
    3. at the equivalence point
    4. when excess titrant has been added

7. On a molecular level, describe what is happening during the titration of a weak base, such as ammonia, with a strong acid, such as HCl, at the following points along the titration curve. Which of these points corresponds to pOH = pK_b?

    1. at the beginning of the titration
    2. at the midpoint of the titration
    3. at the equivalence point
    4. when excess titrant has been added

8. For the titration of a weak acid with a strong base, use the K_a expression to show that pH = pK_a at the midpoint of the titration.

9. Chemical indicators can be used to monitor pH rapidly and inexpensively. Nevertheless, electronic methods are generally preferred. Why?

10. Why does adding ammonium chloride to a solution of ammonia in water decrease the pH of the solution?

11. Given the equilibrium system $CH_3CO_2H(aq) \diamondsuit CH_3CO_2^-(aq) + H^+(aq)$, explain what happens to the position of the equilibrium and the pH in each case.

    1. Dilute HCl is added.
    2. Dilute NaOH is added.
    3. Solid sodium acetate is added.

12. Given the equilibrium system $CH_3NH_2(aq) + H_2O(l) \diamondsuit CH_3NH_3^+(aq) + OH^-(aq)$, explain what happens to the position of the equilibrium and the pH in each case.

    1. Dilute HCl is added.
    2. Dilute NaOH is added.
    3. Solid $CH_3NH_3^+Cl^-$ is added.

Answer

1.
2.
3.
4.
5.
6.
7.
8.
9.
10.
11. 1. shifts to left; pH decreases
    2. shifts to right; pH increases
    3. shifts to left; pH increases
12.

Numerical Problems

1. Calculate the pH of each solution.

    1. A volume of 25.0 mL of 6.09 M HCl is added to 100.0 mL of distilled water
    2. A volume of 5.0 mL of 2.55 M NaOH is added to 75.0 mL of distilled water.

2. What is the pH of a solution prepared by mixing 50.0 mL of 0.225 M HCl with 100.0 mL of a 0.184 M solution of NaOH?

3. What volume of 0.50 M HCl is needed to completely neutralize 25.00 mL of 0.86 M NaOH?

4. Calculate the final pH when each pair of solutions is mixed.

    1. 100 mL of 0.105 M HCl and 100 mL of 0.115 M sodium acetate
    2. 50 mL of 0.10 M HCl and 100 mL of 0.15 M sodium acetate
    3. 100 mL of 0.109 M acetic acid and 100 mL of 0.118 M NaOH
    4. 100 mL of 0.998 M acetic acid and 50.0 mL of 0.110 M NaOH

5. Calculate the final pH when each pair of solutions is mixed.

    1. 100 mL of 0.983 M HCl and 100 mL of 0.102 M sodium fluoride
    2. 50.0 mL of 0.115 M HCl and 100 mL of 0.109 M sodium fluoride
    3. 100 mL of 0.106 M hydrofluoric acid and 50.0 mL of 0.996 M NaOH
    4. 100 mL of 0.107 M sodium acetate and 50.0 mL of 0.987 M acetic acid

6. Calcium carbonate is a major contributor to the “hardness” of water. The amount of $CaCO_3$ in a water sample can be determined by titrating the sample with an acid, such as HCl, which produces water and CO_2. Write a balanced chemical equation for this reaction. Generate a plot of solution pH versus volume of 0.100 M HCl added for the titration of a solution of 250 mg of $CaCO_3$ in 200.0 mL of water with 0.100 M HCl; assume that the HCl solution is added in 5.00 mL increments. What volume of HCl corresponds to the equivalence point?

7. For a titration of 50.0 mL of 0.288 M NaOH, you would like to prepare a 0.200 M HCl solution. The only HCl solution available to you, however, is 12.0 M.

    1. How would you prepare 500 mL of a 0.200 M HCl solution?
    2. Approximately what volume of your 0.200 M HCl solution is needed to neutralize the NaOH solution?
    3. After completing the titration, you find that your “0.200 M” HCl solution is actually 0.187 M. What was the exact volume of titrant used in the neutralization?

8. While titrating 50.0 mL of a 0.582 M solution of HCl with a solution labeled “0.500 M KOH,” you overshoot the endpoint. To correct the problem, you add 10.00 mL of the HCl solution to your flask and then carefully continue the titration. The total

volume of titrant needed for neutralization is 71.9 mL.

1. What is the actual molarity of your KOH solution?
2. What volume of titrant was needed to neutralize 50.0 mL of the acid?

9. Complete the following table and generate a titration curve showing the pH versus volume of added base for the titration of 50.0 mL of 0.288 M HCl with 0.321 M NaOH. Clearly indicate the equivalence point.

Base Added (mL)	10.0	30.0	40.0	45.0	50.0	55.0	65.0	75.0
pH								

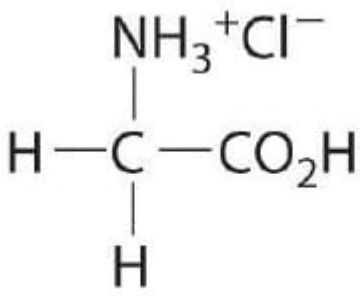
10. The following data were obtained while titrating 25.0 mL of 0.156 M NaOH with a solution labeled "0.202 M HCl." Plot the pH versus volume of titrant added. Then determine the equivalence point from your graph and calculate the exact concentration of your HCl solution.

Volume of HCl (mL)	5	10	15	20	25	30	35
pH	11.46	11.29	10.98	4.40	2.99	2.70	2.52

11. Fill in the data for the titration of 50.0 mL of 0.241 M formic acid with 0.0982 M KOH. The pK_a of formic acid is 3.75. What is the pH of the solution at the equivalence point?

Volume of Base Added (mL)	0	5	10	15	20	25
pH						

12. Glycine hydrochloride, which contains the fully protonated form of the amino acid glycine, has the following structure:



glycine hydrochloride

It is a strong electrolyte that completely dissociates in water. Titration with base gives two equivalence points: the first corresponds to the deprotonation of the carboxylic acid group and the second to loss of the proton from the ammonium group. The corresponding equilibrium equations are as follows:

$$\begin{aligned} {}^{+}NH_3 - CH_2 - CO_2H\,(aq) \rightleftharpoons \quad & pK_{a1} = 2.3 \\ {}^{+}NH_3 - CH_2 - CO_2\,(aq) + H^+ \quad & \end{aligned} \tag{11.7.4}$$

$$\begin{aligned} {}^{+}NH_3 - CH_2 - CO_2\,(aq) \rightleftharpoons \quad & pK_{a2} = 9.6 \\ NH_2 - CH_2 - COO\,(aq) + H^+ \quad & \end{aligned}$$

1. Given 50.0 mL of solution that is 0.430 M glycine hydrochloride, how many milliliters of 0.150 M KOH are needed to fully deprotonate the carboxylic acid group?
2. How many additional milliliters of KOH are needed to deprotonate the ammonium group?
3. What is the pH of the solution at each equivalence point?

4. How many milliliters of titrant are needed to obtain a solution in which glycine has no net electrical charge? The pH at which a molecule such as glycine has no net charge is its *isoelectric point*. What is the isoelectric point of glycine?

13. What is the pH of a solution prepared by adding 38.2 mL of 0.197 M HCl to 150.0 mL of 0.242 M pyridine? The pK_b of pyridine is 8.77.

14. What is the pH of a solution prepared by adding 40.3 mL of 0.289 M NaOH to 150.0 mL of 0.564 M succinic acid ($HO_2CCH_2CH_2CO_2H$)? (For succinic acid, pK_{a1} = 4.21 and pK_{a2} = 5.64).

15. Calculate the pH of a 0.15 M solution of malonic acid ($HO_2CCH_2CO_2H$), whose pK_a values are as follows: pK_{a1} = 2.85 and pK_{a2} = 5.70.

Answers

1.
2.

3. 43 mL

4. Video Solution
5. Video Solution
6. Video Solution
7. 1. dilute 8.33 mL of 12.0 M HCl to 500.0 mL
   2. 72 mL
   3. 77.0 mL
8.
9.
10.

11. pH at equivalence point = 8.28

Volume of Base Added (mL)	0	5	10	15	20	25
pH	2.19	2.38	2.70	2.89	3.04	3.15

12.
13.
14.

15. 1.85

Contributors

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Modified by Joshua B. Halpern

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12: IONIC COMPOUNDS HAVE COMMON PROPERTIES AND REACTIONS

12.1: Overview and Objectives
12.2: Solubility and Molecular Structure
12.3: Determining the Solubility of Ionic Compounds
12.4: Solubility and pH
12.5: Qualitative Analysis Using Selective Precipitation

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12.1: Overview and Objectives

> "*The quantity of a solid which can dissolve in a given volume of solvent is a perfectly definite choice, depending only upon the temperature and pressure. [...] A state of equilibrium is finally reached between the solid substance and the solution, where the rate of dissolution equals the rate of separation.*" *(Wilhelm Ostwald)*

You may have noticed that some recipes involve the preparation of a s*imple syrup;* that is, a solution of sugar and water that you must heat up to fully dissolve the sugar. That's because the amount of sugar is simply too high to dissolve at room temperature. Although sucrose (table sugar) is a covalent compound that we won't be considering, this chapter considers some of the same principles as applied to ionic compounds. We will define the chemical equilibrium and equilibrium constant that describes ionic solids dissolving in water, use this equilibrium constant to estimate the solubility of salts under a variety of conditions, and examine ways to manipulate that solubility by changing concentrations, temperature, or pressure.

Chapter Objectives

- Determine the equilibrium constant and/or the equilibrium composition of a mixture containing a sparingly soluble salt.
- Evaluate the status of a solubility equilbrium (precipitate vs. no precipitate) based on the ion product.
- Predict how stresses in concentration, temperature, and pressure affect the solubility of a sparingly soluble salt.

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12.2: Solubility and Molecular Structure

Learning Objectives

- To understand the relationship between solubility and molecular structure.

When a solute dissolves, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution (part (a) in Figure 13.4). This is not, however, a unidirectional process. If the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called crystallization. Dissolution and crystallization continue as long as excess solid is present, resulting in a dynamic equilibrium analogous to the equilibrium that maintains the vapor pressure of a liquid. We can represent these opposing processes as follows:

$$\text{solute} + \text{solvent} \underset{\text{dissolution}}{\overset{\text{crystallization}}{\rightleftharpoons}} \text{solution} \tag{13.4}$$

Although the terms precipitation and crystallization are both used to describe the separation of solid solute from a solution, crystallization refers to the formation of a solid with a well-defined crystalline structure, whereas precipitation refers to the formation of any solid phase, often one with very small particles.

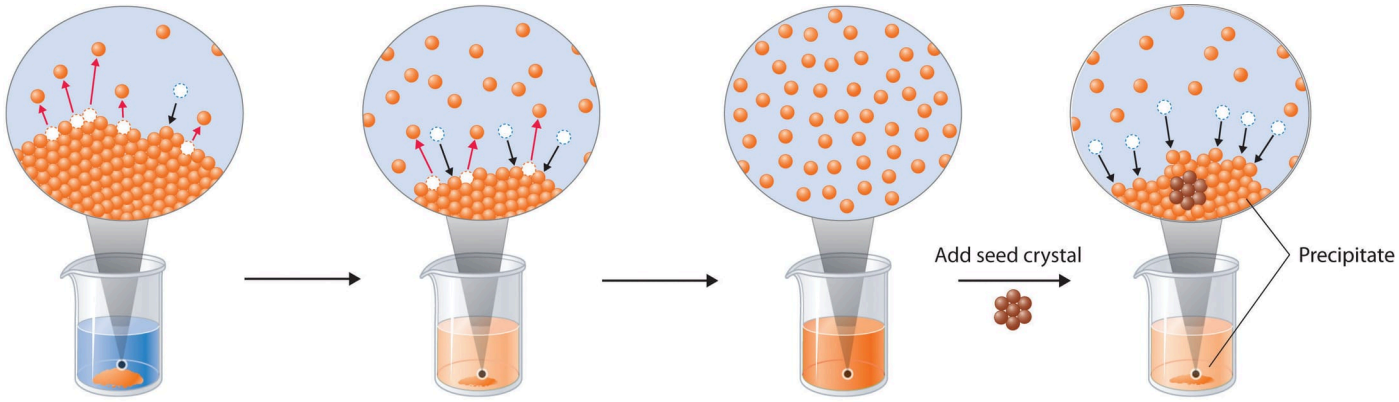


Figure 13.4 Dissolution and Precipitation. (a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.

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12.3: Determining the Solubility of Ionic Compounds

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Determine the equilibrium constant and/or the equilibrium composition of a mixture containing a sparingly soluble salt.
- Evaluate the status of a solubility equilbrium (precipitate vs. no precipitate) based on the ion product.

We begin our discussion of solubility and solubility equilibria by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibriua, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{17.1.1}$$

The equilibrium constant for the dissolution of a sparingly soluble salt is the solubility product (K_{sp})The equilibrium constant expression for the dissolution of a sparingly soluble salt that includes the concentration of a pure solid, which is a constant. of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. (For more information on the equilibrium constant expression, see Section 15.2.) The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\mathrm{Ca}^{2+}]^3[\mathrm{PO}_4^{3-}]^2}{[\mathrm{Ca}_3(\mathrm{PO}_4)_2]} \tag{17.1.2a}$$

$$[\mathrm{Ca}_3(\mathrm{PO}_4)_2]K = K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}]^3[\mathrm{PO}_4^{3-}]^2 \tag{17.1.2b}$$

At 25°C and pH 7.00, K_{sp} for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table 17.1.1; they show that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equation 17.1, changes in pH can affect the solubility of a compound, as you will discover in Section 17.4.

Note the Pattern

As with K, the concentration of a pure solid does not appear explicitly in K_{sp}.

Table 17.1.1 Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	K_{sp}		Solid	Color	K_{sp}
Acetates				**Iodides**		
$Ca(O_2CCH_3)_2{\cdot}3H_2O$	white	4×10^{-3}		Hg_2I_2*	yellow	5.2×10^{-29}
Bromides				PbI_2	yellow	9.8×10^{-9}
***These contain the Hg_2^{2+} ion.**						

Solid	Color	K_{sp}		Solid	Color	K_{sp}
AgBr	off-white	5.35×10^{-13}		**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}		$Ag_2C_2O_4$	white	5.40×10^{-12}
Carbonates				$MgC_2O_4 \cdot 2H_2O$	white	4.83×10^{-6}
$CaCO_3$	white	3.36×10^{-9}		PbC_2O_4	white	4.8×10^{-10}
$PbCO_3$	white	7.40×10^{-14}		**Phosphates**		
Chlorides				Ag_3PO_4	white	8.89×10^{-17}
AgCl	white	1.77×10^{-10}		$Sr_3(PO_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2*	white	1.43×10^{-18}		$FePO_4 \cdot 2H_2O$	pink	9.91×10^{-16}
$PbCl_2$	white	1.70×10^{-5}		**Sulfates**		
Chromates				Ag_2SO_4	white	1.20×10^{-5}
$CaCrO_4$	yellow	7.1×10^{-4}		$BaSO_4$	white	1.08×10^{-10}
$PbCrO_4$	yellow	2.8×10^{-13}		$PbSO_4$	white	2.53×10^{-8}
Fluorides				**Sulfides**		
BaF_2	white	1.84×10^{-7}		Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}		CdS	yellow	8.0×10^{-27}
Hydroxides				PbS	black	8.0×10^{-28}
$Ca(OH)_2$	white	5.02×10^{-6}		ZnS	white	1.6×10^{-24}
$Cu(OH)_2$	pale blue	1×10^{-14}				
$Mn(OH)_2$	light pink	1.9×10^{-13}				
$Cr(OH)_3$	gray-green	6.3×10^{-31}				
$Fe(OH)_3$	rust red	2.79×10^{-39}				
***These contain the Hg_2^{2+} ion.**						



Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of *mass* of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the *molar* concentrations of the component ions.

A kidney stone. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2) \cdot H_2O$ and $Ca_3(PO_4)_2$.

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Example 17.1.1

Calcium oxalate monohydrate [$Ca(O_2CCO_2) \cdot H_2O$, also written as $CaC_2O_4 \cdot H_2O$] is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp}.

Given: solubility in g/100 mL

Asked for: K_{sp}

Strategy:

A Write the balanced dissolution equilibrium and the corresponding solubility product expression.

B Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp}.

Solution:

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:

$$\mathrm{Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {^-O_2CCO_2^-}(aq) + H_2O(l)} \qquad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{ox^{2-}}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine $[Ca^{2+}]$ and $[ox^{2-}]$ at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36 \times 10^{-4}\ \mathrm{g}}{146.1\ \mathrm{g/mol}} = 5.04 \times 10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2)\cdot H_2O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2\cdot)H_2O}}{100\ \mathrm{mL}}\right)\left(\frac{1000\ \mathrm{mL}}{1.00\ \mathrm{L}}\right) = 5.04 \times 10^{-5}\ \mathrm{mol/L} = 5.04 \times 10^{-5}\ \mathrm{M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04×10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

Exercise

One crystalline form of calcium carbonate ($CaCO_3$) is the mineral sold as “calcite” in mineral and gem shops. The solubility of calcite in water is 0.67 mg/100 mL. Calculate its K_{sp}.

Answer: 4.5×10^{-9}

Note the Pattern

The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see *two* images of the letters.

Calcite, a structural material for many organisms, is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations as we did in Chapter 15, remembering that the concentration of the pure solid is essentially constant.

Example 17.1.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

1. the molarity of ions produced in solution
2. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.

B Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

1. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 17.1) is shown in the following table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$			
	$Ca_3(PO_4)_2$	$[Ca^{2+}]$	$[PO_4^{3-}]$
initial	pure solid	0	0
change	—	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

Although the *amount* of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its *molar concentration* does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.1.2):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2$$
$$2.07 \times 10^{-33} = 108x^5$$
$$1.92 \times 10^{-35} = x^5$$
$$1.14 \times 10^{-7}\ M = x$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is 2*x* and 3*x*, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

2. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water: $\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g}\ Ca_3(PO_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g}\ Ca_3(PO_4)_2$

Exercise

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

1. the molarity of a saturated solution
2. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer

1. 1.28×10^{-4} M
2. 3.54 mg

The Ion Product

The ion product (Q)A quantity that has precisely the same form as the solubility product for the dissolution of a sparingly soluble salt, except that the concentrations used are not necessarily equilibrium concentrations. of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (Q) discussed for gaseous equilibriums in Chapter 15. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are *not* necessarily equilibrium concentrations.

Note the Pattern

The ion product Q is analogous to the reaction quotient Q for gaseous equilibriums.

As summarized in Figure 17.1.1 , there are three possible conditions for an aqueous solution of an ionic solid:

1. $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
2. $Q = K_{sp}$. The solution is saturated and at equilibrium.
3. $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

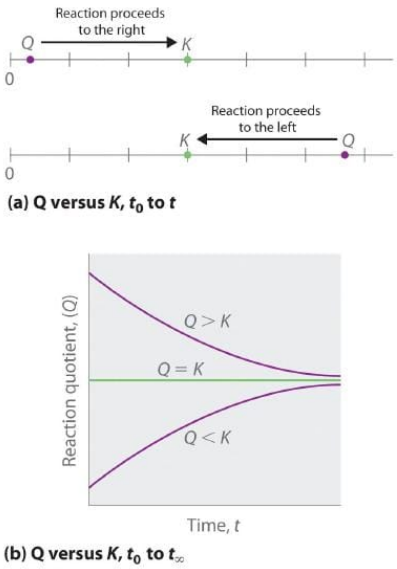


Figure 17.1.1 The Relationship between Q and K_{sp} If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 17.1.3

We mentioned that barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a "barium milkshake" is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

A Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp}.

B Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).

C Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution:

A The only slightly soluble salt that can be formed when these two solutions are mixed is $BaSO_4$ because NaCl is highly soluble. The equation for the precipitation of $BaSO_4$ is as follows:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The solubility product expression is as follows:

$$K_{sp} = [Ba^{2+}][SO_4{}^{2-}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product—$Q = [Ba^{2+}][SO_4^{2-}]$—using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of $BaCl_2$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles } Ba^{2+} = 100 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}}\right) = 3.2 \times 10^{-5} \text{ mol } Ba^{2+}$$

$$[Ba^{2+}] = \left(\frac{3.2 \times 10^{-5} \text{ mol } Ba^{2+}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 2.9 \times 10^{-4} \text{ M } Ba^{2+}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles } SO_4^{2-} = 10.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.0020 \text{ mol}}{1 \text{ L}}\right) = 2.0 \times 10^{-5} \text{ mol } SO_4^{2-}$$

$$[SO_4^{2-}] = \left(\frac{2.0 \times 10^{-5} \text{ mol } SO_4^{2-}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 1.8 \times 10^{-4} \text{ M } SO_4^{2-}$$

We can now calculate Q:

$$Q = [Ba^{2+}][SO_4^{2-}] = (2.9\times10^{-4})(1.8\times10^{-4}) = 5.2\times10^{-8}$$

C We now compare Q with the K_{sp}. If $Q > K_{sp}$, then $BaSO_4$ will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when $[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

Exercise

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5} M solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer: yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)

The Common Ion Effect and Solubility

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. This dependency is another example of the common ion effect discussed in Section 16.6 : adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, *the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion*.The exceptions generally involve the formation of complex ions, which is discussed in Section 17.3 .

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains $3 \times (1.14 \times 10^{-7}$ M) = 3.42×10^{-7} M Ca^{2+} and $2 \times (1.14 \times 10^{-7}$ M) = 2.28×10^{-7} M PO_4^{3-}, according to the stoichiometry shown in Equation 17.1.1 (neglecting hydrolysis to form HPO_4^{2-} as described in Chapter 16). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 17.1.1 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

Note the Pattern

The common ion effect usually decreases the solubility of a sparingly soluble salt.

Example 17.1.4

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.

B Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution:

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in [Ca^{2+}] is once again +3x, and the change in [PO_4^{3-}] is +2x. We can insert these values into the table.

$Ca_3(PO_4)_2(s) = 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$			
	$Ca_3(PO_4)_2$	$[Ca^{2+}]$	$[PO_4^{3-}]$
initial	pure solid	0.20	0
change	—	+3x	+2x
final	pure solid	0.20 + 3x	2x

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07\times10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that x << 0.20. Thus (0.20 + 3x) M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$\begin{aligned} K_{sp} = (0.20)^3(2x)^2 &= 2.07 \times 10^{-33} \\ x^2 &= 6.5 \times 10^{-32} \\ x &= 2.5 \times 10^{-16}\ \text{M} \end{aligned}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 2—here the initial [Ca^{2+}] was 0.20 M rather than 0.

Exercise

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45 × 10^{-12} at 25°C.

Answer: 2.9 × 10^{-6} M (versus 1.3 × 10^{-4} M in pure water)

Summary

The equilibrium constant for a dissolution reaction, called the **solubility product (K_{sp})**, is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of *mass* of solute per 100 mL of solvent, K_{sp} is defined in terms of the *molar* concentrations of the component ions. In contrast, the **ion product (Q)** describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

Key Takeaway

- The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium.

Conceptual Problems

1. Write an expression for K_{sp} for each salt.
    1. AgI
    2. CaF_2
    3. $PbCl_2$
    4. Ag_2CrO_4
2. Some species are not represented in a solubility product expression. Why?
3. Describe the differences between Q and K_{sp}.
4. How can an ion product be used to determine whether a solution is saturated?
5. When using K_{sp} to directly compare the solubilities of compounds, why is it important to compare only the K_{sp} values of salts that have the same stoichiometry?
6. Describe the effect of a common ion on the solubility of a salt. Is this effect similar to the common ion effect found in buffers? Explain your answer.
7. Explain why the presence of $MgCl_2$ decreases the molar solubility of the sparingly soluble salt $MgCO_3$.

Answers

1.
    1. $K_{sp} = [Ag^+][I^-]$
    2. $K_{sp} = [Ca^{2+}][F^-]^2$
    3. $K_{sp} = [Pb^{2+}][Cl^-]^2$
    4. $K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]$
2.
3.
4.
5. For a 1:1 salt, the molar solubility is simply $\sqrt{K_{sp}}$; for a 2:1 salt, the molar solubility is $\sqrt[3]{K_{sp}/4}$> Consequently, the magnitudes of K_{sp} can be correlated with molar solubility *only* if the salts have the same stoichiometry.
6.
7. Because of the common ion effect. Adding a soluble Mg^{2+} salt increases $[Mg^{2+}]$ in solution, and Le Chatelier's principle predicts that this will shift the solubility equilibrium of $MgCO_3$ to the left, decreasing its solubility.

Numerical Problems

1. Predict the molar solubility of each compound using the K_{sp} values given in Table E3.

    1. $Cd(IO_3)_2$
    2. AgCN
    3. HgI_2

2. Predict the molar solubility of each compound using the K_{sp} values given.

    1. Li_3PO_4: 2.37×10^{-11}
    2. $Ca(IO_3)_2$: 6.47×10^{-6}
    3. $Y(IO_3)_3$: 1.12×10^{-10}

3. A student prepared 750 mL of a saturated solution of silver sulfate (Ag_2SO_4). How many grams of Ag_2SO_4 does the solution contain? $K_{sp} = 1.20 \times 10^{-5}$.

4. Given the K_{sp} values in Table 17.1.1 and Table E3, predict the molar concentration of each species in a saturated aqueous solution.

    1. silver bromide
    2. lead oxalate
    3. iron(II) carbonate
    4. silver phosphate
    5. copper(I) cyanide

5. Given the K_{sp} values in Table 17.1.1 and Table E3, predict the molar concentration of each species in a saturated aqueous solution.

    1. copper(I) chloride
    2. lanthanum(III) iodate
    3. magnesium phosphate
    4. silver chromate
    5. strontium sulfate

6. Silicon dioxide, the most common binary compound of silicon and oxygen, constitutes approximately 60% of Earth's crust. Under certain conditions, this compound can react with water to form silicic acid, which can be written as either H_4SiO_4 or $Si(OH)_4$. Write a balanced chemical equation for the dissolution of SiO_2 in basic solution. Write an equilibrium constant expression for the reaction.

7. The K_{sp} of $Mg(OH)_2$ is 5.61×10^{-12}. If you tried to dissolve 24.0 mg of $Mg(OH)_2$ in 250 mL of water and then filtered the solution and dried the remaining solid, what would you predict to be the mass of the undissolved solid? You discover that only 1.0 mg remains undissolved. Explain the difference between your expected value and the actual value.

8. The K_{sp} of lithium carbonate is 8.15×10^{-4}. If 2.34 g of the salt is stirred with 500 mL of water and any undissolved solid is filtered from the solution and dried, what do you predict to be the mass of the solid? You discover that all of your sample dissolves. Explain the difference between your predicted value and the actual value.

9. You have calculated that 24.6 mg of $BaSO_4$ will dissolve in 1.0 L of water at 25°C. After adding your calculated amount to 1.0 L of water and stirring for several hours, you notice that the solution contains undissolved solid. After carefully filtering the solution and drying the solid, you find that 22.1 mg did not dissolve. According to your measurements, what is the K_{sp} of barium sulfate?

10. In a saturated silver chromate solution, the molar solubility of chromate is 6.54×10^{-5}. What is the K_{sp}?

11. A saturated lead(II) chloride solution has a chloride concentration of 3.24×10^{-2} mol/L. What is the K_{sp}?

12. From the solubility data given, calculate K_{sp} for each compound.

    1. AgI: 2.89×10^{-7} g/100 mL
    2. SrF_2: 1.22×10^{-2} g/100 mL
    3. $Pb(OH)_2$: 78 mg/500 mL
    4. $BiAsO_4$: 14.4 mg/2.0 L

13. From the solubility data given, calculate K_{sp} for each compound.

    1. $BaCO_3$: 10.0 mg/500 mL
    2. CaF_2: 3.50 mg/200 mL
    3. $Mn(OH)_2$: 6.30×10^{-4} g/300 mL
    4. Ag_2S: 1.60×10^{-13} mg/100 mL

14. Given the following solubilities, calculate K_{sp} for each compound.

    1. $BaCO_3$: 7.00×10^{-5} mol/L
    2. CaF_2: 1.70 mg/100 mL
    3. $Pb(IO_3)_2$: 2.30 mg/100 mL
    4. SrC_2O_4: 1.58×10^{-7}mol/L

15. Given the following solubilities, calculate K_{sp} for each compound.

    1. Ag_2SO_4: 4.2×10^{-1} g/100 mL
    2. $SrSO_4$: 1.5×10^{-3} g/100 mL
    3. CdC_2O_4: 6.0×10^{-3} g/100 mL
    4. $Ba(IO_3)_2$: 3.96×10^{-2} g/100 mL

16. The K_{sp} of the phosphate fertilizer $CaHPO_4 \cdot 2H_2O$ is 2.7×10^{-7} at 25°C. What is the molar concentration of a saturated solution? What mass of this compound will dissolve in 3.0 L of water at this temperature?

17. The K_{sp} of zinc carbonate monohydrate is 5.5×10^{-11} at 25°C. What is the molar concentration of a saturated solution? What mass of this compound will dissolve in 2.0 L of water at this temperature?

18. Silver nitrate eye drops were formerly administered to newborn infants to guard against eye infections contracted during birth. Although silver nitrate is highly water soluble, silver sulfate has a K_{sp} of 1.20×10^{-5} at 25°C. If you add 25.0 mL of 0.015 M $AgNO_3$ to 150 mL of 2.8×10^{-3} M Na_2SO_4, will you get a precipitate? If so, what will its mass be?

19. Use the data in Table E3 to predict whether precipitation will occur when each pair of solutions is mixed.

    1. 150 mL of 0.142 M $Ba(NO_3)_2$ with 200 mL of 0.089 M NaF
    2. 250 mL of 0.079 M K_2CrO_4 with 175 mL of 0.087 M $CaCl_2$
    3. 300 mL of 0.109 M $MgCl_2$ with 230 mL of 0.073 M $Na_2(C_2O_4)$

20. What is the maximum volume of 0.048 M $Pb(NO_3)_2$ that can be added to 250 mL of 0.10 M NaSCN before precipitation occurs? $K_{sp} = 2.0 \times 10^{-5}$ for $Pb(SCN)_2$.

21. Given 300 mL of a solution that is 0.056 M in lithium nitrate, what mass of solid sodium carbonate can be added before precipitation occurs (assuming that the volume of solution does not change after adding the solid)? $K_{sp} = 8.15 \times 10^{-4}$ for Li_2CO_3.

22. Given the information in the following table, calculate the molar solubility of each sparingly soluble salt in 0.95 M $MgCl_2$.

Saturated Solution	K_{sp}
$MgCO_3 \cdot 3H_2O$	2.4×10^{-6}
$Mg(OH)_2$	5.6×10^{-12}
$Mg_3(PO_4)_2$	1.04×10^{-24}

Answers

1. 1. 1.84×10^{-3} M
   2. 7.73×10^{-9} M
   3. 1.9×10^{-10} M
2.
3. 3.37 g
4.
5. 1. 4.15×10^{-4} M
   2. 7.26×10^{-4} M
   3. 6.26×10^{-6} M
   4. 6.54×10^{-5} M
   5. 5.86×10^{-4} M
6.
7. 22.4 mg; a secondary reaction occurs, where OH^- from the dissociation of the salt reacts with H^+ from the dissociation of water. This reaction causes further dissociation of the salt (Le Chatelier's principle).
8.
9. 1.2×10^{-10}
10.
11. 1.70×10^{-5}
12.
13.
14.
15. 1. 8.8×10^{-6}
    2. 6.7×10^{-9}
    3. 9.0×10^{-8}
    4. 2.16×10^{-9}
16.
17. 7.4×10^{-6} M; 2.1 mg
18.
19. Precipitation will occur in all cases.
20.
21. 8.27 g

22.

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12.4: Solubility and pH

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Predict how stresses in concentration, temperature, and pressure affect the solubility of a sparingly soluble salt.

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. In this section, we discuss the relationship between the solubility of these classes of compounds and pH.

Why Can Acid–Base Equilibrium Influence Solubility?

We begin our discussion by examining the effect of pH on the solubility of a representative salt, M^+A^-, where A^- is the conjugate base of the weak acid HA. When the salt dissolves in water, the following reaction occurs:

$$MA_{(s)} \rightleftharpoons M^+_{(aq)} + A^-_{(aq)} \tag{17.4.1a}$$

with

$$K_{sp} = [M^+][A^-] \tag{17.4.1b}$$

The anion can also react with water in a hydrolysis reaction:

$$A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HA_{(aq)} \tag{17.4.2}$$

Because of the reaction described in Equation 17.4.2, the predicted solubility of a sparingly soluble salt that has a basic anion such as S^{2-}, PO_4^{3-}, or CO_3^{2-}.

If instead a strong acid is added to the solution, the added H^+ will react essentially completely with A^- to form HA. This reaction decreases $[A^-]$, which decreases the magnitude of the ion product ($Q = [M^+][A^-]$). According to Le Chatelier's principle, more MA will dissolve until $Q = K_{sp}$. Hence *an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid*. In contrast, pH has little to no effect on the solubility of salts whose anion is the conjugate base of a stronger weak acid or a *strong* acid, respectively (e.g., chlorides, bromides, iodides, and sulfates). For example, the hydroxide salt $Mg(OH)_2$ is relatively insoluble in water:

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{17.4.3a}$$

with

$$K_{sp} = 5.61 \times 10^{-12} \tag{17.4.3b}$$

When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing OH^- from solution:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \tag{17.4.5}$$

The overall equation for the reaction of $Mg(OH)_2$ with acid is thus

$$Mg(OH)_{2(s)} + 2H^+_{(aq)} \rightleftharpoons Mg^{2+}_{(aq)} + 2H_2O_{(l)} \tag{17.4.6}$$

As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in Equation 17.4.6 is driven to the right, so more $Mg(OH)_2$ dissolves.

Such pH-dependent solubility is not restricted to salts that contain anions derived from water. For example, CaF_2 is a sparingly soluble salt:

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^{-}_{(aq)} \tag{17.4.7a}$$

with

$$K_{sp} = 3.45 \times 10^{-11} \tag{17.4.7b}$$

When strong acid is added to a saturated solution of CaF_2, the following reaction occurs:

$$H^{+}_{(aq)} + F^{-}_{(aq)} \rightleftharpoons HF_{(aq)} \tag{17.4.8}$$

Because the forward reaction decreases the fluoride ion concentration, more CaF_2 dissolves to relieve the stress on the system. The net reaction of CaF_2 with strong acid is thus

$$CaF_{2(s)} + 2H^{+}_{(aq)} \rightarrow Ca^{2+}_{(aq)} + 2HF_{(aq)} \tag{17.4.9}$$

Example 7 shows how to calculate the solubility effect of adding a strong acid to a solution of a sparingly soluble salt.

Note the Pattern

Sparingly soluble salts derived from weak acids tend to be more soluble in an acidic solution.

Example 17.4.1

Lead oxalate (PbC_2O_4), lead iodide (PbI_2), and lead sulfate ($PbSO_4$) are all rather insoluble, with K_{sp} values of 4.8×10^{-10}, 9.8×10^{-9}, and 2.53×10^{-8}, respectively. What effect does adding a strong acid, such as perchloric acid, have on their relative solubilities?

Given: K_{sp} values for three compounds

Asked for: relative solubilities in acid solution

Strategy:

Write the balanced chemical equation for the dissolution of each salt. Because the strongest conjugate base will be most affected by the addition of strong acid, determine the relative solubilities from the relative basicity of the anions.

Solution:

The solubility equilibria for the three salts are as follows:

$$PbC_2O_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + C_2O^{2-}_{4(aq)}$$

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2I^{-}_{(aq)}$$

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The addition of a strong acid will have the greatest effect on the solubility of a salt that contains the conjugate base of a weak acid as the anion. Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of PbI_2 will not greatly affect its solubility; the acid will simply dissociate to form $H^+(aq)$ and the corresponding anion. In contrast, oxalate is the fully deprotonated form of oxalic acid (HO_2CCO_2H), which is a weak diprotic acid (pK_{a1} = 1.23 and pK_{a2} = 4.19). Consequently, the oxalate ion has a significant affinity for one proton and a lower affinity for a second proton. Adding a strong acid to a saturated

solution of lead oxalate will result in the following reactions:

$$C_2O_{4(aq)}^{2-} + H_{(aq)}^{+} \rightarrow HO_2CCO_{2(aq)}^{-}$$

$$HO_2CCO_{2(aq)}^{-} + H_{(aq)}^{+} \rightarrow HO_2CCO_2H_{(aq)}$$

These reactions will decrease [$C_2O_4^{2-}$], causing more lead oxalate to dissolve to relieve the stress on the system.The pK_a of HSO_4^- (1.99) is similar in magnitude to the pK_{a1} of oxalic acid, so adding a strong acid to a saturated solution of $PbSO_4$ will result in the following reaction:

$$SO_{4(aq)}^{2-} + H_{(aq)}^{+} \rightleftharpoons HSO_{4(aq)}^{-}$$

Because HSO_4^- has a pKa of 1.99, this reaction will lie largely to the left as written. Consequently, we predict that the effect of added strong acid on the solubility of $PbSO_4$ will be significantly less than for PbC_2O_4.

Exercise

Which of the following insoluble salts—AgCl, Ag_2CO_3, Ag_3PO_4, and/or AgBr—will be substantially more soluble in 1.0 M HNO_3 than in pure water?

Answer: Ag_2CO_3 and Ag_3PO_4

Caves and their associated pinnacles and spires of stone provide one of the most impressive examples of pH-dependent solubility equilibria (part (a) in Figure 17.6). Perhaps the most familiar caves are formed from limestone, such as Carlsbad Caverns in New Mexico, Mammoth Cave in Kentucky, and Luray Caverns in Virginia. The primary reactions that are responsible for the formation of limestone caves are as follows:

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_{(aq)}^{+} + HCO_{3(aq)}^{-} \tag{17.4.10}$$

$$HCO_{3(aq)}^{-} \rightleftharpoons H + (aq) + CO_{3(aq)}^{2-} \tag{17.4.11}$$

$$Ca_{(aq)}^{2+} + CO_{3(aq)}^{2-} \rightleftharpoons CaCO_{3(s)} \tag{17.4.12}$$



Figure 17.4.1 The Chemistry of Cave Formation (a) This cave in Campanet, Mallorca, Spain, and its associated formations are examples of pH-dependent solubility equilibria. (b) A cave forms when groundwater containing atmospheric CO_2, forming an acidic solution, dissolves limestone ($CaCO_3$) in a process that may take tens of thousands of years. As groundwater seeps into a cave, water evaporates from the solution of $CaCO_3$ in CO_2-rich water, producing a supersaturated solution and a shift in equilibrium that causes precipitation of the $CaCO_3$. The deposited limestone eventually forms stalactites and stalagmites.

Limestone deposits that form caves consist primarily of $CaCO_3$ from the remains of living creatures such as clams and corals, which used it for making structures such as shells. When a saturated solution of $CaCO_3$ in CO_2-rich water rises toward Earth's

surface or is otherwise heated, CO_2 gas is released as the water warms. $CaCO_3$ then precipitates from the solution according to the following equation (part (b) in Figure 17.4.1):

$$Ca^{2+}_{(aq)} + 2HCO^{-}_{3(aq)} \rightleftharpoons CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)} \tag{17.4.13}$$

The forward direction is the same reaction that produces the solid called *scale* in teapots, coffee makers, water heaters, boilers, and other places where hard water is repeatedly heated.

When groundwater-containing atmospheric CO_2 (Equation 17.4.10 and Equation 17.4.11) finds its way into microscopic cracks in the limestone deposits, $CaCO_3$ dissolves in the acidic solution in the reverse direction of Equation 17.4.13. The cracks gradually enlarge from 10–50 μm to 5–10 mm, a process that can take as long as 10,000 yr. Eventually, after about another 10,000 yr, a cave forms. Groundwater from the surface seeps into the cave and clings to the ceiling, where the water evaporates and causes the equilibrium in Equation 17.4.13 to shift to the right. A circular layer of solid $CaCO_3$ is deposited, which eventually produces a long, hollow spire of limestone called a *stalactite* that grows down from the ceiling. Below, where the droplets land when they fall from the ceiling, a similar process causes another spire, called a *stalagmite*, to grow up. The same processes that carve out hollows below ground are also at work above ground, in some cases producing fantastically convoluted landscapes like that of Yunnan Province in China (Figure 17.4.2).

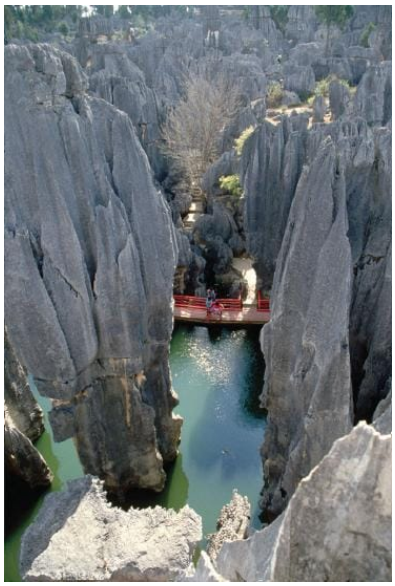


Figure 17.4.2 Solubility Equilibriua in the Formation of Karst **Landscapes**Landscapes such as the steep limestone pinnacles of the Stone Forest in Yunnan Province, China, are formed from the same process that produces caves and their associated formations.

Selective Precipitation Using pH

Many dissolved metal ions can be separated by the selective precipitation of the cations from solution under specific conditions. In this technique, pH is often used to control the concentration of the anion in solution, which controls which cations precipitate.

Suppose, for example, we have a solution that contains 1.0 mM Zn^{2+} and 1.0 mM Cd^{2+} and want to separate the two metals by selective precipitation as the insoluble sulfide salts, ZnS and CdS. The relevant solubility equilibria can be written as follows:

$$ZnS_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + S^{2-}_{(aq)} \tag{17.4.19a}$$

with

$$K_{sp} = 1.6 \times 10^{-24} \tag{17.4.19b}$$

and

$$CdS_{(s)} \rightleftharpoons Cd^{2+}_{(aq)} + S^{2-}_{(aq)} \tag{17.4.20a}$$

with

$$K_{sp} = 8.0 \times 10^{-27} \tag{17.4.20b}$$

Because the S^{2-} ion is quite basic and reacts extensively with water to give HS^- and OH^-, the solubility equilibria are more accurately written as MS(s) = M^{2+}(aq) +HS^-(aq) + $OH^{-(aq)}$ rather than MS(s) = M^{2+}(aq) +$S2^-$(aq) Here we use the simpler form involving S^{2-}, which is justified because we take the reaction of S^{2-} with water into account later in the solution, arriving at the same answer using either equilibrium equation.

The sulfide concentrations needed to cause ZnS and CdS to precipitate are as follows:

$$K_{sp} = [Zn^{2+}][S^{2-}] \tag{17.4.21a}$$

$$1.6 \times 10^{-24} = (0.0010\ M)[S^{2-}] \tag{17.4.21b}$$

$$1.6 \times 10^{-21}\ M = [S^{2-}] \tag{17.4.21c}$$

and

$$K_{sp} = [Cd^{2+}][S^{2-}] \tag{17.4.22a}$$

$$8.0 \times 10^{-27} = (0.0010\ M)[S^{2-}] \tag{17.4.22b}$$

$$8.0 \times 10^{-24}\ M = [S^{2-}] \tag{17.4.22c}$$

Thus sulfide concentrations between 1.6 × 10^{-21} M and 8.0 × 10^{-24} M will precipitate CdS from solution but not ZnS. How do we obtain such low concentrations of sulfide? A saturated aqueous solution of H_2S contains 0.10 M H_2S at 20°C. The pK_{a1} for H_2S is 6.97, and pK_{a2} corresponding to the formation of [S^{2-}] is 12.90. The equations for these reactions are as follows:

$$H_2S_{(aq)} \rightleftharpoons H^+_{(aq)} + HS^-_{(aq)} \tag{17.4.24a}$$

with

$$pK_{a1} = 6.97 \text{ and hence } K_{a1} = 1.1 \times 10^{-7} \tag{17.4.24b}$$

$$HS^-_{(aq)} \rightleftharpoons H^+_{(aq)} + S^{2-}_{(aq)} \tag{17.4.24c}$$

with

$$pK_{a2} = 12.90 \text{ and hence } K_{a2} = 1.3 \times 10^{-13} \tag{17.4.24d}$$

We can show that the concentration of S^{2-} is 1.3 × 10^{-13} by comparing K_{a1} and K_{a2} and recognizing that the contribution to [H^+] from the dissociation of HS^- is negligible compared with [H^+] from the dissociation of H_2S. Thus substituting 0.10 M in the equation for K_{a1} for the concentration of H_2S, which is essentially constant regardless of the pH, gives the following:

$$K_{a1} = 1.1 \times 10^{-7} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{x^2}{0.10\ M} \tag{17.4.5}$$
$$x = 1.1 \times 10^{-4}\ M = [H^+] = [HS^-]$$

Substituting this value for [H^+] and [HS^-] into the equation for K_{a2},

$$K_{a2} = 1.3 \times 10^{-13} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(1.1 \times 10^{-4}\ M)x}{1.1 \times 10^{-4}\ M} = x = [S^{2-}]$$

Although [S^{2-}] in an H_2S solution is very low (1.3 × 10^{-13} M), bubbling H_2S through the solution until it is saturated would precipitate both metal ions because the concentration of S^{2-} would then be much greater than 1.6 × 10^{-21} M. Thus we must adjust

$[S^{2-}]$ to stay within the desired range. The most direct way to do this is to adjust $[H^+]$ by adding acid to the H_2S solution (recall Le Chatelier's principle), thereby driving the equilibrium in Equation 17.4.244 to the left. The overall equation for the dissociation of H_2S is as follows:

$$H_2S_{(aq)} \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)} \tag{17.4.26}$$

Now we can use the equilibrium constant K for the overall reaction, which is the product of K_{a1} and K_{a2}, and the concentration of H_2S in a saturated solution to calculate the H^+ concentration needed to produce $[S^{2-}]$ of 1.6×10^{-21} M:

$$K = K_{a1}K_{a2} = (1.1 \times 10^{-7})(1.3 \times 10^{-13}) = 1.4 \times 10^{-20} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \tag{17.4.27}$$

$$[H^+]^2 = \frac{K[H_2S]}{[S^{2-}]} = \frac{(1.4 \times 10^{-20})(0.10\ M)}{1.6 \times 10^{-21}\ M} = 0.88$$

$$[H^+] = 0.94$$

Thus adding a strong acid such as HCl to make the solution 0.94 M in H^+ will prevent the more soluble ZnS from precipitating while ensuring that the less soluble CdS will precipitate when the solution is saturated with H_2S.

Example 17.4.3

A solution contains 0.010 M Ca^{2+} and 0.010 M La^{3+}. What concentration of HCl is needed to precipitate $La_2(C_2O_4)_3{\cdot}9H_2O$ but not $Ca(C_2O_4){\cdot}H_2O$ if the concentration of oxalic acid is 1.0 M? K_{sp} values are 2.32×10^{-9} for $Ca(C_2O_4)$ and 2.5×10^{-27} for $La_2(C_2O_4)_3$; $pK_{a1} = 1.25$ and $pK_{a2} = 3.81$ for oxalic acid.

Given: concentrations of cations, K_{sp} values, and concentration and pK_a values for oxalic acid

Asked for: concentration of HCl needed for selective precipitation of $La_2(C_2O_4)_3$

Strategy:

A Write each solubility product expression and calculate the oxalate concentration needed for precipitation to occur. Determine the concentration range needed for selective precipitation of $La_2(C_2O_4)_3{\cdot}9H_2O$.

B Add the equations for the first and second dissociations of oxalic acid to get an overall equation for the dissociation of oxalic acid to oxalate. Substitute the $[ox^{2-}]$ needed to precipitate $La_2(C_2O_4)_3{\cdot}9H_2O$ into the overall equation for the dissociation of oxalic acid to calculate the required $[H^+]$.

Solution:

A Because the salts have different stoichiometries, we cannot directly compare the magnitudes of the solubility products. Instead, we must use the equilibrium constant expression for each solubility product to calculate the concentration of oxalate needed for precipitation to occur. Using ox^{2-} for oxalate, we write the solubility product expression for calcium oxalate as follows:

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (0.010)[ox^{2-}] = 2.32 \times 10^{-9}$$

$$[ox^{2-}] = 2.32 \times 10^{-7}\ M$$

The expression for lanthanum oxalate is as follows:

$$K_{sp} = [La^{3+}]^2[ox^{2-}]^3 = (0.010)^2[ox^{2-}]^3 = 2.5 \times 10^{-27}$$

$$[ox^{2-}] = 2.9 \times 10^{-8}\ M$$

Thus lanthanum oxalate is less soluble and will selectively precipitate when the oxalate concentration is between 2.9×10^{-8} M and 2.32×10^{-7} M.

B To prevent Ca^{2+} from precipitating as calcium oxalate, we must add enough H^+ to give a maximum oxalate concentration of 2.32×10^{-7} M. We can calculate the required $[H^+]$ by using the overall equation for the dissociation of oxalic acid to oxalate:

$$HO_2CCO_2H_{(aq)} \rightleftharpoons 2H^+_{(aq)} + C_2O^{2-}_{4(aq)}$$

$$K = K_{a1}K_{a2} = (10^{-1.25})(10^{-3.81}) = 10^{-5.06} = 8.7\times10^{-6}$$

Substituting the desired oxalate concentration into the equilibrium constant expression,

$$8.7 \times 10^{-6} = \frac{[\mathrm{H^+}]^2[\mathrm{ox^{2-}}]}{[\mathrm{HO_2CCO_2H}]} = \frac{[\mathrm{H^+}]^2(2.32 \times 10^{-7})}{1.0}$$

$$[\mathrm{H^+}] = 6.1\ \mathrm{M}$$

Thus adding enough HCl to give $[H^+]$ = 6.1 M will cause only $La_2(C_2O_4)_3{\cdot}9H_2O$ to precipitate from the solution.

Exercise

A solution contains 0.015 M Fe^{2+} and 0.015 M Pb^{2+}. What concentration of acid is needed to ensure that Pb^{2+} precipitates as PbS in a saturated solution of H_2S, but Fe^{2+} does not precipitate as FeS? K_{sp} values are 6.3×10^{-18} for FeS and 8.0×10^{-28} for PbS.

Answer: 0.018 M H^+

Summary

The anion in many sparingly soluble salts is the conjugate base of a weak acid. At low pH, protonation of the anion can dramatically increase the solubility of the salt. Oxides can be classified as acidic oxides or basic oxides. **Acidic oxides** either react with water to give an acidic solution or dissolve in strong base; most acidic oxides are nonmetal oxides or oxides of metals in high oxidation states. **Basic oxides** either react with water to give a basic solution or dissolve in strong acid; most basic oxides are oxides of metallic elements. Oxides or hydroxides that are soluble in both acidic and basic solutions are called **amphoteric oxides**. Most elements whose oxides exhibit amphoteric behavior are located along the diagonal line separating metals and nonmetals in the periodic table. In solutions that contain mixtures of dissolved metal ions, the pH can be used to control the anion concentration needed to selectively precipitate the desired cation.

Key Takeaway

- The anion in sparingly soluble salts is often the conjugate base of a weak acid that may become protonated in solution, so the solubility of simple oxides and sulfides, both strong bases, often depends on pH.

Conceptual Problems

1. Which of the following will show the greatest increase in solubility if 1 M HNO_3 is used instead of distilled water? Explain your reasoning.

    1. $CuCl_2$
    2. $K[Pb(OH)_3]$
    3. $Ba(CH_3CO_2)_2$
    4. $CaCO_3$

2. Of the compounds $Sn(CH_3CO_2)_2$ and SnS, one is soluble in dilute HCl and the other is soluble only in hot, concentrated HCl. Which is which? Provide a reasonable explanation.

3. Where in the periodic table do you expect to find elements that form basic oxides? Where do you expect to find elements that form acidic oxides?

4. Because water can autoionize, it reacts with oxides either as a base (as OH^-) or as an acid (as H_3O^+). Do you expect oxides of elements in high oxidation states to be more acidic (reacting with OH^-) or more basic (reacting with H_3O^+) than the corresponding oxides in low oxidation states? Why?

5. Given solid samples of CrO, Cr_2O_3, and CrO_3, which would you expect to be the most acidic (reacts most readily with OH^-)? Which would be the most basic (reacts most readily with H_3O^+)? Why?

6. Which of these elements—Be, B, Al, N, Se, In, Tl, Pb—do you expect to form an amphoteric oxide? Why?

Numerical Problems

1. A 1.0 L solution contains 1.98 M $Al(NO_3)_3$. What are $[OH^-]$ and $[H^+]$? What pH is required to precipitate the cation as $Al(OH)_3$? $K_{sp} = 1.3 \times 10^{-33}$ and $K_a = 1.05 \times 10^{-5}$ for the hydrated Al^{3+} ion.

2. A 1.0 L solution contains 2.03 M $CoCl_2$. What is $[H^+]$? What pH is required to precipitate the cation as $Co(OH)_2$? $K_{sp} = 5.92 \times 10^{-15}$ and $K_a = 1.26 \times 10^{-9}$ for the hydrated Co^{2+} ion.

3. Given 100 mL of a solution that contains 0.80 mM Ag^+ and 0.80 mM Cu^+, can the two metals be separated by selective precipitation as the insoluble bromide salts by adding 10 mL of an 8.0 mM solution of KBr? K_{sp} values are 6.27×10^{-9} for CuBr and 5.35×10^{-13} for AgBr. What maximum $[Br^-]$ will separate the ions?

4. Given 100 mL of a solution that is 1.5 mM in Tl^+, Zn^{2+}, and Ni^{2+}, which ions can be separated from solution by adding 5.0 mL of a 12.0 mM solution of $Na_2C_2O_4$?

Precipitate	K_{sp}
$Tl_2C_2O_4$	2×10^{-4}
$ZnC_2O_4 \cdot 2H_2O$	1.38×10^{-9}
NiC_2O_4	4×10^{-10}

How many milliliters of 12.0 mM $Na_2C_2O_4$ should be added to separate Tl^+ and Zn^{2+} from Ni^{2+}?

Answers

1. $[H^+] = 4.56 \times 10^{-3}$; $[OH^-] = 2.19 \times 10^{-12}$; pH = 2.94

2.

3. No; both metal ions will precipitate; AgBr will precipitate as Br^- is added, and CuBr will begin to precipitate at $[Br^-] = 8.6 \times 10^{-6}$ M.

4.

Contributors

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12.5: Qualitative Analysis Using Selective Precipitation

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Predict how stresses in concentration, temperature, and pressure affect the solubility of a sparingly soluble salt.

The composition of relatively complex mixtures of metal ions can be determined using qualitative analysis. This is a procedure that allows for discovering the *identity* of metal ions present in the mixture (rather than quantitative information about their amounts).

The procedure used to separate and identify more than 20 common metal cations from a single solution consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively *less* selective until almost all of the metal ions are precipitated, as illustrated in Figure 17.5.1.

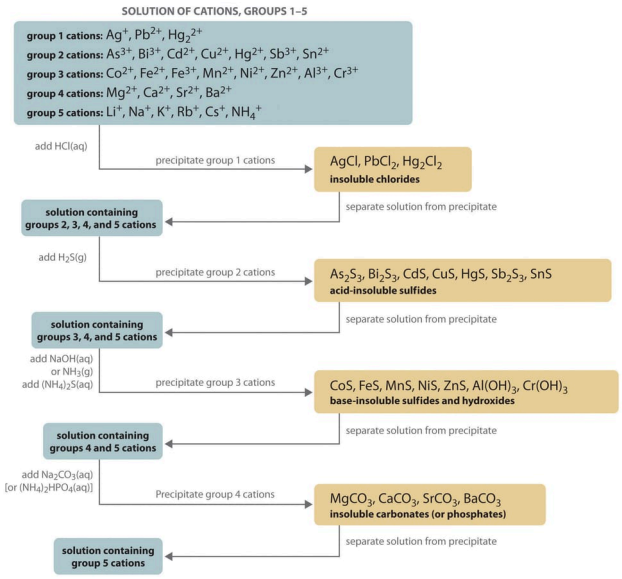


Figure 17.5.1 Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

Group 1: Insoluble Chlorides

Most metal chloride salts are soluble in water; only Ag^+, Pb^{2+}, and Hg_2^{2+} form chlorides that precipitate from water. Thus the first step in a qualitative analysis is to add about 6 M HCl, thereby causing AgCl, $PbCl_2$, and/or Hg_2Cl_2 to precipitate. If no precipitate forms, then these cations are not present in significant amounts. The precipitate can be collected by filtration or centrifugation.

Group 2: Acid-Insoluble Sulfides

Next, the acidic solution is saturated with H_2S gas. Only those metal ions that form very insoluble sulfides, such as As^{3+}, Bi^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Sb^{3+}, and Sn^{2+}, precipitate as their sulfide salts under these acidic conditions. All others, such as Fe^{2+} and Zn^{2+}, remain in solution. Once again, the precipitates are collected by filtration or centrifugation.

Group 3: Base-Insoluble Sulfides (and Hydroxides)

Ammonia or NaOH is now added to the solution until it is basic, and then $(NH_4)_2S$ is added. This treatment removes any remaining cations that form insoluble hydroxides or sulfides. The divalent metal ions Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} precipitate as their sulfides, and the trivalent metal ions Al^{3+} and Cr^{3+} precipitate as their hydroxides: $Al(OH)_3$ and $Cr(OH)_3$. If the mixture contains Fe^{3+}, sulfide reduces the cation to Fe^{2+}, which precipitates as FeS.

Group 4: Insoluble Carbonates or Phosphates

The next metal ions to be removed from solution are those that form insoluble carbonates and phosphates. When Na_2CO_3 is added to the basic solution that remains after the precipitated metal ions are removed, insoluble carbonates precipitate and are collected. Alternatively, adding $(NH_4)_2HPO_4$ causes the same metal ions to precipitate as insoluble phosphates.

Group 5: Alkali Metals

At this point, we have removed all the metal ions that form water-insoluble chlorides, sulfides, carbonates, or phosphates. The only common ions that might remain are any alkali metals (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium (NH_4^+). We now take a second sample from the *original* solution and add a small amount of NaOH to neutralize the ammonium ion and produce NH_3. (We cannot use the same sample we used for the first four groups because we added ammonium to that sample in earlier steps.) Any ammonia produced can be detected by either its odor or a litmus paper test. A flame test on another original sample is used to detect sodium, which produces a characteristic bright yellow color. As discussed in Chapter 2, the other alkali metal ions also give characteristic colors in flame tests, which allows them to be identified if only one is present.

Summary

In **qualitative analysis**, the identity, not the amount, of metal ions present in a mixture is determined. The technique consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively *less* selective until almost all the metal ions are precipitated. Other additional steps are needed to separate metal ions that precipitate together.

Key Takeaway

- Several common metal cations can be identified in a solution using selective precipitation.

Conceptual Problem

1. Given a solution that contains a mixture of NaCl, $CuCl_2$, and $ZnCl_2$, propose a method for separating the metal ions.

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13: REDOX REACTIONS DESCRIBE THE MOVEMENT OF ELECTRONS

13.1: Overview and Objectives
13.2: Oxidation-Reduction Reactions
13.3: Balancing Redox Reactions
13.4: Describing Electrochemical Cells
13.5: Standard Potentials
13.6: Comparing Strengths of Oxidants and Reductants
13.7: Electrochemical Cells and Thermodynamics
13.8: Electrolysis

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13.1: Overview and Objectives

> "The metals alone, are the true motors of this electricity... that electric fluid is set in motion by the simple contact of different conducting substances." (Alessandro Volta)

Volta, from whom we get the name for the unit of electrical potential known as the *volt*, was one of the first scientists to show that it was possible to take advantage of the movement of electrons associated with some types of chemical reactions, called *oxidation-reduction (redox) reaction*s, to produce electrical current. In this chapter, we'll look more closely at redox reactions, discover what sorts of chemicals make good reducing and oxidizing agents, and examine the specific application of redox reactions to electrochemical cells, like batteries.

Chapter Objectives

- Balance redox reactions in acidic and basic solutions, identifying the oxidizing agent and reducing agent.
- Rank chemicals by their oxidizing or reducing ability.
- Write the balanced chemical equation or shorthand notation for a galvanic cell and calculate its $E°$.
- Use appropriate mathematical expressions to convert between ΔG, K, Q, and E_{cell}.

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13.2: Oxidation-Reduction Reactions

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Balance redox reactions in acidic and basic solutions, identifying the oxidizing agent and reducing agent.

Oxidation–Reduction Reactions

The term oxidation refers to the loss of one or more electrons in a chemical reaction. The substance that loses electrons is said to be oxidized. was first used to describe reactions in which metals react with oxygen in air to produce metal oxides. When iron is exposed to air in the presence of water, for example, the iron turns to rust—an iron oxide. When exposed to air, aluminum metal develops a continuous, coherent, transparent layer of aluminum oxide on its surface. In both cases, the metal acquires a positive charge by transferring electrons to the neutral oxygen atoms of an oxygen molecule. As a result, the oxygen atoms acquire a negative charge and form oxide ions (O^{2-}). Because the metals have lost electrons to oxygen, they have been *oxidized*; oxidation is therefore the loss of electrons. Conversely, because the oxygen atoms have gained electrons, they have been *reduced*, so reduction is the gain of electrons. For every oxidation, there must be an associated reduction.

Note the Pattern

Any oxidation *must* be accompanied by a reduction and vice versa.

The term reduction refers to the gain of one or more electrons in a chemical reaction. The substance that gains electrons is said to be reduced. referred to the decrease in mass observed when a metal oxide was heated with carbon monoxide, a reaction that was widely used to extract metals from their ores. When solid copper(I) oxide is heated with hydrogen, for example, its mass decreases because the formation of pure copper is accompanied by the loss of oxygen atoms as a volatile product (water). The reaction is as follows:

$$Cu_2O\,(s) + H_2\,(g) \rightarrow 2Cu\,(s) + H_2O\,(g)$$

Oxidation and reduction reactions are now defined as reactions that exhibit a change in the oxidation states of one or more elements in the reactants, which follows the mnemonic *oxidation is loss reduction is gain*, or *oil rig*. The oxidation state: The charge that each atom in a compound would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons. of each atom in a compound is the charge an atom would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons. Atoms in their elemental form, such as O_2 or H_2, are assigned an oxidation state of zero. For example, the reaction of aluminum with oxygen to produce aluminum oxide is

$$4Al\,(s) + 3O_2\,(g) \rightarrow 2Al_2O_3\,(s)$$

Each neutral oxygen atom gains two electrons and becomes negatively charged, forming an oxide ion; thus, oxygen has an oxidation state of –2 in the product and has been reduced. Each neutral aluminum atom loses three electrons to produce an aluminum ion with an oxidation state of +3 in the product, so aluminum has been oxidized. In the formation of Al_2O_3, electrons are transferred as follows (the superscript 0 emphasizes the oxidation state of the elements):

$$4Al^0 + 3O_2^0 \rightarrow 4Al^+6O^{2-}$$

Equation 13.2.1 and Equation 13.2.2 are examples of oxidation–reduction (redox) reactions. In redox reactions, there is a net transfer of electrons from one reactant to another. In any redox reaction, the total number of electrons lost must equal the total of electrons gained to preserve electrical neutrality. In Equation 13.2.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$\begin{aligned} electrons\ lost &= 4\ \cancel{Al\ atoms} \times \frac{3\ e^-\ lost}{\cancel{Al\ atoms}} = 12\ e^-\ lost \\ electrons\ gained &= 6\ \cancel{O\ atoms} \times \frac{2\ e^-\ gained}{\cancel{O\ atoms}} = 12\ e^-\ gained \end{aligned} \tag{13.2.1}$$

The same pattern is seen in all oxidation–reduction reactions: the number of electrons lost must equal the number of electrons gained.

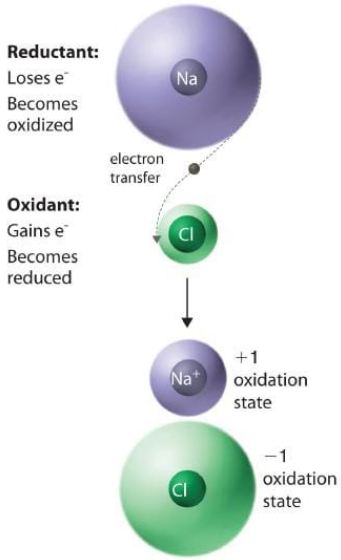
Note the Pattern

In all oxidation–reduction (redox) reactions, the number of electrons lost equals the number of electrons gained.

Assigning Oxidation States

Assigning oxidation states to the elements in binary ionic compounds is straightforward: the oxidation states of the elements are identical to the charges on the monatomic ions. In an earlier chapter, you learned how to predict the formulas of simple ionic compounds based on the sign and magnitude of the charge on monatomic ions formed by the neutral elements. Examples of such compounds are sodium chloride (NaCl; Figure 13.2.1, magnesium oxide (MgO), and calcium chloride ($CaCl_2$). In covalent compounds, in contrast, atoms share electrons. Oxidation states in covalent compounds can be understood in terms of polar covalent bonds and electronegativity. Oxidation states assume that electrons are completely transferred. While this is not true, it is almost true, and the oxidation state model can help you understand and predict many reactions. For example, in water, the oxidation state of the oxygen atom is -2 and that of each hydrogen is +1. That is the oxidation state model assumes that the hydrogen atoms transfer an electron completely to the oxygen atom. We know this is not the case, but that the electrons from the hydrogen atoms are found closter to the oxygen atom. A more extreme case is carbon dioxide, where the oxidation states of the more electronegative oxygen atoms are -2 and that of the carbon atom is +4. Again, the idea is that the oxidation state model assumes complete transfer, and the atomic bond model tell us that the transfer is only partial. Still, the oxidation state model is useful as we shall see

Figure 13.2.1 The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom



The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.

A set of rules for assigning oxidation states to atoms in chemical compounds follows.

Rules for Assigning Oxidation States:

1. The oxidation state of an atom in any pure element, whether monatomic, diatomic, or polyatomic, is zero.
2. The oxidation state of a monatomic ion is the same as its charge—for example, Na^+ = +1, Cl^- = –1.
3. The oxidation state of fluorine in chemical compounds is always –1. Other halogens usually have oxidation states of –1 as well, except when combined with oxygen or other halogens.
4. Hydrogen is assigned an oxidation state of +1 in its compounds with nonmetals and –1 in its compounds with metals.
5. Oxygen is normally assigned an oxidation state of –2 in compounds, with two exceptions: in compounds that contain oxygen–fluorine or oxygen–oxygen bonds, the oxidation state of oxygen is determined by the oxidation states of the other elements present.
6. The sum of the oxidation states of all the atoms in a neutral molecule or ion must equal the charge on the molecule or ion.

In any chemical reaction, the net charge must be conserved; that is, in a chemical reaction, the total number of electrons is constant, just like the total number of atoms. Consistent with this, rule 1 states that the sum of the individual oxidation states of the atoms in a molecule or ion must equal the net charge on that molecule or ion. In NaCl, for example, Na has an oxidation state of +1 and Cl is –1. The net charge is zero, as it must be for any compound.

Rule 3 is required because fluorine attracts electrons more strongly than any other element, for reasons you discovered in Chapter 7 . Hence fluorine provides a reference for calculating the oxidation states of other atoms in chemical compounds. Rule 4 reflects the difference in chemistry observed for compounds of hydrogen with nonmetals (such as chlorine) as opposed to compounds of hydrogen with metals (such as sodium). For example, NaH contains the H^- ion, whereas HCl forms H^+ and Cl^- ions when dissolved in water. Rule 5 is necessary because fluorine has a greater attraction for electrons than oxygen does; this rule also prevents violations of rule 2. So the oxidation state of oxygen is +2 in OF_2 but –½ in KO_2. Note that an oxidation state of –½ for O in KO_2 is perfectly acceptable. Nonintegral oxidation states are encountered occasionally. They are usually due to the presence of two or more atoms of the same element with different oxidation states, so that the "average" oxidation state is a fraction. As with resonance structures, this is a failure of the model.

The reduction of copper(I) oxide shown in Equation $13.2.5$ demonstrates how to apply these rules. Rule 1 states that atoms in their elemental form have an oxidation state of zero, which applies to H_2 and Cu. From rule 4, hydrogen in H_2O has an oxidation state of +1, and from rule 5, oxygen in both Cu_2O and H_2O has an oxidation state of –2. Rule 6 states that the sum of the oxidation states in a molecule or formula unit must equal the net charge on that compound. This means that each Cu atom in Cu_2O must have a charge of +1: 2(+1) + (–2) = 0. So the oxidation states are as follows:

$$\overset{+1}{Cu}_2\overset{}{O}_{-2}\,(s) + \overset{0}{H}_2 \rightarrow 2\overset{0}{Cu}\,(s) + \overset{+1}{H}_2\overset{}{O}_{-2}\,(g) \tag{13.2.2}$$

Assigning oxidation states allows us to see that there has been a net transfer of electrons from hydrogen (0 → +1) to copper (+1 → 0). So this is a redox reaction. Once again, the number of electrons lost equals the number of electrons gained, and there is a net conservation of charge:

$$\begin{aligned} electrons\ lost &= 2\ \cancel{H\ atoms} \times \frac{1\ e^-\ lost}{\cancel{H\ atoms}} = 2\ e^-\ lost \\ electrons\ gained &= 2\ \cancel{Cu\ atoms} \times \frac{1\ e^-\ gained}{\cancel{Cu\ atoms}} = 2\ e^-\ gained \end{aligned} \tag{13.2.3}$$

Remember that oxidation states are useful for visualizing the transfer of electrons in oxidation–reduction reactions, but the oxidation state of an atom and its actual charge are the same only for simple ionic compounds. Oxidation states are a convenient way of assigning electrons to atoms, and they are useful for predicting the types of reactions that substances undergo.

Example 13.2.1

Assign oxidation states to all atoms in each compound.

1. sulfur hexafluoride (SF_6)

2. methanol (CH_3OH)
3. ammonium sulfate [$(NH_4)_2SO_4$]
4. magnetite (Fe_3O_4)
5. ethanoic (acetic) acid (CH_3CO_2H)

Given: molecular or empirical formula

Asked for: oxidation states

Strategy:

Begin with atoms whose oxidation states can be determined unambiguously from the rules presented (such as fluorine, other halogens, oxygen, and monatomic ions). Then determine the oxidation states of other atoms present according to rule 1.

Solution:

1. We know from rule 3 that fluorine always has an oxidation state of –1 in its compounds. The six fluorine atoms in sulfur hexafluoride give a total negative charge of –6. Because rule 1 requires that the sum of the oxidation states of all atoms be zero in a neutral molecule (here SF_6), the oxidation state of sulfur must be +6: [(6 F atoms)(–1)] + [(1 S atom) (+6)] = 0
2. According to rules 4 and 5, hydrogen and oxygen have oxidation states of +1 and –2, respectively. Because methanol has no net charge, carbon must have an oxidation state of –2: [(4 H atoms)(+1)] + [(1 O atom)(–2)] + [(1 C atom)(–2)] = 0
3. Note that $(NH_4)_2SO_4$ is an ionic compound that consists of both a polyatomic cation (NH_4^+) and a polyatomic anion (SO_4^{2-}) (see Table 6.2.1). We assign oxidation states to the atoms in each polyatomic ion separately. For NH_4^+, hydrogen has an oxidation state of +1 (rule 4), so nitrogen must have an oxidation state of –3: [(4 H atoms)(+1)] + [(1 N atom)(–3)] = +1, the charge on the NH_4^+ ion

   For SO_4^{2-}, oxygen has an oxidation state of –2 (rule 5), so sulfur must have an oxidation state of +6:

   [(4 O atoms) (–2)] + [(1 S atom)(+6)] = –2, the charge on the sulfate ion
4. Oxygen has an oxidation state of –2 (rule 5), giving an overall charge of –8 per formula unit. This must be balanced by the positive charge on three iron atoms, giving an oxidation state of +8/3 for iron:

   Fractional oxidation states are allowed because oxidation states are a somewhat arbitrary way of keeping track of electrons. In fact, Fe_3O_4 can be viewed as having two Fe^{3+} ions and one Fe^{2+} ion per formula unit, giving a net positive charge of +8 per formula unit. Fe_3O_4 is a magnetic iron ore commonly called magnetite. In ancient times, magnetite was known as lodestone because it could be used to make primitive compasses that pointed toward Polaris (the North Star), which was called the “lodestar.”

5. Initially, we assign oxidation states to the components of CH_3CO_2H in the same way as any other compound. Hydrogen and oxygen have oxidation states of +1 and –2 (rules 4 and 5, respectively), resulting in a total charge for hydrogen and oxygen of [

$$(4Hatoms)(+1)] + [(2Oatoms)(-2)] = 0 \tag{13.2.4}$$

   So the oxidation state of carbon must also be zero (rule 6). This is, however, an *average* oxidation state for the two carbon atoms present. Because each carbon atom has a different set of atoms bonded to it, they are likely to have different oxidation states. To determine the oxidation states of the individual carbon atoms, we use the same rules as before but with the additional assumption that bonds between atoms of the same element do not affect the oxidation states of those atoms. The carbon atom of the methyl group ($–CH_3$) is bonded to three hydrogen atoms and one carbon atom. We know from rule 4 that hydrogen has an oxidation state of +1, and we have just said that the carbon–carbon bond can be ignored in calculating the oxidation state of the carbon atom. For the methyl group to be electrically neutral, its carbon atom must have an oxidation state of –3. Similarly, the carbon atom of the carboxylic acid group ($–CO_2H$) is bonded to one carbon atom and two oxygen atoms. Again ignoring the bonded carbon atom, we assign oxidation states of –2 and +1 to the oxygen and hydrogen atoms, respectively, leading to a net charge of

   [(2 O atoms)(–2)] + [(1 H atom)(+1)] = –3

To obtain an electrically neutral carboxylic acid group, the charge on this carbon must be +3. The oxidation states of the individual atoms in acetic acid are thus

$$\overset{+1}{\underset{-3}{C}}\overset{+1}{H_3}\overset{+3}{\underset{-2}{C}}\overset{-2}{O_2}\overset{+1}{H} \tag{13.2.5}$$

Thus the sum of the oxidation states of the two carbon atoms is indeed zero.

Exercise 13.2.1

Assign oxidation states to all atoms in each compound.

1. barium fluoride (BaF_2)
2. formaldehyde (CH_2O)
3. potassium dichromate ($K_2Cr_2O_7$)
4. cesium oxide (CsO_2)
5. ethanol (CH_3CH_2OH)

Answer available at the end of this section.

Oxidants and Reductants

Compounds that are capable of accepting electrons, such as O_2 or F_2, are called oxidants (or oxidizing agents) because they are capable of oxidizing other substances.. *In the process of accepting electrons, an oxidant is reduced.* Compounds that are capable of donating electrons, such as sodium metal or cyclohexane (C_6H_{12}), are called reductants (or reducing agents) because they can cause the reduction of another compound. *In the process of donating electrons, a reductant is oxidized.* These relationships are summarized in Equation 7.5.7:

$$oxidant + reductant \rightarrow oxidation - reduction \tag{13.2.6}$$

$$\underset{gains\ e^-}{\overset{(is\ reduced)}{O_2}}(g) + \underset{loses\ e^-}{\overset{(is\ oxidized)}{4Na}}(s) \rightarrow \underset{redox\ reaction}{2Na_2O} \tag{7.5.7}$$

Some oxidants have a greater ability than others to remove electrons from other compounds. Oxidants can range from very powerful, capable of oxidizing most compounds with which they come in contact, to rather weak. Both F_2 and Cl_2 are powerful oxidants: for example, F_2 will oxidize H_2O in a vigorous, potentially explosive reaction. In contrast, S_8 is a rather weak oxidant, and O_2 falls somewhere in between. Conversely, reductants vary in their tendency to donate electrons to other compounds. Reductants can also range from very powerful, capable of giving up electrons to almost anything, to weak. The alkali metals are powerful reductants, so they must be kept away from atmospheric oxygen to avoid a potentially hazardous redox reaction.

Summary

Chemical reactions may be classified as an a**cid–base reaction**, an **exchange reaction**, a **condensation reaction** and its reverse, a **cleavage reaction**, and an **oxidation–reduction (or redox)** reaction. To keep track of electrons in chemical reactions, oxidation states are assigned to atoms in compounds. The **oxidation state** is the charge an atom would have if all its bonding electrons were transferred completely to the atom that has the greater attraction for electrons. In an **oxidation–reduction reaction**, one atom must lose electrons and another must gain electrons. **Oxidation** is the loss of electrons, and an element whose oxidation state increases is said to be *oxidized*. **Reduction** is the gain of electrons, and an element whose oxidation state decreases is said to be *reduced*. **Oxidants** are compounds that are capable of accepting electrons from other compounds, so they are reduced during an oxidation–reduction reaction. In contrast, **reductants** are compounds that are capable of donating

electrons to other compounds, so they are oxidized during an oxidation–reduction reaction.

Key Takeaway

- Chemical reactions may be classified as acid–base, exchange, condensation, cleavage, and oxidation–reduction (redox).

Conceptual Problems

1. What is a combustion reaction? How can it be distinguished from an exchange reaction?
2. What two products are formed in the combustion of an organic compound containing only carbon, hydrogen, and oxygen? Is it possible to form only these two products from a reaction that is not a combustion reaction? Explain your answer.
3. What factors determine whether a reaction can be classified as a redox reaction?
4. Name three characteristics of a balanced redox reaction.
5. Does an oxidant accept electrons or donate them?
6. Does the oxidation state of a reductant become more positive or more negative during a redox reaction?
7. Nitrogen, hydrogen, and ammonia are known to have existed on primordial earth, yet mixtures of nitrogen and hydrogen do not usually react to give ammonia. What natural phenomenon would have enough energy to initiate a reaction between these two primordial gases?
8. Catalysts are not added to reactions in stoichiometric quantities. Why?
9. State whether each of the following uses a homogeneous catalyst or a heterogeneous catalyst.
    1. Platinum metal is used in the catalytic converter of an automobile.
    2. Nitrogen is biologically converted to ammonia by an enzyme.
    3. Carbon monoxide and hydrogen combine to form methane and water with a nickel catalyst.
    4. A dissolved rhodium compound is used as a catalyst for the conversion of an alkene to an alkane.
10. State whether each of the following uses a homogeneous catalyst or a heterogeneous catalyst.
    1. Pellets of ZSM-5, an aluminum- and silicon-containing mineral, are used to catalyze the conversion of methanol to gasoline.
    2. The conversion of glucose to a carboxylic acid occurs with catalysis by the enzyme glucose oxidase.
    3. Metallic rhodium is used to the conversion of carbon monoxide and water to carbon dioxide and hydrogen.
11. Complete the following table to describe some key differences between homogeneous and heterogeneous catalysis.

	Homogeneous	Heterogeneous
number of phases		
ease of separation from product		
ease of recovery of catalyst		

12. To increase the rate of a reaction, a scientist decided to use a catalyst. Unexpectedly, the scientist discovered that the catalyst decreased the yield of the desired product, rather than increasing it. What might have happened?

Answer

1.
2.
3.

4.
5.
6.
7.
8.
9.
10.
11.

	Homogeneous	Heterogeneous
number of phases	single phase	at least two phases
ease of separation from product	difficult	easy
ease of recovery of catalyst	difficult	easy

12.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 7.7) before proceeding to the Numerical Problems.

1. Classify each chemical reaction according to the types listed in Table 7.5.1

    1. $12FeCl_2(s) + 3O_2(g) \rightarrow 8FeCl_3(s) + 2Fe_2O_3(s)$
    2. $CaCl_2(aq) + K_2SO_4(aq) \rightarrow CaSO_4(s) + 2KCl(aq)$
    3. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
    4. $Br_2(l) + C_2H_4(g) \rightarrow BrCH_2CH_2Br(l)$

2. Assign oxidation states to the atoms in each compound or ion.

    1. $(NH_4)_2S$
    2. the phosphate ion
    3. $[AlF_6]^{3-}$
    4. CuS
    5. HCO_3^-
    6. NH_4^+
    7. H_2SO_4
    8. formic acid
    9. *n*-butanol

3. Assign oxidation states to the atoms in each compound or ion.

    1. ClO_2
    2. HO_2^-
    3. sodium bicarbonate
    4. MnO_2
    5. PCl_5
    6. $[Mg(H_2O)_6]^{2+}$
    7. N_2O_4
    8. butanoic acid
    9. methanol

4. Assign oxidation states to the atoms in each compound.

    1. iron(III) nitrate

2. Al_2O_3
3. potassium sulfate
4. Cr_2O_3
5. sodium perchlorate
6. Cu_2S
7. hydrazine (N_2H_4)
8. NO_2
9. *n*-pentanol

5. Assign oxidation states to the atoms in each compound.

   1. calcium carbonate
   2. NaCl
   3. CO_2
   4. potassium dichromate
   5. $KMnO_4$
   6. ferric oxide
   7. $Cu(OH)_2$
   8. Na_2SO_4
   9. *n*-hexanol

6. For each redox reaction, determine the identities of the oxidant, the reductant, the species oxidized, and the species reduced.

   1. $H_2(g) + I_2(s) \rightarrow 2HI(g)$
   2. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
   3. $2F_2(g) + 2NaOH(aq) \rightarrow OF_2(g) + 2NaF(aq) + H_2O(l)$

7. For each redox reaction, determine the identities of the oxidant, the reductant, the species oxidized, and the species reduced.

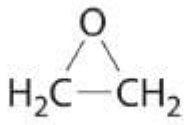
   1. $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
   2. $SiCl_4(l) + 2Mg(s) \rightarrow 2MgCl_2(s) + Si(s)$
   3. $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

8. Balance each chemical equation. Then identify the oxidant, the reductant, the species oxidized, and the species reduced. (Δ indicates that the reaction requires heating.)

   1. $H_2O(g) + CO(g) \rightarrow CO_2(g) + H_2(g)$
   2. the reaction of aluminum oxide, carbon, and chlorine gas at 900°C to produce aluminum chloride and carbon monoxide

9. Balance each chemical equation. Then identify the oxidant, the reductant, the species oxidized, and the species reduced. (Δ indicates that the reaction requires heating.)

   1. the reaction of water and carbon at 800°C to produce hydrogen and carbon monoxide
   2. $Mn(s) + S_8(s) + CaO(s) \rightarrow CaS(s) + MnO(s)$
   3. the reaction of ethylene and oxygen at elevated temperature in the presence of a silver catalyst to produce ethylene oxide



Ethylene oxide

   4. $ZnS(s) + H_2SO_4(aq) + O_2(g) \rightarrow ZnSO_4(aq) + S_8(s) + H_2O(l)$

10. Silver is tarnished by hydrogen sulfide, an atmospheric contaminant, to form a thin layer of dark silver sulfide (Ag_2S) along with hydrogen gas.

1. Write a balanced chemical equation for this reaction.
2. Which species has been oxidized and which has been reduced?
3. Assuming 2.2 g of Ag has been converted to silver sulfide, construct a table showing the reaction in terms of the number of atoms in the reactants and products, the moles of reactants and products, the grams of reactants and products, and the molecules of reactants and products.

11. The following reaction is used in the paper and pulp industry:

$$Na_2SO_4(aq) + C(s) + NaOH(aq) \rightarrow Na_2CO_3(aq) + Na_2S(aq) + H_2O(l)$$

1. Balance the chemical equation.
2. Identify the oxidant and the reductant.
3. How much carbon is needed to convert 2.8 kg of sodium sulfate to sodium sulfide?
4. If the yield of the reaction were only 78%, how many kilograms of sodium carbonate would be produced from 2.80 kg of sodium sulfate?
5. If 240 g of carbon and 2.80 kg of sodium sulfate were used in the reaction, what would be the limiting reactant (assuming an excess of sodium hydroxide)?

12.

Contributors

- Anonymous

Modified by Joshua Halpern

Answers

Exercise 13.2.1

1. Ba, +2; F, −1
2. C, 0; H, +1; O, −2
3. K, +1; Cr, +6; O, −2
4. Cs, +1; O, −½
5. C, −3; H, +1; C, −1; H, +1; O, −2; H, +1

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13.3: Balancing Redox Reactions

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Balance redox reactions in acidic and basic solutions, identifying the oxidizing agent and reducing agent.

Balancing Redox Equations

The unbalanced equation below describes the decomposition of molten sodium chloride:

$$\mathrm{NaCl\,(l)} \longrightarrow \mathrm{Na\,(l)} + \mathrm{Cl_2\,(g)} \qquad \text{(unbalanced)}$$

This reaction satisfies the criterion for redox classification, since the oxidation number for Na is decreased from +1 to 0 (it undergoes *reduction*) and that for Cl is increased from –1 to 0 (it undergoes *oxidation*). The equation in this case is easily balanced by inspection, requiring stoichiometric coefficients of 2 for the NaCl and Na:

$$2\,\mathrm{NaCl\,(l)} \longrightarrow 2\,\mathrm{Na\,(l)} + \mathrm{Cl_2\,(g)} \qquad \text{(balanced)}$$

Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, $H^+(aq)$ and $OH^-(aq)$, as reactants or products. In these cases, equations representing the redox reaction can be very challenging to balance by inspection, and the use of a systematic approach called the *half-reaction method* is helpful.

Balancing REDOX reactions via the half-reaction Method

This approach involves the following steps:

1. Write skeletal equations for the oxidation and reduction half-reactions.
2. Balance each half-reaction for all elements except H and O.
3. Balance each half-reaction for O by adding H_2O.
4. Balance each half-reaction for H by adding H^+.
5. Balance each half-reaction for charge by adding electrons.
6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

The examples below demonstrate the application of this method to balancing equations for aqueous redox reactions.

Example 13.3.1: Balancing Equations for Redox Reactions in Acidic Solutions

Write the balanced equation representing reaction between solid copper and nitric acid to yield aqueous copper(II) ions and nitrogen monoxide gas.

Solution

Following the steps of the half-reaction method:

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\begin{aligned}\text{oxidation:}&\quad \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq)}\\ \text{reduction:}&\quad \mathrm{HNO_3\,(aq) \longrightarrow NO\,(g)}\end{aligned}$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\begin{aligned}\text{oxidation:}&\quad \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq)}\\ \text{reduction:}&\quad \mathrm{HNO_3\,(aq) \longrightarrow NO\,(g)}\end{aligned}$$

Step 3: Balance each half-reaction for O by adding $\mathrm{H_2O}$.

$$\begin{aligned}\text{oxidation:}&\quad \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq)}\\ \text{reduction:}&\quad \mathrm{HNO_3\,(aq) \longrightarrow NO\,(g) + \mathbf{2H2O(l)}}\end{aligned}$$

Step 4: Balance each half-reaction for H by adding $\mathrm{H^+}$.

$$\begin{aligned}\text{oxidation:}&\quad \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq)}\\ \text{reduction:}&\quad \mathrm{\mathbf{3H^+(aq)} + HNO_3\,(aq) \longrightarrow NO\,(g) + 2\,H_2O\,(l)}\end{aligned}$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\begin{aligned}\text{oxidation:}&\quad \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq) + \mathbf{2e^-}}\\ \text{reduction:}&\quad \mathrm{\mathbf{3e^-} + 3\,H^+\,(aq) + HNO_3\,(aq) \longrightarrow NO\,(g) + 2\,H_2O\,(l)}\end{aligned}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

$$\begin{aligned}\text{oxidation }(\times 3):&\quad \mathrm{\mathbf{3}\ Cu\,(s) \longrightarrow \mathbf{3}\ Cu^{2+}\,(aq) + \mathbf{6}\ \cancel{\mathbf{2}}\ e^-}\\ \text{reduction }(\times 2):&\quad \mathrm{\mathbf{6}\ \cancel{\mathbf{3}}\ e^- + \mathbf{6}\ \cancel{\mathbf{3}}\ H^+\,(aq) + \mathbf{2}\ HNO_3\,(aq) \longrightarrow \mathbf{2}\ NO\,(g) + \mathbf{4}\ \cancel{\mathbf{2}}\ H_2O\,(l)}\end{aligned}$$

Step 7: Add the two half-reactions and simplify.

$$\mathrm{3\,Cu\,(s) + \cancel{6e^-} + 6\,H^+\,(aq) + 2\,HNO_3\,(aq) \longrightarrow 3\,Cu^{2+}\,(aq) + \cancel{6e^-} + 2\,NO\,(g) + 4\,H_2O\,(l)}$$

$$\mathrm{3\,Cu\,(s) + 6\,H^+\,(aq) + 2\,HNO_3\,(aq) \longrightarrow 3\,Cu^{2+}\,(aq) + 2\,NO\,(g) + 4\,H_2O\,(l)}$$

Step 8: If the reaction takes place in a basic medium, add $\mathrm{OH^-}$ ions the equation obtained in step 7 to neutralize the $\mathrm{H^+}$ ions (add in equal numbers to both sides of the equation) and simplify.

This step not necessary since the solution is stipulated to be acidic.

The balanced equation for the reaction in an acidic solution is then

$$\mathrm{3\,Cu\,(s) + 6\,H^+\,(aq) + 2\,HNO_3\,(aq) \longrightarrow 3\,Cu^{2+}\,(aq) + 2\,NO\,(g) + 4\,H_2O\,(l)}$$

Exercise 13.3.1

The reaction above results when using relatively diluted nitric acid. If concentrated nitric acid is used, nitrogen dioxide is produced instead of nitrogen monoxide. Write a balanced equation for this reaction.

Answer available at the end of this section.

Example 13.3.2: Balancing Equations for Redox Reactions in Basic Solutions

Write the balanced equation representing reaction between aqueous permanganate ion, , and solid chromium(III) hydroxide, $Cr(OH)_3$, to yield solid manganese(IV) oxide, MnO_2, and aqueous chromate ion, The reaction takes place in a basic solution.

Solution

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\begin{aligned} &\text{oxidation:} \quad \mathrm{Cr(OH)_3\,(s) \longrightarrow CrO_4{}^{2-}\,(aq)} \\ &\text{reduction:} \quad \mathrm{MnO_4{}^-\,(aq) \longrightarrow MnO_2\,(s)} \end{aligned}$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\begin{aligned} &\text{oxidation:} \quad \mathrm{Cr(OH)_3\,(s) \longrightarrow CrO_4{}^{2-}\,(aq)} \\ &\text{reduction:} \quad \mathrm{MnO_4{}^-\,(aq) \longrightarrow MnO_2\,(s)} \end{aligned}$$

Step 3: Balance each half-reaction for O by adding $\mathrm{H_2O}$.

$$\begin{aligned} &\text{oxidation:} \quad \mathbf{H2O(l)} + \mathrm{Cr(OH)_3\,(s) \longrightarrow CrO_4{}^{2-}\,(aq)} \\ &\text{reduction:} \quad \mathrm{MnO_4{}^-\,(aq) \longrightarrow MnO_2\,(s)} + \mathbf{2H2O(l)} \end{aligned}$$

Step 4: Balance each half-reaction for H by adding $\mathrm{H^+}$.

$$\begin{aligned} &\text{oxidation:} \quad \mathrm{H_2O\,(l) + Cr(OH)_3\,(s) \longrightarrow CrO_4{}^{2-}\,(aq)} + \mathbf{5H^+(aq)} \\ &\text{reduction:} \quad \mathbf{4H^+(aq)} + \mathrm{MnO_4{}^-\,(aq) \longrightarrow MnO_2\,(s) + 2\,H_2O\,(l)} \end{aligned}$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\begin{aligned} &\text{oxidation:} \quad \mathrm{H_2O\,(l) + Cr(OH)_3\,(s) \longrightarrow CrO_4{}^{2-}\,(aq) + 5\,H^+\,(aq)} + \mathbf{3e^-} \\ &\text{reduction:} \quad \mathbf{3e^-} + \mathrm{4\,H^+\,(aq) + MnO_4{}^-\,(aq) \longrightarrow MnO_2\,(s) + 2\,H_2O\,(l)} \end{aligned}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

This step is not necessary since the number of electrons is already in balance.

Step 7: Add the two half-reactions and simplify.

$$\begin{aligned} &\cancel{H2O(l)} + \mathrm{Cr(OH)_3\,(s) \longrightarrow CrO_4{}^{2-}\,(aq)} + \cancel{5}^{\,1}\mathrm{H^+\,(aq)} + \cancel{3e^-} \\ + \quad &\cancel{3e^-} + \cancel{4H^+(aq)} + \mathrm{MnO_4{}^-\,(aq) \longrightarrow MnO_2\,(s)} + \cancel{2}^{\,1}\,\mathrm{H_2O\,(l)} \\ &\mathrm{Cr(OH)_3\,(s) + MnO_4{}^-\,(aq) \longrightarrow CrO_4{}^{2-}\,(aq) + MnO_2\,(s) + H^+\,(aq) + H_2O\,(l)} \end{aligned}$$

Step 8: If the reaction takes place in a basic medium, add $\mathrm{OH^-}$ ions the equation obtained in step 7 to neutralize the $\mathrm{H^+}$ ions (add in equal numbers to both sides of the equation) and simplify.

$$\mathrm{OH^-\,(aq) + Cr(OH)_3\,(s) + MnO_4{}^-\,(aq) \longrightarrow CrO_4{}^{2-}\,(aq) + MnO_2\,(s)} + \cancel{H^+(aq)} + \mathrm{H_2O\,(l)} + \cancel{OH^-(aq)}$$

after neutralizing the $\mathrm{H^+}$, we get the balanced equation for the reaction in a basic solution

$$\mathrm{OH^-\,(aq) + Cr(OH)_3\,(s) + MnO_4{}^-\,(aq) \longrightarrow CrO_4{}^{2-}\,(aq) + MnO_2\,(s) + 2\,H_2O\,(l)}$$

Exercise 13.3.2

Aqueous permanganate ion may also be reduced using aqueous bromide ion, $\mathrm{Br^-}$, the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, $\mathrm{BrO_3{}^-}$. Write the balanced equation for this reaction occurring in a basic medium.

Answer available at the end of this section.

Answers

Exercise 13.3.1

$$\mathrm{Cu\,(s) + 2\,H^+\,(aq) + 2\,HNO_3\,(aq) \longrightarrow Cu^{2+}\,(aq) + 2\,NO_2\,(g) + 2\,H_2O\,(l)}$$

Exercise 13.3.2

$$\mathrm{H_2O\,(l) + 2\,MnO_4{}^-\,(aq) + Br^-\,(aq) \longrightarrow 2\,MnO_2\,(s) + BrO_3{}^-\,(aq) + 2\,OH^-\,(aq)}$$

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13.4: Describing Electrochemical Cells

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Write the balanced chemical equation or shorthand notation for a galvanic cell and calculate its *E*°.

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. As we described in Chapter 7, a redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The reductant (a substance that is capable of donating electrons and in the process is oxidized) is the substance that loses electrons and is oxidized in the process; the oxidant (A substance that is capable of accepting electrons and in the process is reduced) is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two half-reactions (reactions that represent either the oxidation half or the reduction half of an oxidation–reduction (redox) reaction), one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$Zn\,(s) + Br_2\,(l) \rightarrow Zn^{2+}\,(aq) + 2Br^{-}\,(aq) \tag{19.1.1}$$

The half-reactions are as follows:

$$reduction\ half\ reaction: Br_2\,(l) + 2e^{-} \rightarrow 2Br^{-}\,(aq) \tag{19.1.2}$$

$$oxidation\ half\ reaction: Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^{-} \tag{19.1.3}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the reductant in this reaction (it loses electrons), and Br_2 is the oxidant (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 19.1). A redox reaction is balanced when *the number of electrons lost by the reductant equals the number of electrons gained by the oxidant*. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

Note the Pattern

In any redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an electrochemical cell (an apparatus that generates electricity from a spontaneous oxidation–reduction (redox) reaction or, conversely, uses electricity to drive a nonspontaneous redox reaction).

There are two types of electrochemical cells: galvanic cells and electrolytic cells. A galvanic (voltaic) cell (an electrochemical cell that uses the energy released during a spontaneous oxidation–reduction (redox) reaction (ΔG^{o}) to generate electricity). Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to *generate* electricity. This type of electrochemical cell is often called a *voltaic cell* after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an electrolytic cellAn electrochemical cell

that consumes electrical energy from an external source to drive a nonspontaneous (ΔG^{o}) oxidation–reduction (redox) reaction. *consume*s electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two electrodesA solid metal connected by an electrolyte and an external circuit that provides an electrical connection between systems in an electrochemical cell (galvanic or electrolytic)., which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 19.1.1). The oxidation half-reaction occurs at one electrode (the anodeOne of two electrodes in an electrochemical cell, it is the site of the oxidation half-reaction.), and the reduction half-reaction occurs at the other (the cathodeOne of two electrodes in an electrochemical cell, it is the site of the reduction half-reaction.). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an *electrolyte*, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells. We discuss electrolytic cells in Section 19.7.

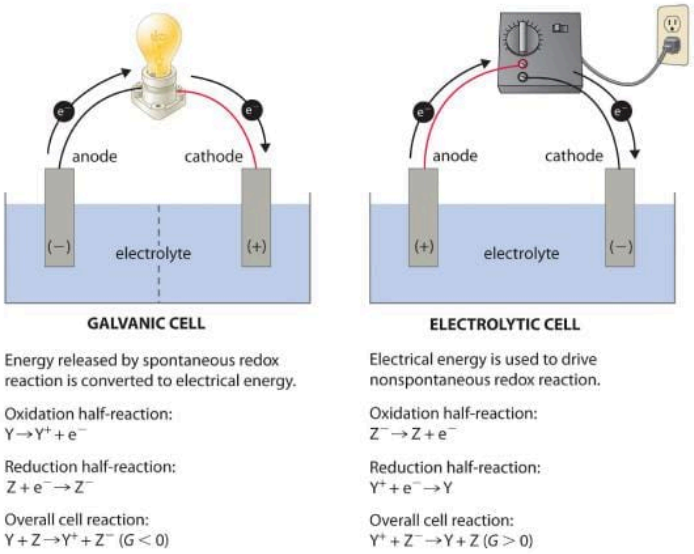


Figure 19.1.1 Electrochemical **Cells** A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Galvanic (Voltaic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s)$$

We can cause this reaction to occur by inserting zinc powder into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc dissolves, and a mass of metallic copper forms (Figure 19.1.2). These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.

Figure 19.1.2 The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment When zinc powder is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give Zn^{2+}(aq) ions, while Cu^{2+}(aq) ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. The reaction demonstration starts at 3:00 in the video, the chemistry of the reaction is discussed in the first three minutes and at the end

This same reaction can be carried out using the galvanic cell illustrated in part (a) in Figure 19.1.3. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of Cu^{2+} ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of Zn^{2+} ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a salt bridge (a U-shaped tube inserted into both solutions of a galvanic cell that contains a concentrated liquid or gelled electrolyte and completes the circuit between the anode and the cathode), a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are Na^+ or K^+ and NO_3^- or SO_4^{2-}, respectively. (The ions in the salt bridge do *not* have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the Zn^{2+} solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the Cu^{2+} solution decreases (part (b) in Figure 19.1.3). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

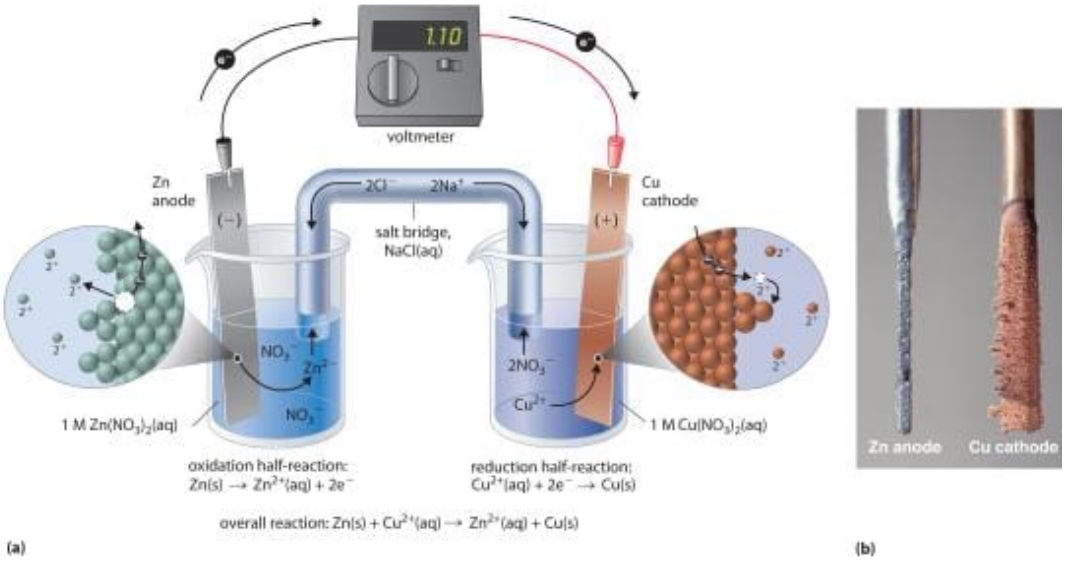


Figure 19.1.3 The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give Zn^{2+}(aq) ions, while the Cu cathode gains mass as Cu^{2+}(aq) ions are reduced to copper metal that is deposited on the cathode.

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

A galvanic cell. This galvanic cell illustrates the use of a salt bridge to connect two solutions generating a voltage.

A *voltmeter* can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The potential (E_{cell})Related to the energy needed to move a charged particle in an electric field, it is the difference in electrical potential beween two half-reactions. of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (part (a) in Figure 19.1.3). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example 1.

Note the Pattern

A galvanic (voltaic) cell converts the energy released by a spontaneous chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a nonspontaneous chemical reaction.

Example 19.1.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3Sn(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Sn^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

For this galvanic cell,

1. write the half-reaction that occurs at each electrode.
2. indicate which electrode is the cathode and which is the anode.
3. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.

B From the direction of electron flow, assign each electrode as either positive or negative.

Solution:

1. **A** In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows: reduction: $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$ oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$

   Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

2. Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.
3. **B** Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow *from* the tin electrode, it must be electrically negative. In contrast, electrons flow *toward* the Pt electrode, so that electrode must be electrically positive.

Exercise

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of MnO_4^- in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of Sn^{2+} in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2MnO_4^-(aq) + 5Sn^{2+}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Sn^{4+}(aq) + 8H_2O(l)$$

For this galvanic cell,

1. write the half-reaction that occurs at each electrode.
2. indicate which electrode is the cathode and which is the anode.
3. indicate which electrode is positive and which is negative.

Answer

1. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$; $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$
2. The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.
3. The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.

Constructing a Cell Diagram

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a *cell diagram*, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the Zn/Cu cell shown in part (a) in Figure 19.1.3 is written as follows:

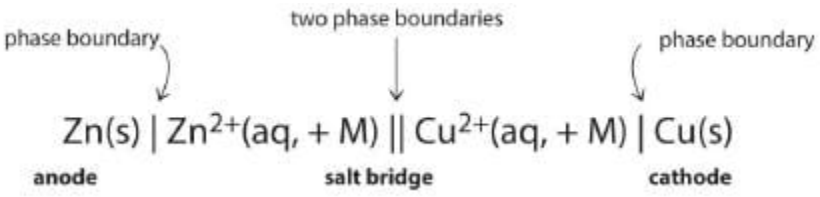


Figure 19.1.4 A cell diagram includes solution concentrations when they are provided.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the

junction potential. One example of this type of galvanic cell is as follows:

$$Pt\,(s)\mid H_2\,(g)\mid HCl\,(aq)\mid AgCl\,(s)\mid Ag\,(s)$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

$$cathode\ \ reaction: AgCl\,(s)+e^-\rightarrow Ag\,(s)+Cl^-\,(aq)$$

$$anode\ \ reaction: \frac{1}{2}H_2\,(g)\rightarrow H^+\,(aq)+e^-$$

$$overall: AgCl\,(s)+\frac{1}{2}H_2\,(g)\rightarrow Ag\,(s)+Cl^-\,(aq)+H^+\,(aq)$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

Example 19.1.2

Draw a cell diagram for the galvanic cell described in Example 1. The balanced chemical reaction is as follows:

$$3Sn(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Sn^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution:

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus Sn(s)|Sn^{2+}(aq). We could include H_2SO_4(aq) with the contents of the anode compartment, but the sulfate ion (as HSO_4^-) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as HNO_3(aq)|NO(g)|Pt(s), with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$Sn(s)|Sn^{2+}(aq)||HNO_3(aq)|NO(g)|Pt(s)$$

The solution concentrations were not specified, so they are not included in this cell diagram.

Exercise

Draw a cell diagram for the following reaction, assuming the concentration of Ag^+ and Mg^{2+} are each 1 M:

$$Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$$

Answer: Mg(s)|Mg^{2+}(aq, 1 M)||Ag^+(aq, 1 M)|Ag(s)

Summary

Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two **half-reactions**, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the **reductant** equals the number of electrons gained by the **oxidant**. An electric current is produced from the flow of electrons from the reductant to the oxidant. An **electrochemical cell** can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a **galvanic (voltaic) cell**, the energy from a spontaneous reaction generates electricity, whereas in an **electrolytic cell**, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two **electrodes** that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the **anode**, and the reductive half-reaction occurs at the **cathode**. A **salt bridge** connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The **potential** of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

Key Takeaway

- A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur.

Conceptual Problems

1. Is $2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ an oxidation–reduction reaction? Why or why not?
2. If two half-reactions are physically separated, how is it possible for a redox reaction to occur? What is the name of the apparatus in which two half-reactions are carried out simultaneously?
3. What is the difference between a galvanic cell and an electrolytic cell? Which would you use to generate electricity?
4. What is the purpose of a salt bridge in a galvanic cell? Is it always necessary to use a salt bridge in a galvanic cell?
5. One criterion for a good salt bridge is that it contains ions that have similar rates of diffusion in aqueous solution, as K^+ and Cl^- ions do. What would happen if the diffusion rates of the anions and cations differed significantly?
6. It is often more accurate to measure the potential of a redox reaction by immersing two electrodes in a single beaker rather than in two beakers. Why?

Answer

1.
2.
3.
4.
5. A large difference in cation/anion diffusion rates would increase resistance in the salt bridge and limit electron flow through the circuit.
6.

Numerical Problems

1. Copper(I) sulfate forms a bright blue solution in water. If a piece of zinc metal is placed in a beaker of aqueous $CuSO_4$ solution, the blue color fades with time, the zinc strip begins to erode, and a black solid forms around the zinc strip. What is happening? Write half-reactions to show the chemical changes that are occurring. What will happen if a piece of copper

metal is placed in a colorless aqueous solution of $ZnCl_2$?

2. Consider the following spontaneous redox reaction: $NO_3^-(aq) + H^+(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + HNO_2(aq)$.

    1. Write the two half-reactions for this overall reaction.
    2. If the reaction is carried out in a galvanic cell using an inert electrode in each compartment, which electrode corresponds to which half-reaction?
    3. Which electrode is negatively charged, and which is positively charged?

3. The reaction $Pb(s) + 2VO^{2+}(aq) + 4H^+(aq) \rightarrow Pb^{2+}(aq) + 2V^{3+}(aq) + 2H_2O(l)$ occurs spontaneously.

    1. Write the two half-reactions for this redox reaction.
    2. If the reaction is carried out in a galvanic cell using an inert electrode in each compartment, which reaction occurs at the cathode and which occurs at the anode?
    3. Which electrode is positively charged, and which is negatively charged?

4. Phenolphthalein is an indicator that turns pink under basic conditions. When an iron nail is placed in a gel that contains $[Fe(CN)_6]^{3-}$, the gel around the nail begins to turn pink. What is occurring? Write the half-reactions and then write the overall redox reaction.

5. Sulfate is reduced to HS^- in the presence of glucose, which is oxidized to bicarbonate. Write the two half-reactions corresponding to this process. What is the equation for the overall reaction?

6. Write the spontaneous half-reactions and the overall reaction for each proposed cell diagram. State which half-reaction occurs at the anode and which occurs at the cathode.

    1. $Pb(s)|PbSO_4(s)|SO_4^{2-}(aq)||Cu^{2+}(aq)|Cu(s)$
    2. $Hg(l)|Hg_2Cl_2(s)|Cl^-(aq) \parallel Cd^{2+}(aq)|Cd(s)$

7. For each galvanic cell represented by these cell diagrams, determine the spontaneous half-reactions and the overall reaction. Indicate which reaction occurs at the anode and which occurs at the cathode.

    1. $Zn(s)|Zn^{2+}(aq) \parallel H^+(aq)|H_2(g), Pt(s)$
    2. $Ag(s)|AgCl(s)|Cl^-(aq) \parallel H^+(aq)|H_2(g)|Pt(s)$
    3. $Pt(s)|H_2(g)|H^+(aq) \parallel Fe^{2+}(aq), Fe^{3+}(aq)|Pt(s)$

8. For each redox reaction, write the half-reactions and draw the cell diagram for a galvanic cell in which the overall reaction occurs spontaneously. Identify each electrode as either positive or negative.

    1. $Ag(s) + Fe^{3+}(aq) \rightarrow Ag^+(aq) + Fe^{2+}(aq)$
    2. $Fe^{3+}(aq) + 1/2H_2(g) \rightarrow Fe^{2+}(aq) + H^+(aq)$

9. Write the half-reactions for each overall reaction, decide whether the reaction will occur spontaneously, and construct a cell diagram for a galvanic cell in which a spontaneous reaction will occur.

    1. $2Cl^-(aq) + Br_2(l) \rightarrow Cl_2(g) + 2Br^-(aq)$
    2. $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$
    3. $2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$
    4. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

10. Write the half-reactions for each overall reaction, decide whether the reaction will occur spontaneously, and construct a cell diagram for a galvanic cell in which a spontaneous reaction will occur.

    1. $Co(s) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe(s)$
    2. $O_2(g) + 4H^+(aq) + 4Fe^{2+}(aq) \rightarrow 2H_2O(l) + 4Fe^{3+}(aq)$

3. $6Hg^{2+}(aq) + 2NO_3^-(aq) + 8H^+ \rightarrow 3Hg_2^{2+}(aq) + 2NO(g) + 4H_2O(l)$
4. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

Answers

1.
2.
3.
4.
5. reduction: $SO_4^{2-}(aq) + 9H^+(aq) + 8e^- \rightarrow HS^-(aq) + 4H_2O(l)$ oxidation: $C_6H_{12}O_6(aq) + 12H_2O(l) \rightarrow 6HCO_3^-(g) + 30H^+(aq) + 24e^-$ overall: $C_6H_{12}O_6(aq) + 3SO_4^{2-}(aq) \rightarrow 6HCO_3^-(g) + 3H^+(aq) + 3HS^-(aq)$
6.
7. 1. reduction: $2H^+(aq) + 2e^- \rightarrow H_2(aq)$; cathode;

      oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; anode;

      overall: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(aq)$

   2. reduction: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$; cathode;

      oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; anode;

      overall: $AgCl(s) + H_2(g) \rightarrow 2H^+(aq) + Ag(s) + Cl^-(aq)$

   3. reduction: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$; cathode;

      oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; anode;

      overall: $2Fe^{3+}(aq) + H_2(g) \rightarrow 2H^+(aq) + 2Fe^{2+}(aq)$
8.
9.
10.

Contributors

- Anonymous

Modified by Joshua B. Halpern

Figure 9.1.2 the reaction between Zn and Cu^{2+} from YouTube courtesy of UC Berkeley Chemistry and Respect Chemistry

Galvanic Cell demonstration from YouTube courtesy of Angela Stott

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13.5: Standard Potentials

Learning Objectives

By the end of this chapter, you will have background information that will help you to be able to:

- Write the balanced chemical equation or shorthand notation for a galvanic cell and calculate its $E°$.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the *s* electrons of zinc by the electrons in filled *d* orbitals. (For more information on atomic orbitals, see Section 2.5.) Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper (Figure 19.2.1). Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

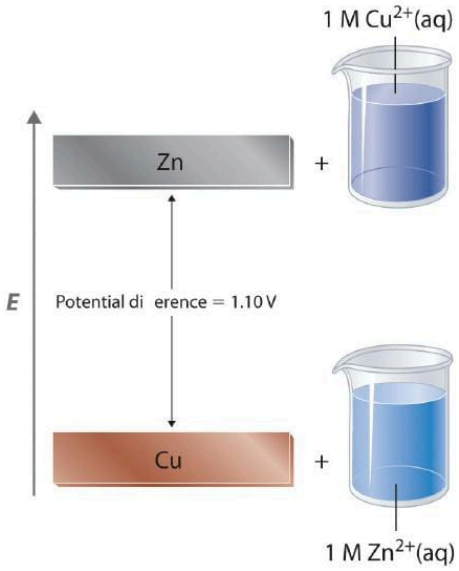


Figure 19.2.1 Potential Energy Difference in the Zn/Cu System The potential energy of a system consisting of metallic Zn and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous Zn^{2+} ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure 19.1.3 but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the *concentrations* of the reacting species and the *temperature* of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the standard cell potentialThe potential of an electrochemical cell measured under standard conditions (1 M for solutions, 1 atm for gases, and pure solids or pure liquids for other substances) and at a fixed temperature (usually 298 K). ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions,Concentrated solutions of salts (about 1 M) generally do not exhibit

ideal behavior, and the actual standard state corresponds to an *activity* of 1 rather than a concentration of 1 M. Corrections for nonideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

Note the Pattern

Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the *difference* between the potentials of two electrodes can be measured. (This is analogous to measuring absolute enthalpies or free energies. Recall from Chapter 18 that only *differences* in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential ($E°$) for the Zn/Cu system is 1.10 V, whereas $E°$ for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V – 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co\,(s)\mid Co^{2+}\,(aq,\ 1M)\parallel Cu^{2+}\,(aq,\ 1M)\mid Cu\,(s)$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of *standard electrode potentials* by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances. (Standard electrode potentials for various reduction reactions are given in Table P1.) The standard cell potential ($E°_{cell}$) is therefore the *difference* between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the *sum* of the two half-reactions. According to Equation 19.2.1, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

Note the Pattern

The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials: $E°_{cell} = E°_{cathode} - E°_{anode}$.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The standard hydrogen electrode (SHE)The electrode chosen as the reference for all other electrodes, which has been assigned a standard potential of 0 V and consists of a Pt wire in contact with an aqueous solution that contains 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface. is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 19.2.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+\,(aq) + 2e^- \rightleftharpoons H_2\,(g)$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

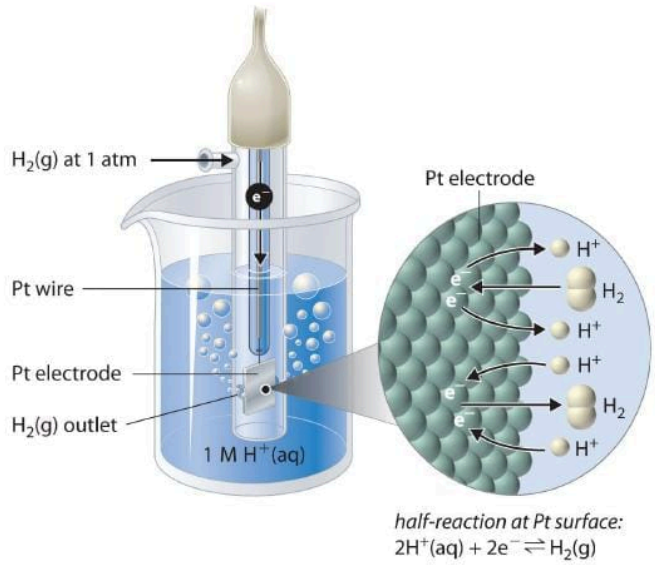


Figure 19.2.2 The Standard Hydrogen Electrode The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Figure 19.2.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn\,(s)\mid Zn^{2+}\,(aq)\parallel H^+\,(aq,\ 1M)\mid H_2\,(g, 1\ atm)\mid Pt\,(s)$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

$$cathode: 2H^+\,(aq,\ 1M) + 2e^- \rightarrow H_2\,(g) \qquad E^o_{cathode} = 0\ \ V$$

$$anode: Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^- \qquad E^o_{anode} = -0.76\ \ V$$

$$overall: Zn\,(s) + 2H^+\,(aq) \rightarrow Zn^{2+}\,(aq) + H_2\,(g)$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.76$$

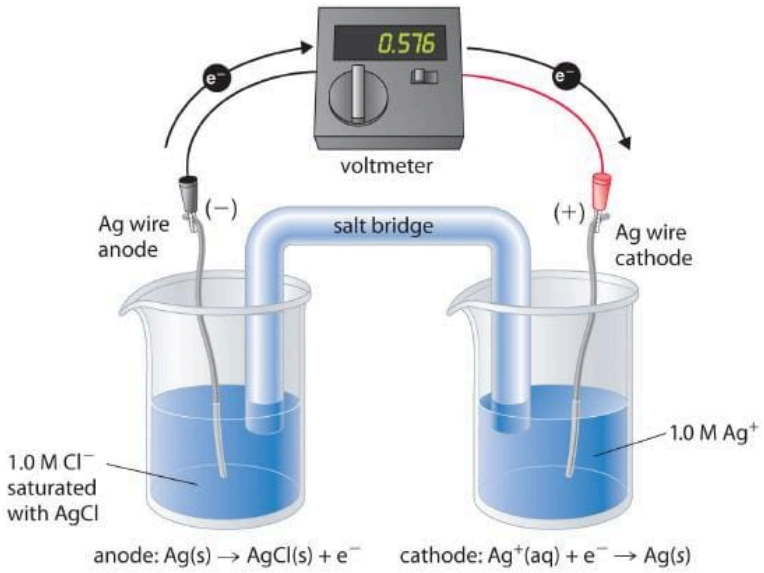


Figure 19.2.3 Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form $Zn^{2+}(aq)$ ions while $H^+(aq)$ ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Although the reaction at the anode is an oxidation, by convention its tabulated $E°$ value is reported as a *reduction* potential. The potential of a half-reaction measured against the SHE under standard conditions is called the standard electrode potentialThe potential of a half-reaction measured against the SHE under standard conditions. for that half-reaction.In this example, the standard reduction potential for $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the *oxidation* of Zn to Zn^{2+}, often called the Zn/Zn^{2+} *redox couple*, or the Zn/Zn^{2+} *couple*, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain $E°_{cell}$: 0 − (−0.76 V) = 0.76 V.

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, *$E°$ values are independent of the stoichiometric coefficients for the half-reaction*, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

Note the Pattern

$E°$ values do not depend on the stoichiometric coefficients for a half-reaction.

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure 19.2.3 but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the *cathode*, and the hydrogen electrode is the *anode*. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt\,(s) \mid H_2\,(g, 1\ atm) \mid H^+\,(aq,\ 1M) \parallel Cu^{2+}\,(aq) \mid Cu\,(s)$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

$$cathode: Cu^{2+}\,(aq) + 2e^- \rightarrow Cu\,(s) \qquad E^o_{cathode} = 0.34\ V$$

$$anode: H_2\,(g) \rightarrow 2H^+\,(aq) + 2e^- \qquad E^o_{anode} = 0\ V$$

$$overall: H_2(g) + Cu^{2+}(aq) \rightarrow Cu(s) + 2H^+(aq)$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.34$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called *voltage*. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s)$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E°_{cell}$:

$$cathode: \quad Cu^{2+}(aq, 1M) + 2e^- \rightarrow Cu(s) \qquad E^o_{cathode} = 0.34 \ V$$

$$anode: \quad Zn(s) \rightarrow Zn^{2+}(aq, 1M) + 2e^- \qquad E^o_{anode} = -0.76 \ V$$

$$overall \quad Zn(s) + Cu^{2+}(aq, 1M) \rightarrow Zn^{2+}(aq, 1M) + Cu(s)$$

$$E_{cell} = E^o_{cathode} - E_{anode} = 1.10 \ V$$

This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction.As we shall see in Section 19.7, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example 4 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

Note the Pattern

A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.

Example 19.2.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

$$cathode: \quad Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$
$$anode: \quad Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the

half-reaction.

B Use Equation 19.2.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution:

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

B Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 19.2.2:

$$\begin{aligned} E_{cell} &= E^o_{cathode} - E_{anode} \\ 0.27\ V &= E^o_{cathode} - (-0.55\ V) \\ E^o_{cathode} &= -0.28\ V \end{aligned}$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the *oxidation* of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus $E° = -(-0.28\ V) = 0.28$ V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are *independent* of stoichiometry.

Exercise

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate [$Hg(CH_3CO_2)_2$] and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

$$\begin{aligned} cathode: &\quad Hg^{2+}(aq) + 2e^- \rightarrow Hg(l) \\ anode: &\quad Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \end{aligned}$$

If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the anode?

Answer: 0.85 V

Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called indicator electrodeThe electrode of a galvanic cell whose potential is related to the concentration of the substance being measured., whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the reference electrodeAn electrode in an galvanic cell whose potential is unaffected by the properties of the solution., must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

Note the Pattern

The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference

electrodes. One is the silver–silver chloride electrodeA reference electrode that consists of a silver wire coated with a very thin layer of AgCl and dipped into a chloride ion solution with a fixed concentration., which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

$$Cl^-\,(aq)\mid AgCl\,(s)\mid Ag\,(s)$$
$$AgCl\,(s)+e^-\rightarrow Ag\,(s)+Cl^-\,(aq)$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the saturated calomel electrode (SCE)A reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; $\mathrm{Hg_2Cl_2}$) and KCl in an interior cell, which is surrounded by an aqueous KCl solution., which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called *calomel* in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure 19.2.5). Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$Pt\,(s)\mid Hg_2Cl_2\,(s)\mid KCl\,(aq,sat)$$
$$Hg_2Cl_2\,(s)+2e^-\rightarrow 2Hg\,(l)+2Cl^-\,(aq)$$

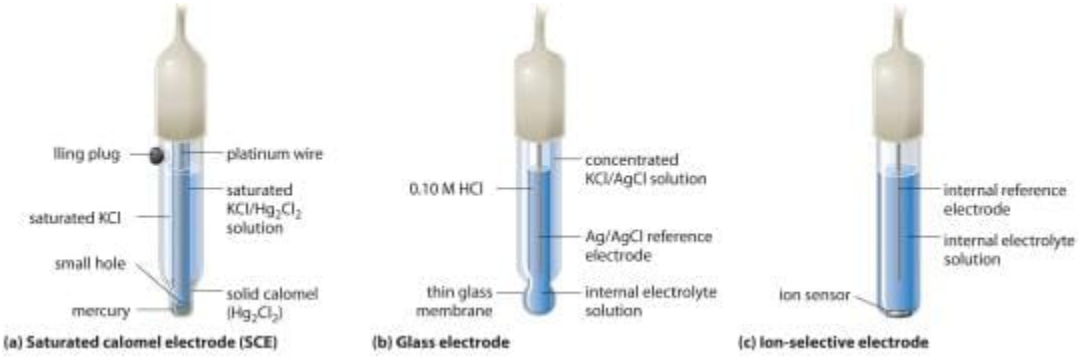


Figure 19.2.5 Three Common Types of Electrodes: (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution.

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A glass electrodeAn electrode used to measure the $\mathrm{H^+}$ ion concentration of a solution and consisting of an internal Ag/AgCl electrode immersed in a 1 M HCl solution that is separated from the solution by a very thin glass membrane. is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure 19.2.5). The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that pH = –log$[H^+]$:

$$E_{glass}=E'+(0.0591\ V\times log\,[H^+])=E'-0.0591\ \ V\times pH$$

The voltage *E*′ is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is *calibrated*; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodesAn electrode whose potential depends on only the concentration of a particular species in solution. are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure 19.2.5). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called *fluoride electrode*. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 19.2.1.

Table 19.2.1 Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the **standard cell potential ($E°_{cell}$)**. Only the *difference* between the potentials of two electrodes can be measured. By convention, all tabulated values of *standard electrode potentials* are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} - E°_{anode}$). The potential of the **standard hydrogen electrode (SHE)** is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its **standard electrode potential**. The standard cell potential is a measure of the driving force for a given redox reaction. All $E°$ values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of $E°$ corresponding to that reaction must also be reversed. If $E°_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E°_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an **indicator electrode** is related to the concentration of the substance being measured, whereas the potential of the **reference electrode** is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the **silver–silver chloride electrode**; the **saturated calomel electrode (SCE)**; the **glass electrode**, which is commonly used to measure pH; and **ion-selective electrodes**, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for $E°$.

Key Takeaways

- Redox reactions can be balanced using the half-reaction method.
- The standard cell potential is a measure of the driving force for the reaction.

Key Equation

Standard cell potential

Equation 19.2.2: $E°_{cell} = E°_{cathode} - E°_{anode}$

Conceptual Problems

1. Is a hydrogen electrode chemically inert? What is the major disadvantage to using a hydrogen electrode?
2. List two factors that affect the measured potential of an electrochemical cell and explain their impact on the measurements.
3. What is the relationship between electron flow and the potential energy of valence electrons? If the valence electrons of substance A have a higher potential energy than those of substance B, what is the direction of electron flow between them in a galvanic cell?
4. If the components of a galvanic cell include aluminum and bromine, what is the predicted direction of electron flow? Why?
5. Write a cell diagram representing a cell that contains the Ni/Ni^{2+} couple in one compartment and the SHE in the other compartment. What are the values of $E°_{cathode}$, $E°_{anode}$, and $E°_{cell}$?
6. Explain why $E°$ values are independent of the stoichiometric coefficients in the corresponding half-reaction.
7. Identify the oxidants and the reductants in each redox reaction.
    1. $Cr(s) + Ni^{2+}(aq) \rightarrow Cr^{2+}(aq) + Ni(s)$
    2. $Cl_2(g) + Sn^{2+}(aq) \rightarrow 2Cl^-(aq) + Sn^{4+}(aq)$
    3. $H_3AsO_4(aq) + 8H^+(aq) + 4Zn(s) \rightarrow AsH_3(g) + 4H_2O(l) + 4Zn^{2+}(aq)$
    4. $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$
8. Identify the oxidants and the reductants in each redox reaction.
    1. $Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$
    2. $Cu^{2+}(aq) + 2Ag(s) \rightarrow Cu(s) + 2Ag^+(aq)$
    3. $H^+(aq) + 2MnO_4^-(aq) + 5H_2SO_3(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5HSO_4^-(aq)$
    4. $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(s) + 3H_2O(l)$
9. All reference electrodes must conform to certain requirements. List the requirements and explain their significance.
10. For each application, describe the reference electrode you would use and explain why. In each case, how would the measured potential compare with the corresponding $E°$?
    1. measuring the potential of a Cl^-/Cl_2 couple
    2. measuring the pH of a solution
    3. measuring the potential of a $MnO_4–/Mn^{2+}$ couple

Answers

1.
2.
3.
4.
5. $Ni\,(s) \mid Ni^{2+}\,(aq) \parallel H^+\,(aq, 1\ M) \mid H_2\,(g, 1\ atm) \mid Pt\,(s)$

E^o_{anode}	$Ni^{2+}\,(aq) + 2e^- \rightarrow Ni\,(s)$	$-0.257\ V$
$E^o_{cathode}$	$2H^+\,(aq) + 2e^- \rightarrow H_2\,(g,)$	$0.000\ V$
E^o_{cell}	$2H^+\,(aq) + Ni\,(s) \rightarrow H_2\,(g,) + Ni^{2+}\,(aq)$	$0.257\ V$

6.
7. 1. oxidant: Ni^{2+}(aq); reductant: Cr(s)
   2. oxidant: Cl_2(g); reductant: Sn^{2+}(aq)
   3. oxidant: H_3AsO_4(aq); reductant: Zn(s)
   4. oxidant: NO_2(g); reductant: NO_2(g)
8.
9.
10.

Numerical Problems

1. Draw the cell diagram for a galvanic cell with an SHE and a copper electrode that carries out this overall reaction:

   H_2(g) + Cu^{2+}(aq) → $2H^+$(aq) + Cu(s).

2. Draw the cell diagram for a galvanic cell with an SHE and a zinc electrode that carries out this overall reaction:

   Zn(s) + $2H^+$(aq) → Zn^{2+}(aq) + H_2(g).

3. Balance each reaction and calculate the standard electrode potential for each. Be sure to include the physical state of each product and reactant.

   1. Cl_2(g) + H_2(g) → $2Cl^-$(aq) + $2H^+$(aq)
   2. Br_2(aq) + Fe^{2+}(aq) → $2Br^-$(aq) + Fe^{3+}(aq)
   3. Fe^{3+}(aq) + Cd(s) → Fe^{2+}(aq) + Cd^{2+}(aq)

4. Balance each reaction and calculate the standard reduction potential for each. Be sure to include the physical state of each product and reactant.

   1. Cu^+(aq) + Ag^+(aq) → Cu^{2+}(aq) + Ag(s)
   2. Sn(s) + Fe^{3+}(aq) → Sn^{2+}(aq) + Fe^{2+}(aq)
   3. Mg(s) + Br_2(l) → $2Br^-$(aq) + Mg^{2+}(aq)

5. Write a balanced chemical equation for each redox reaction.

   1. $H_2PO_2^-$(aq) + SbO_2^-(aq) → HPO_3^{2-}(aq) + Sb(s) in basic solution
   2. HNO_2(aq) + I^-(aq) → NO(g) + I_2(s) in acidic solution
   3. N_2O(g) + ClO^-(aq) → Cl^-(aq) + NO_2^-(aq) in basic solution
   4. Br_2(l) → Br^-(aq) + BrO_3^-(aq) in basic solution
   5. $Cl(CH_2)_2OH$(aq) + $K_2Cr_2O_7$(aq) → $ClCH_2CO_2H$(aq) + Cr^{3+}(aq) in acidic solution

6. Write a balanced chemical equation for each redox reaction.

   1. I^-(aq) + $HClO_2$(aq) → IO_3^-(aq) + Cl_2(g) in acidic solution
   2. Cr^{2+}(aq) + O_2(g) → Cr^{3+}(aq) + H_2O(l) in acidic solution
   3. CrO_2^-(aq) + ClO^-(aq) → CrO_4^{2-}(aq) + Cl^-(aq) in basic solution
   4. S(s) + HNO_2(aq) → H_2SO_3(aq) + N_2O(g) in acidic solution
   5. $F(CH_2)_2OH$(aq) + $K_2Cr_2O_7$(aq) → FCH_2CO_2H(aq) + Cr^{3+}(aq) in acidic solution

7. The standard cell potential for the oxidation of Pb to Pb^{2+} with the concomitant reduction of Cu^{+} to Cu is 0.39 V. You know that $E°$ for the Pb^{2+}/Pb couple is −0.13 V. What is $E°$ for the Cu^{+}/Cu couple?

8. You have built a galvanic cell similar to the one in Figure 19.2.3 using an iron nail, a solution of $FeCl_2$, and an SHE. When the cell is connected, you notice that the iron nail begins to corrode. What else do you observe? Under standard conditions, what is E_{cell}?

9. Carbon is used to reduce iron ore to metallic iron. The overall reaction is as follows:

$$2Fe_2O_3{\cdot}xH_2O(s) + 3C(s) \rightarrow 4Fe(l) + 3CO_2(g) + 2xH_2O(g)$$

   Write the two half-reactions for this overall reaction.

10. Will each reaction occur spontaneously under standard conditions?

    1. $Cu(s) + 2H^{+}(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$
    2. $Zn^{2+}(aq) + Pb(s) \rightarrow Zn(s) + Pb^{2+}(aq)$

11. Each reaction takes place in acidic solution. Balance each reaction and then determine whether it occurs spontaneously as written under standard conditions.

    1. $Se(s) + Br_2(l) \rightarrow H_2SeO_3(aq) + Br^{-}(aq)$
    2. $NO_3^{-}(aq) + S(s) \rightarrow HNO_2(aq) + H_2SO_3(aq)$
    3. $Fe^{3+}(aq) + Cr^{3+}(aq) \rightarrow Fe^{2+}(aq) + Cr_2O_7^{2-}(aq)$

12. Calculate $E°_{cell}$ and $\Delta G°$ for the redox reaction represented by the cell diagram $Pt(s)|Cl_2(g, 1\ atm)||ZnCl_2(aq, 1\ M)|Zn(s)$. Will this reaction occur spontaneously?

13. If you place Zn-coated (galvanized) tacks in a glass and add an aqueous solution of iodine, the brown color of the iodine solution fades to a pale yellow. What has happened? Write the two half-reactions and the overall balanced chemical equation for this reaction. What is $E°_{cell}$?

14. Your lab partner wants to recover solid silver from silver chloride by using a 1.0 M solution of HCl and 1 atm H_2 under standard conditions. Will this plan work?

Answers

1. $Pt(s)|H_2(g, 1\ atm)\ |\ H^{+}(aq, 1M)||Cu^{2+}(aq)|Cu(s)$
2.
3.
    1. $Cl_2(g) + H_2(g) \rightarrow 2Cl^{-}(aq) + 2H^{+}(aq)$; $E° = 1.358$ V
    2. $Br_2(l) + 2Fe^{2+}(aq) \rightarrow 2Br^{-}(aq) + 2Fe^{3+}(aq)$; $E° = 0.316$ V
    3. $2Fe^{3+}(aq) + Cd(s) \rightarrow 2Fe^{2+}(aq) + Cd^{2+}(aq)$; $E° = 1.174$ V
4.
5.
6.
7.
8.
9.
10.
11.
12.
13.
14.

Contributors

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13.6: Comparing Strengths of Oxidants and Reductants

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Rank chemicals by their oxidizing or reducing ability.

We can use the procedure described in Section 19.2 to measure the standard potentials for a wide variety of chemical substances, some of which are listed in Table 19.3.1 (Table P1 contains a more extensive listing.) These data allow us to compare the oxidative and reductive strengths of a variety of substances. The half-reaction for the standard hydrogen electrode (SHE) lies more than halfway down the list in Table 19.3.1 . All reactants that lie *above* the SHE in the table are stronger oxidants than H^+, and all those that lie below the SHE are weaker. The strongest oxidant in the table is F_2, with a standard electrode potential of 2.87 V. This high value is consistent with the high electronegativity of fluorine and tells us that fluorine has a stronger tendency to accept electrons (it is a stronger oxidant) than any other element.

Table 19.3.1 Standard Potentials for Selected Reduction Half-Reactions at 25°C

Half-Reaction	$E°$ (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	1.78
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	1.72
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	1.69
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.22
$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$	1.09
$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow HNO_2(aq) + H_2O(l)$	0.93
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$H_2SeO_3(aq) + 4H^+ + 4e^- \rightarrow Se(s) + 3H_2O(l)$	0.74
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	0.70
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	0.60
$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	0.60
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$H_2SO_3(aq) + 4H^+(aq) + 4e^- \rightarrow S(s) + 3H_2O(l)$	0.45
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	0.40

Half-Reaction	$E°$ (V)
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.22
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.15
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14
$2SO_4^{2-}(aq) + 4H+(aq) + 2e^- \rightarrow S_2O_6^{2-}(aq) + 2H_2O(l)$	−0.22
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.26
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.36
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	−0.40
$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$	−0.41
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.45
$Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}(aq)$	−0.69
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.662
$Be^{2+}(aq) + 2e^- \rightarrow Be(s)$	−1.85
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.04

Similarly, all species in Table 19.3.1 that lie *below* H_2 are stronger reductants than H_2, and those that lie above H_2 are weaker. The strongest reductant in the table is thus metallic lithium, with a standard electrode potential of −3.04 V. This fact might be surprising because cesium, not lithium, is the least electronegative element. The apparent anomaly can be explained by the fact that electrode potentials are measured in aqueous solution, where intermolecular interactions are important, whereas ionization potentials and electron affinities are measured in the gas phase. Due to its small size, the Li^+ ion is stabilized in aqueous solution by strong electrostatic interactions with the negative dipole end of water molecules. These interactions result in a significantly greater $\Delta H_{hydration}$ for Li^+ compared with Cs^+. Lithium metal is therefore the strongest reductant (most easily oxidized) of the alkali metals in aqueous solution.

Note the Pattern

Species in Table 19.3.1 that lie below H_2 are stronger reductants (more easily oxidized) than H_2. Species that lie above H_2 are stronger oxidants.

Because the half-reactions shown in Table 19.3.1 are arranged in order of their $E°$ values, we can use the table to quickly predict the relative strengths of various oxidants and reductants. Any species on the left side of a half-reaction will spontaneously oxidize any species on the right side of another half-reaction that lies *below* it in the table. Conversely, any species on the right side of a half-reaction will spontaneously reduce any species on the left side of another half-reaction that lies *above* it in the table. We can use these generalizations to predict the spontaneity of a wide variety of redox reactions ($E°_{cell} > 0$), as illustrated in Example 5.



Example 19.3.1

The black tarnish that forms on silver objects is primarily Ag_2S. The half-reaction for reversing the tarnishing process is as follows:

$$AgS\,(s)\,2e^- \rightarrow Ag\,(s) + S^{2-}\,(aq) \qquad E^o = -0.69\ V$$

1. Referring to Table 19.3.1 , predict which species—H_2O_2(aq), Zn(s), I^-(aq), Sn^{2+}(aq)—can reduce Ag_2S to Ag under standard conditions.
2. Of these species—H_2O_2(aq), Zn(s), I^-(aq), Sn^{2+}(aq), identify which is the strongest reducing agent in aqueous solution and thus the best candidate for a commercial product.
3. From the data in Table 19.3.1 , suggest an alternative reducing agent that is readily available, inexpensive, and possibly more effective at removing tarnish.

Given: reduction half-reaction, standard electrode potential, and list of possible reductants

Asked for: reductants for Ag_2S, strongest reductant, and potential reducing agent for removing tarnish

Strategy:

A From their positions in Table 19.3.1, decide which species can reduce Ag_2S. Determine which species is the strongest reductant.

B Use Table 19.3.1 to identify a reductant for Ag_2S that is a common household product.

Solution:

We can solve the problem in one of two ways: (1) compare the relative positions of the four possible reductants with that of the Ag_2S/Ag couple in Table 19.3.1 or (2) compare $E°$ for each species with $E°$ for the Ag_2S/Ag couple (−0.69 V).

1. **A** The species in Table 19.3.1 are arranged from top to bottom in order of increasing reducing strength. Of the four species given in the problem, I^-(aq), Sn^{2+}(aq), and H_2O_2(aq) lie above Ag_2S, and one [Zn(s)] lies below it. We can therefore conclude that Zn(s) can reduce Ag_2S(s) under standard conditions, whereas I^-(aq), Sn^{2+}(aq), and H_2O_2(aq) cannot. Sn^{2+}(aq) and H_2O_2(aq) appear twice in the table: on the left side (oxidant) in one half-reaction and on the right side (reductant) in another.
2. The strongest reductant is Zn(s), the species on the right side of the half-reaction that lies closer to the bottom of Table 19.3.1 than the half-reactions involving I^-(aq), Sn^{2+}(aq), and H_2O_2(aq). (Commercial products that use a piece of zinc are often marketed as a “miracle product” for removing tarnish from silver. All that is required is to add warm water and salt for electrical conductivity.)
3. **B** Of the reductants that lie below Zn(s) in Table 19.3.1 , and therefore are stronger reductants, only one is commonly available in household products: Al(s), which is sold as aluminum foil for wrapping foods.

Exercise

Refer to Table 19.3.1 to predict

1. which species—Sn^{4+}(aq), Cl^-(aq), Ag^+(aq), Cr^{3+}(aq), and/or H_2O_2(aq)—can oxidize MnO_2(s) to MNO_4^- under standard

conditions.

2. which species—$Sn^{4+}(aq)$, $Cl^{-}(aq)$, $Ag^{+}(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—is the strongest oxidizing agent in aqueous solution.

Answer

1. $Ag^{+}(aq)$; $H_2O_2(aq)$
2. $H_2O_2(aq)$

Example 19.3.2

Use the data in Table 19.3.1 to determine whether each reaction is likely to occur spontaneously under standard conditions:

1. $Sn(s) + Be^{2+}(aq) \rightarrow Sn^{2+}(aq) + Be(s)$
2. $MnO_2(s) + H_2O_2(aq) + 2H^{+}(aq) \rightarrow O_2(g) + Mn^{2+}(aq) + 2H_2O(l)$

Given: redox reaction and list of standard electrode potentials (Table 19.3.1)

Asked for: reaction spontaneity

Strategy:

A Identify the half-reactions in each equation. Using Table 19.3.1, determine the standard potentials for the half-reactions in the appropriate direction.

B Use Equation 19.2.2 to calculate the standard cell potential for the overall reaction. From this value, determine whether the overall reaction is spontaneous.

Solution:

1. **A** Metallic tin is oxidized to $Sn^{2+}(aq)$, and $Be^{2+}(aq)$ is reduced to elemental beryllium. We can find the standard electrode potentials for the latter (reduction) half-reaction (–1.85 V) and for the former (oxidation) half-reaction (–0.14 V) directly from Table 19.3.1.

   B Adding the two half-reactions gives the overall reaction:

$$\begin{array}{lcc} cathode: & MnO_2\,(s) + 4H^+\,(aq) + 2e^- \rightarrow Mn^{2+}\,(aq) + 2H_2O\,(l) & E^o_{cathode} = 1.22\ V \\ anode: & H_2O_2\,(aq) \rightarrow O_2\,(g) + 2H^+\,(aq) + 2e^- & E^o_{anode} = 1.22\ V \\ overall: & MnO_2\,(s) + 2H^+\,(aq) + H_2O_2\,(aq) \rightarrow & E^o_{cell} = E^o_{cathode} - E^o_{anode} \\ & O_2\,(g) + Mn^{2+}\,(aq) + 2H_2O\,(l) & -0.53\ V \end{array}$$

   The standard cell potential is quite negative, so the reaction will *not* occur spontaneously as written. That is, metallic tin cannot be used to reduce Be^{2+} to beryllium metal under standard conditions. Instead, the reverse process, the reduction of stannous ions (Sn^{2+}) by metallic beryllium, which has a positive value of $E°_{cell}$, will occur spontaneously.

2. **A** MnO_2 is the oxidant (Mn^{4+} is reduced to Mn^{2+}), while H_2O_2 is the reductant (O^{2-} is oxidized to O_2). We can obtain the standard electrode potentials for the reduction and oxidation half-reactions directly from Table 19.2.

   B The two half-reactions and their corresponding potentials are as follows:

$$\begin{array}{lcc} cathode: & MnO_2\,(s) + 4H^+\,(aq) + 2e^- \rightarrow Mn^{2+}\,(aq) + 2H_2O\,(l) & E^o_{cathode} = 1.22\ V \\ anode: & H_2O_2\,(aq) \rightarrow O_2\,(g) + 2H^+\,(aq) + 2e^- & E^o_{anode} = 1.22\ V \\ overall: & MnO_2\,(s) + 2H^+\,(aq) + H_2O_2\,(aq) \rightarrow & E^o_{cell} = E^o_{cathode} - E^o_{anode} \\ & O_2\,(g) + Mn^{2+}\,(aq) + 2H_2O\,(l) & -0.53\ V \end{array}$$

   The standard potential for the reaction is positive, indicating that under standard conditions, it will occur spontaneously as written. Hydrogen peroxide will reduce MnO_2, and oxygen gas will evolve from the solution.

Exercise

Use the data in Table 19.3.2 to determine whether each reaction is likely to occur spontaneously under standard conditions:

1. $2Ce^{4+}(aq) + 2Cl^{-}(aq) \rightarrow 2Ce^{3+}(aq) + Cl_2(g)$
2. $4MnO_2(s) + 3O_2(g) + 4OH^{-}(aq) \rightarrow 4MnO_4^{-}(aq) + 2H_2O$

Answer

1. spontaneous ($E°_{cell}$ = 0.36 V)
2. nonspontaneous ($E°_{cell}$ = −0.20 V)

Although the sign of $E°_{cell}$ tells us whether a particular redox reaction will occur spontaneously under standard conditions, it does not tell us to what *extent* the reaction proceeds, and it does not tell us what will happen under nonstandard conditions. To answer these questions requires a more quantitative understanding of the relationship between electrochemical cell potential and chemical thermodynamics, as described in Section 19.4.

Summary

The oxidative and reductive strengths of a variety of substances can be compared using standard electrode potentials. Apparent anomalies can be explained by the fact that electrode potentials are measured in aqueous solution, which allows for strong intermolecular electrostatic interactions, and not in the gas phase.

Key Takeaway

- The relative strengths of various oxidants and reductants can be predicted using $E°$ values.

Conceptual Problems

1. The order of electrode potentials cannot always be predicted by ionization potentials and electron affinities. Why? Do you expect sodium metal to have a higher or a lower electrode potential than predicted from its ionization potential? What is its approximate electrode potential?

2. Without referring to tabulated data, of Br_2/Br^{-}, Ca^{2+}/Ca, O_2/OH^{-}, and Al^{3+}/Al, which would you expect to have the *least* negative electrode potential and which the *most* negative? Why?

3. Because of the sulfur-containing amino acids present in egg whites, eating eggs with a silver fork will tarnish the fork. As a chemist, you have all kinds of interesting cleaning products in your cabinet, including a 1 M solution of oxalic acid ($H_2C_2O_4$). Would you choose this solution to clean the fork that you have tarnished from eating scrambled eggs?

4. The electrode potential for the reaction $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ is 0.34 V under standard conditions. Is the potential for the oxidation of 0.5 mol of Cu equal to −0.34/2 V? Explain your answer.

Answer

1.
2.

3. No; $E°$ = −0.691 V for $Ag_2S(s) + 2e^{-} \rightarrow Ag(s) + S^{2-}(aq)$, which is too negative for Ag_2S to be spontaneously reduced by oxalic acid [$E°$ = 0.49 V for $2CO_2(g) + 2H^{+}(aq) + 2e^{-} \rightarrow H_2C_2O_4(aq)$]

4.

Contributors

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13.7: Electrochemical Cells and Thermodynamics

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Use appropriate mathematical expressions to convert between ΔG, K, Q, and E_{cell}.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of Co(s) with Ni^{2+}(aq) to form Ni(s) and Co^{2+}(aq) occurs spontaneously, but if we reduce the concentration of Ni^{2+} by a factor of 100, so that [Ni^{2+}] is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential and Free Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in coulombs (C)The SI unit of measure for the number of electrons that pass a given point in 1 second; it is defined as 6.25×10^{18} e^-/s and relates electron potential (in volts) to energy (in joules): 1 J/1 V = 1 C., an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in amperes (A)The fundamental SI unit of electric current; it is defined as the flow of 1 C/s past a given point: 1A = 1 C/s.; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ J}{1\ V} = 1\ \ C = 1\ \ A \cdot s$$

In chemical reactions, however, we need to relate the coulomb to the charge on a *mole* of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the faraday (*F*)The charge on 1 mol of electrons; it is obtained by multiplying the charge on the electron by Avogadro's number., named after the English physicist and chemist Michael Faraday (1791–1867):

$$F = \left(1.60218 \times 10^{-19}\ C\right) \frac{6.02214 \times 10^{23}}{1\ mole}$$

$$F = 9.64855 \times 10^{4}\ \ C/mole \simeq 96,486 C/\left(mol\ e^{-}\right)$$

The total charge transferred from the reductant to the oxidant is therefore *nF*, where *n* is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E_{cell}) and the total charge transferred during the reaction (*nF*):

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done *by* a system (an electrochemical cell with a positive potential) *on* its surroundings.

As you learned in Chapter 18, the change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG, the most important thermodynamic quantity discussed in Chapter 18. This relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a *negative* value of ΔG and a *positive* value of E_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between $\Delta G°$ and $E°_{cell}$ is as follows:

$$\Delta G^o = -nFE^o_{cell}$$

Note the Pattern

A spontaneous redox reaction is characterized by a negative value of $\Delta G°$, which corresponds to a positive value of $E°_{cell}$.

Example 19.4.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table 19.3.1, calculate the free-energy change ($\Delta G°$) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: $\Delta G°$ for the reaction and spontaneity

Strategy:

A From the relevant half-reactions and the corresponding values of $E°$, write the overall reaction and calculate $E°_{cell}$ using Equation 19.2.2.

B Determine the number of electrons transferred in the overall reaction. Then use Equation 19.4.5 to calculate $\Delta G°$. If $\Delta G°$ is negative, then the reaction is spontaneous.

Solution:

A As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of $E°$. From Table 19.3.1, we can find the reduction and oxidation half-reactions and corresponding $E°$ values:

$$\begin{array}{lcl} cathode: & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) & E^o_{cathode} = 1.23\ V \\ anode: & 2Br^-(aq) \rightarrow Br_2(aq) + 2e^- & E^o_{anode} = 1.09\ V \end{array}$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of $E°$ is not affected:

$$\begin{array}{lcl} cathode: & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) & E^o_{cathode} = 1.23\ V \\ anode: & 6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^- & E^o_{anode} = 1.09\ V \\ overall: & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6BrI^- \rightarrow & E^o_{cell} = 0.14\ V \\ & 2Cr^{3+}(aq) + 7H_2O(l) + 3Br_2(aq) & \end{array}$$

B We can now calculate $\Delta G°$ using Equation 19.4.1⓪ Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\Delta G^o = -nFE^o_{cell} = \left(6 \cancel{mol}\right)\left(96,468\ J/\left(\cancel{V}\cdot\cancel{mol}\right)\right)\left(0.14\ \cancel{V}\right)$$
$$-8.1\times10^4\ J$$
$$-81\ kJ/mol\ Cr_2O_7$$

Thus Δ*G*° is –81 kJ for the reaction as written, and the reaction is spontaneous.

Exercise

Use the data in Table 19.3.1 to calculate Δ*G*° for the reduction of ferric ion by iodide:

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$

Is the reaction spontaneous?

Answer: –44 kJ/mol I_2; yes

Potentials for the Sums of Half-Reactions

Although Table 19.3.1 and Table P1 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of $Fe^{3+}(aq)$ to Fe(s) is not listed in the table, but two related reductions are given:

$$Fe^{3+}\,(aq) + e^- \rightarrow Fe^{2+}\,(aq) \qquad E^o = 0.77\ V$$

$$Fe^{2+}\,(aq) + 2e^- \rightarrow Fe\,(aq) \qquad E^o = -0.45\ V$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction *because E° is not a state function*. However, because Δ*G*° is a state function, the sum of the Δ*G*° values for the individual reactions gives us Δ*G*° for the overall reaction, which is proportional to *both* the potential *and* the number of electrons (*n*) transferred. To obtain the value of *E*° for the overall half-reaction, we first must add the values of Δ*G*° (= –*nFE*°) for each individual half-reaction to obtain Δ*G*° for the overall half-reaction:

$$Fe^{3+}\,(aq) + e^- \rightarrow \cancel{Fe^{2+}\,(aq)} \quad \Delta G^o = (-1)\,F\,(0.77\ V) \tag{19.4.8}$$

$$\cancel{Fe^{2+}\,(aq)} + 2e^- \rightarrow Fe\,(s) \quad \Delta G^o = (-2)\,F\,(-0.457\ V)$$

$$Fe^{3+}\,(aq) + e^- \rightarrow Fe\,(s) \quad \Delta G^o = (-1)\,F\,(0.77\ V) + (-2)\,F\,(-0.457\ V)$$

Solving the last expression for Δ*G*° for the overall half-reaction,

$$\Delta G^o = F\,[(-0.77\ V) + (-2)\,(-0.457\ V)] = F\,(0.13\ V)$$

Three electrons (*n* = 3) are transferred in the overall reaction (Equation 19.4.15), so substituting into Equation 19.4.10 and solving for *E*° gives the following:

$$\Delta G^o = -nFE^o_{cell}$$

$$F\,(0.13\ V) = -3FE^o_{cell}$$

$$E^o_{cell} = -\frac{0.13\ V}{3} = -0.043\ V$$

This value of *E*° is *very* different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

Note the Pattern

Values of $E°$ for half-reactions cannot be added to give $E°$ for the sum of the half-reactions; only values of $\Delta G° = -nFE°_{cell}$ for half-reactions can be added.

The Relationship between Cell Potential and the Equilibrium Constant

We can use the relationship between $\Delta G°$ and the equilibrium constant K, defined in Chapter 18, to obtain a relationship between $E°_{cell}$ and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^o = -RTln\ \ K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 19.4.9), we can write

$$-nFE^o_{cell} = -RTln\ \ K$$

Rearranging this equation,

$$E^o_{cell} = \left(\frac{RT}{nF}\right) ln\ \ K$$

For T = 298 K, Equation 19.4.12 can be simplified as follows:

$$E^o_{cell} = \left(\frac{RT}{nF}\right) ln\ \ K = \left[\frac{8.314\ \cancel{J}/\left(\cancel{mol}\cdot\cancel{K}\right)\left(298\ \cancel{K}\right)}{n\left[96,486\ \cancel{J}/\left(V\cdot\cancel{mol}\right)\right]}\right] 2.303\ \ log\ \ K = \left(\frac{0.0591}{n}\right) log\ \ K$$

Thus $E°_{cell}$ is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of $E°_{cell}$ and vice versa.

Example 19.4.2

Use the data in Table 19.3.1 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A Write the relevant half-reactions and potentials. From these, obtain the overall reaction and $E°_{cell}$.

B Determine the number of electrons transferred in the overall reaction. Use Equation 19.4.13 to solve for log K and then K.

Solution:

A The relevant half-reactions and potentials from Table 19.3.1 are as follows:

$$\begin{array}{rcc} cathode: & PbO_2\,(s) + SO_4^{2-}\,(aq) + 4H^+\,(aq) + 2e^- \rightarrow PbSO_4\,(s) + 2H_2O\,(l) & E^o_{cathode} = 1.69\ V \\ anode: & Pb\,(s) + SO_4^{2-}\,(aq) \rightarrow PbSO_4\,(s) + 2e^- & E^o_{anode} = 0.36\ V \\ overall: & Pb\,(s)\,PbO_2\,(s) + 2SO_4^{2-}\,(aq) + 4H^+\,(aq) \rightarrow 2PbSO_4\,(s) + 2H_2O\,(l) & E^o_{cell} = 2.05\ V \end{array}$$

B Two electrons are transferred in the overall reaction, so n = 2. Solving Equation 19.4.13 for log K and inserting the values of n and $E°$,

$$ln\ K = \frac{nE^o}{0.0591\ V} = \frac{2\left(2.05\ \cancel{V}\right)}{0.0591\ \cancel{V}} = 69.37$$

$$K = 2.3 \times 10^{69}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

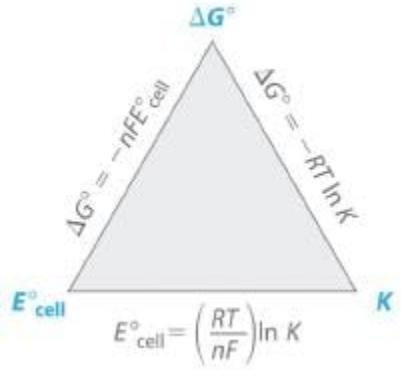
Exercise

Use the data in Table 19.3.1 to calculate the equilibrium constant for the reaction of Sn^{2+}(aq) with oxygen to produce Sn^{4+}(aq) and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2Sn^{2+}\,(aq) + O_2\,(g) + 4H^+\,(aq) \rightleftharpoons 2Sn^{4+}\,(aq) + 2H_2O\,(l)$$

Answer: 1.2×10^{73}

Figure 19.4.1 summarizes the relationships that we have developed based on properties of the *system*—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity ($\Delta G° < 0$). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q developed in Chapter 18 .



$\Delta G°$	$E°_{cell}$	K	Direction of Reaction
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure 19.4.1 The Relationships among Criteria for Thermodynamic **Spontaneity**The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, $\Delta G°$, and $E°_{cell}$. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of $\Delta G°$ and $E°_{cell}$ and the magnitude of K determine the direction of spontaneous reaction under standard conditions.

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall from Chapter 18 that the *actual* free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G^o + RT\ \ ln\ \ Q$$

We also know that $\Delta G = -nFE_{cell}$ and $\Delta G° = -nFE°_{cell}$. Substituting these expressions into Equation 19.4.14, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT\ \ ln\ \ Q$$

Dividing both sides of this equation by $-nF$,

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ \ ln\ \ Q$$

Equation 19.4.16 is called the Nernst equationAn equation for calculating cell potentials E_{cell} under nonstandard conditions; it

can be used to determine the direction of spontaneous reaction for any redox reaction under an conditions:$E_{cell}=E°-(RT/nF)lnQ$, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), Equation 19.4.16 reduces to Equation 19.4.12 because $Q = K$, and there is no net transfer of electrons (i.e., $E_{cell} = 0$).

Substituting the values of the constants into Equation 19.4.16 with T = 298 K and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential ($E°_{cell}$), and the reactant and product concentrations at room temperature (contained in Q):

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{F}\ \ ln\ \ Q$$

Note the Pattern

The Nernst equation can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 19.4.17 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 19.4.17 that the cell potential changes by $0.0591/n$ V for each 10-fold change in the value of Q because log 10 = 1.

Example 19.4.3

In the exercise in Example 6, you determined that the following reaction proceeds spontaneously under standard conditions because $E°_{cell} > 0$ (which you now know means that $\Delta G° < 0$):

$$2Ce^{4+}\,(aq) + 2Cl^{-}\,(aq) \rightarrow 2Ce^{3+}\,(aq) + Cl_2\,(g)$$

Calculate E for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: $[Ce^{4+}]$ = 0.013 M, $[Ce^{3+}]$ = 0.60 M, $[Cl^-]$ = 0.0030 M, Cl_2= 1.0 atm, and T = 25°C.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution:

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 19.4.17 instead of 19.46. The overall reaction involves the net transfer of two electrons:

$2Ce^{4+}(aq) + 2e^- \rightarrow 2Ce^{3+}(aq)$

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl_2, and the value of $E°_{cell}$ into Equation 19.4.17,

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{F}\ \ log\ \ Q$$

$$= 0.25\ V - \frac{0.0591\ V}{2}\ log n\ \left(\frac{\left[Ce^{3+}\right]^2 P_{Cl_2}}{\left[Ce^{4+}\right]^2 \left[Cl^-\right]^2}\right)$$

$$= 0.25\ V - [(0.0296\ V)\ (8.37)] = 0.00\ V$$

Thus the reaction will *not* occur spontaneously under these conditions (because E = 0 V and ΔG = 0). The composition specified is that of an equilibrium mixture.

Exercise

In the exercise in Example 6, you determined that molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4MnO_2\,(s) + 3O_2\,(g) + 4OH^-\,(aq) \rightarrow 4MnO_4^-\,(aq) + 2H_2O\,(l) \;\;\; E_{cell}^{o}=-0.20\;V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, $P(O_2)$ = 0.20 atm, $[MNO_4^-]$ = 1.0 × 10^{-4} M, and T = 25°C.

Answer: E_{cell} = −0.22 V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell discussed in Section 19.2 allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s) \;\;\; E_{cell}^{o}=1.10\;V \tag{19.4.18}$$

The reaction quotient is therefore Q = $[Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0 × 10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 19.4.17:

$$E_{cell} = E_{cell}^{o} - \frac{0.0591\ V}{n}\ log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.10\ V - \frac{0.0591\ V}{2}\ log \frac{1.0 \times 10^{-6}}{1.0} = 1.28\ V$$

Thus the initial voltage is *greater* than $E°$ because Q < 1. As the reaction proceeds, $[Zn^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[Cu^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio Q = $[Zn^{2+}]/[Cu^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[Zn^{2+}] = [Cu^{2+}]$, so Q = 1 and $E_{cell} = E°_{cell}$. Beyond this point, $[Zn^{2+}]$ will continue to increase in the anode compartment, and $[Cu^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0 × 10^{-6} M Cu^{2+}), Q = 1.0 × 10^6, and the cell potential will be reduced to 0.92 V.

The variation of E_{cell} with log Q over this range is linear with a slope of −0.0591/n, as illustrated in Figure 19.4.2. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of Q when E_{cell} = 0 is calculated as follows:

$$E_{cell} = E_{cell}^{o} - \frac{0.0591\ V}{n}\ log\ Q = 0$$

$$E^o = \frac{0.0591\ V}{n}\ log\ Q$$

$$log\ Q) = \frac{E^o\ n}{0.0591\ V} = \frac{\left(1.10\ \cancel{V}\right)(2)}{0.0591\ \cancel{V}} = 37.23$$

$$Q = 10^{37.23} = 1.7 \times 10^{37}$$

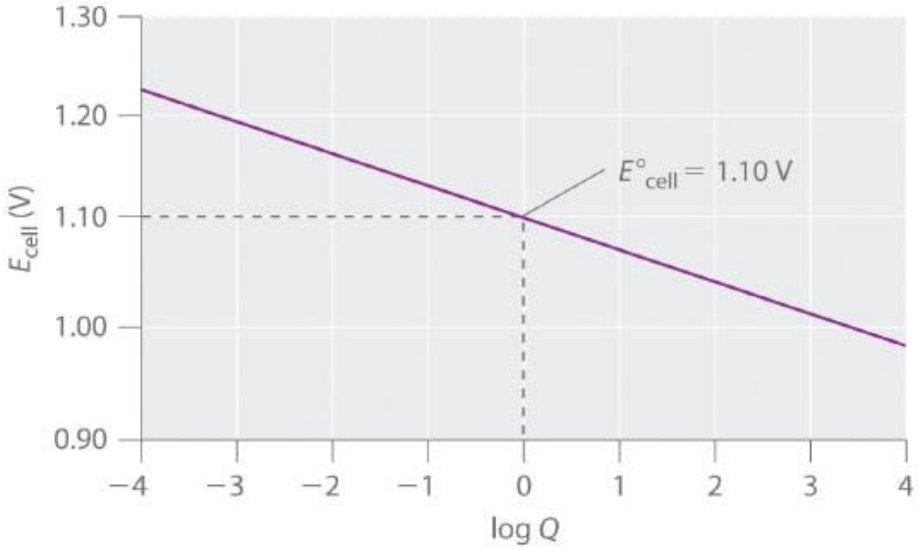


Figure 19.4.2 The Variation of E_{cell} with Log Q for a Zn/Cu **Cell** Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[Zn^{2+}] = [Cu^{2+}]$, log Q = 0 and $E_{cell} = E°_{cell}$ = 1.10 V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until Q = K and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

Recall that at equilibrium, Q = K. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7×10^{37} at 25°C.

Application: Using Cell Potentials to Measure Concentrations

One use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example 11, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated in Example 12.

Example 19.4.6

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment (Figure 19.4.3). The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$Zn(s)|Zn^{2+}(aq, 1.0\ M) \parallel H^+(aq, ?\ M)|H_2(g, 1.0\ atm)|Pt(s)$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A Write the overall cell reaction.

B Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

Solution:

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table 19.3.1):

$$Zn\,(s) + 2H^+\,(aq) \rightarrow Zn^{2+}\,(aq) + H_2\,(g) \qquad E_o = 0.76\ V$$

B By substituting the given values into the simplified Nernst equation (Equation 19.64), we can calculate [H^+] under nonstandard conditions:

\(E_{cell} =E_{cell}^{o}-\dfrac{0.0591\;V}{n}\;log \left (\dfrac{\left [Zn^{2+} \right]P_{H_{2}}}{\left [H^{+} \right]^{2}} \right)

$$0.26\ V = 0.76\ V - \left(\frac{0.0591\ V}{2}\right) log\left(\frac{(1.0)\,(1.0)}{[H^+]^2}\right) = -0.0296\ V\ log\left(\frac{K_{sp}}{1.0}\right)$$

$$16.9 = log\left(\frac{1}{[H^+]^2}\right) = log\,[H^+]^{-2} = -2\ log\,[H^+]$$

$$8.46 = -log\,[H^+]$$

$$8.5 = pH$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows"

Pb(s) $|Pb^{2+}$(aq, ? M)$||H^+$(aq), 1.0 M$|O_2$(g, 1.0 atm)|Pt(s)

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table 19.7.1 and Table T1 to determine the concentration of Pb^{2+} in the groundwater.

Answer: 1.2×10^{-9} M

Summary

A **coulomb (C)** relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in **amperes (A)**, where 1 A is defined as the flow of 1 C/s past a given point. The **faraday (*F*)** is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the Δ*G* values for the half-reactions gives Δ*G* for the overall reaction, which is proportional to *both* the potential *and* the number of electrons (*n*) transferred. Spontaneous redox reactions have a negative Δ*G* and therefore a positive E_{cell}. Because the equilibrium constant *K* is related to Δ*G*, $E°_{cell}$ and *K* are also related. Large equilibrium constants correspond to large positive values of *E*°. The **Nernst equation** allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. **Concentration cells** consist of anode and cathode compartments that are identical except for the concentrations of the reactant. Because Δ*G* = 0 at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

Key Takeaway

- The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution.

Key Equations

Charge on a mole of electrons (faraday)

Equation 19.4.2: $F \approx 96{,}486\ \text{J/(V·mol)}$

Maximum work from an electrochemical cell

Equation 19.4.3: $w_{max} = -nFE_{cell}$

Relationship between Δ *G* ° and Δ *E* °

Equation 19.4.5: $\Delta G° = -nFE°_{cell}$

Relationship between Δ *G* ° and *K* for a redox reaction

Equation 19.4.10: $\Delta G° = -RT \ln K$

Relationship between Δ *E* ° and *K* for a redox reaction at 25°C

Equation 19.4.12: $E^o_{cell} = \left(\frac{RT}{nF}\right) ln\ \ K$

Equation 19.4.13: $E^o_{cell} = \left(\frac{0.0591}{n}\right) log\ \ K$

Relationship between Δ *G* ° and *Q*

Equation 19.4.14: $\Delta G = \Delta G° + RT \ln Q$

Relationship between E_{cell} and *Q* at 25°C

Equation 19.4.17: $E_{cell} = E^o_{cell} - \frac{0.0591\ V}{F}\ \ ln\ \ Q$

Conceptual Problems

1. State whether you agree or disagree with this reasoning and explain your answer: Standard electrode potentials arise from the number of electrons transferred. The greater the number of electrons transferred, the greater the measured potential difference. If 1 mol of a substance produces 0.76 V when 2 mol of electrons are transferred—as in $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$—then 0.5 mol of the substance will produce 0.76/2 V because only 1 mol of electrons is transferred.

2. What is the relationship between the *measured cell potential* and the *total charge* that passes through a cell? Which of these is dependent on concentration? Which is dependent on the identity of the oxidant or the reductant? Which is dependent on the number of electrons transferred?

3. In the equation $w_{max} = -nFE°_{cell}$, which quantities are extensive properties and which are intensive properties?

4. For any spontaneous redox reaction, *E* is positive. Use thermodynamic arguments to explain why this is true.

5. State whether you agree or disagree with this statement and explain your answer: Electrochemical methods are especially useful in determining the reversibility or irreversibility of reactions that take place in a cell.

6. Although the sum of two half-reactions gives another half-reaction, the sum of the potentials of the two half-reactions cannot be used to obtain the potential of the net half-reaction. Why? When does the sum of two half-reactions correspond to the overall reaction? Why?

7. Occasionally, you will find high-quality electronic equipment that has its electronic components plated in gold. What is the advantage of this?

8. Blood analyzers, which measure pH, $P(CO_2)$ and $P(O_2)$ are frequently used in clinical emergencies. For example, blood $P(CO_2)$ is measured with a pH electrode covered with a plastic membrane that is permeable to CO_2. Based on your knowledge of how electrodes function, explain how such an electrode might work. Hint: $CO_2(g) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$.

9. Concentration cells contain the same species in solution in two different compartments. Explain what produces a voltage in a concentration cell. When does V = 0 in such a cell?

10. Describe how an electrochemical cell can be used to measure the solubility of a sparingly soluble salt.

Answers

1.
2.

3. extensive: w_{max} and n; intensive: $E°_{cell}$

4.
5.
6.

7. Gold is highly resistant to corrosion because of its very positive reduction potential.

8.
9.
10.

Numerical Problems

1. The chemical equation for the combustion of butane is as follows:

$$C_4H10\,(g) + \frac{13}{2}O_2\,(g) \rightarrow 2CO_2\,(g) + 5H_2O\,(g)$$

   This reaction has $\Delta H°$ = –2877 kJ/mol. Calculate $E°_{cell}$ and then determine $\Delta G°$. Is this a spontaneous process? What is the change in entropy that accompanies this process at 298 K?

2. How many electrons are transferred during the reaction $Pb(s) + Hg_2Cl_2(s) \rightarrow PbCl_2(aq) + 2Hg(l)$? What is the standard cell potential? Is the oxidation of Pb by Hg_2Cl_2 spontaneous? Calculate $\Delta G°$ for this reaction.

3. For the cell represented as $Al(s)|Al^{3+}(aq)||Sn^{2+}(aq), Sn^{4+}(aq)|Pt(s)$, how many electrons are transferred in the redox reaction? What is the standard cell potential? Is this a spontaneous process? What is $\Delta G°$?

4. Explain why the sum of the potentials for the half-reactions $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ and $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ does not equal the potential for the reaction $Sn^{4+}(aq) + 4e^- \rightarrow Sn(s)$. What is the net cell potential? Compare the values of $\Delta G°$ for the sum of the potentials and the actual net cell potential.

5. Based on Table 19.3.1 and Table P1, do you agree with the proposed potentials for the following half-reactions? Why or why not?

   1. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, $E°$ = 0.68 V
   2. $Ce^{4+}(aq) + 4e^- \rightarrow Ce(s)$, $E°$ = –0.62 V

6. For each reaction, calculate $E°_{cell}$ and then determine $\Delta G°$. Indicate whether each reaction is spontaneous.

   1. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
   2. $K_2S_2O_6(aq) + I_2(s) \rightarrow 2KI(aq) + 2K_2SO_4(aq)$
   3. $Sn(s) + CuSO_4(aq) \rightarrow Cu(s) + SnSO_4(aq)$

7. What is the standard change in free energy for the reaction between Ca^{2+} and Na(s) to give Ca(s) and Na^{+}? Do the sign and magnitude of $\Delta G°$ agree with what you would expect based on the positions of these elements in the periodic table? Why or why not?

8. In acidic solution, permanganate (MnO_4^-) oxidizes Cl^- to chlorine gas, and MnO_4^- is reduced to $Mn^{2+}(aq)$.

    1. Write the balanced chemical equation for this reaction.
    2. Determine $E°_{cell}$.
    3. Calculate the equilibrium constant.

9. Potentiometric titrations are an efficient method for determining the endpoint of a redox titration. In such a titration, the potential of the solution is monitored as measured volumes of an oxidant or a reductant are added. Data for a typical titration, the potentiometric titration of Fe(II) with a 0.1 M solution of Ce(IV), are given in the following table. The starting potential has been arbitrarily set equal to zero because it is the *change* in potential with the addition of the oxidant that is important.

Titrant (mL)	*E* (mV)
2.00	50
6.00	100
9.00	255
10.00	960
11.00	1325
12.00	1625
14.00	1875

    1. Write the balanced chemical equation for the oxidation of Fe^{2+} by Ce^{4+}.
    2. Plot the data and then locate the endpoint.
    3. How many millimoles of Fe^{2+} did the solution being titrated originally contain?

10. The standard electrode potential ($E°$) for the half-reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ is −0.257 V. What pH is needed for this reaction to take place in the presence of 1.00 atm $H_2(g)$ as the reductant if $[Ni^{2+}]$ is 1.00 M?

11. The reduction of Mn(VII) to Mn(s) by $H_2(g)$ proceeds in five steps that can be readily followed by changes in the color of the solution. Here is the redox chemistry:

    1. $MnO_4^-(aq) + e^- \rightarrow MnO_4^{2-}(aq)$; $E° = +0.56$ V (purple → dark green)
    2. $MnO_4^{2-}(aq) + 2e^- + 4H^+(aq) \rightarrow MnO_2(s)$; $E° = +2.26$ V (dark green → dark brown solid)
    3. $MnO_2(s) + e^- + 4H^+(aq) \rightarrow Mn^{3+}(aq)$; $E° = +0.95$ V (dark brown solid → red-violet)
    4. $Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; $E° = +1.51$ V (red-violet → pale pink)
    5. $Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$; $E° = -1.18$ V (pale pink → colorless)
    1. Is the reduction of MnO_4^- to $Mn^{3+}(aq)$ by $H_2(g)$ spontaneous under standard conditions? What is $E°_{cell}$?
    2. Is the reduction of $Mn^{3+}(aq)$ to Mn(s) by $H_2(g)$ spontaneous under standard conditions? What is $E°_{cell}$?

12. Mn(III) can disproportionate (both oxidize and reduce itself) by means of the following half-reactions:

    $Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; $E° = +1.51$ V

    $Mn^{3+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 4H^+(aq) + e^-$; $E° = +0.95$ V

    1. What is $E°$ for the disproportionation reaction?
    2. Is disproportionation more or less thermodynamically favored at low pH than at pH 7.0? Explain your answer.
    3. How could you prevent the disproportionation reaction from occurring?

13. For the reduction of oxygen to water, $E°$ = 1.23 V. What is the potential for this half-reaction at pH 7.00? What is the potential in a 0.85 M solution of NaOH?

14. The biological molecule abbreviated as NADH (reduced nicotinamide adenine dinucleotide) can be formed by reduction of NAD^+ (nicotinamide adenine dinucleotide) via the half-reaction $NAD^+ + H^+ + 2e^- \rightarrow NADH$; $E° = -0.32$ V.

    1. Would NADH be able to reduce acetate to pyruvate?
    2. Would NADH be able to reduce pyruvate to lactate?
    3. What potential is needed to convert acetate to lactate?

    acetate + CO_2 + $2H^+$ + $2e^- \rightarrow$ pyruvate + H_2O; $E° = +0.70$ V

    pyruvare + $2H^+$ + $2e^- \rightarrow$ lactate; $E° = -0.185$ V

15. Given the following biologically relevant half-reactions, will FAD (flavin adenine dinucleotide), a molecule used to transfer electrons whose reduced form is $FADH_2$, be an effective oxidant for the conversion of acetaldehyde to acetate at pH 4.00?

    acetate + $2H^+$ + $2e^- \rightarrow$ acetaldehyde + H_2O; $E° = -0.58$ V

    FAD + $2H^+$ + $2e^- \rightarrow$ $FADH_2$; $E° = -0.18$ V

16. Ideally, any half-reaction with $E° > 1.23$ V will oxidize water as a result of the half-reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.

    1. Will FeO_4^{2-} oxidize water if the half-reaction for the reduction of Fe(VI) → Fe(III) is $FeO_4^{2-}(aq) + 8H^+(aq) + 3e^- \rightarrow Fe^{3+}(aq) + 4H_2O$; $E° = 1.9$ V?
    2. What is the highest pH at which this reaction will proceed spontaneously if $[Fe^{3+}] = [FeO_4^{2-}] = 1.0$ M and $P_{O_2} = 1.0$ atm?

17. Under acidic conditions, ideally any half-reaction with $E° > 1.23$ V will oxidize water via the reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.

    1. Will aqueous acidic $KMnO_4$ evolve oxygen with the formation of MnO_2?
    2. At pH 14.00, what is $E°$ for the oxidation of water by aqueous $KMnO_4$ (1 M) with the formation of MnO_2?
    3. At pH 14.00, will water be oxidized if you are trying to form MnO_2 from MnO_4^{2-} via the reactio $2MnO_4^{2-}(aq) + 2H_2O(l) \rightarrow 2MnO_2(s) + O_2(g) + 4OH^-(aq)$?

18. Complexing agents can bind to metals and result in the net stabilization of the complexed species. What is the net thermodynamic stabilization energy that results from using CN^- as a complexing agent for Mn^{3+}/Mn^{2+}?

    $Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; $E° = +1.51$ V

    $Mn(CN)_6^{3-}(aq) + e^- \rightarrow Mn(CN)_6^{4-}(aq)$; $E° = -0.24$V

19. You have constructed a cell with zinc and lead amalgam electrodes described by the cell diagram $Zn(Hg)(s)|Zn(NO_3)_2(aq)||Pb(NO_3)_2(aq)|Pb(Hg)(s)$. If you vary the concentration of $Zn(NO_3)_2$ and measure the potential at different concentrations, you obtain the following data:

$Zn(NO_3)_2$ (M)	E_{cell} (V)
0.0005	0.7398
0.002	0.7221
0.01	0.7014

    1. Write the half-reactions that occur in this cell.
    2. What is the overall redox reaction?

3. What is $E°_{cell}$? What is $\Delta G°$ for the overall reaction?
4. What is the equilibrium constant for this redox reaction?

20. Hydrogen gas reduces Ni^{2+} according to the following reaction: $Ni^{2+}(aq) + H_2(g) \rightarrow Ni(s) + 2H^+(aq)$; $E°_{cell} = -0.25$ V; $\Delta H = 54$ kJ/mol.

    1. What is K for this redox reaction?
    2. Is this reaction likely to occur?
    3. What conditions can be changed to increase the likelihood that the reaction will occur as written?
    4. Is the reaction more likely to occur at higher or lower pH?

21. The silver–silver bromide electrode has a standard potential of 0.07133 V. What is K_{sp} of AgBr?

Answers

1.
2.

3. $6e^-$; $E°_{cell} = 1.813$ V; the reaction is spontaneous; $\Delta G° = -525$ kJ/mol Al.

4.
5.
6.
7.
8.
9.
10.
11.
12.
13.
14.

15. yes; $E° = 0.40$ V

16.
17.
    1. yes; $E° = 0.45$ V
    2. 0.194 V
    3. yes; $E° = 0.20$ V

18.
19.
20.
21.

Contributors

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Modified by Joshua B. Halpern

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13.8: Electrolysis

Learning Objectives

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called electrolysisAn electrochemical process in which an external voltage is applied to an electrolytic cell to drive a nonspontaneous reaction., occurs: an external voltage is applied to drive a nonspontaneous reaction (Figure 19.1.1). In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Note the Pattern

In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a 1 M Cd^{2+} solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (part (a) in Figure 19.7.19). The overall reaction is as follows:

$$Cd\,(s) + Cu^{2+}\,(aq) \rightarrow Cu\,(s) + Cd^{2+}\,(aq)$$

This reaction is thermodynamically spntaneous as written (

$$\Delta G^o = nFE^o_{cell} = \left(2\ \cancel{mol\ e^-}\right)\left[96,486\ J/\left(\cancel{V}\cdot\cancel{mol}\right)\right]\left(0.74\ \cancel{V}\right) = -140\ \ kJ/mol$$

In this direction, the system is acting as a galvanic cell.

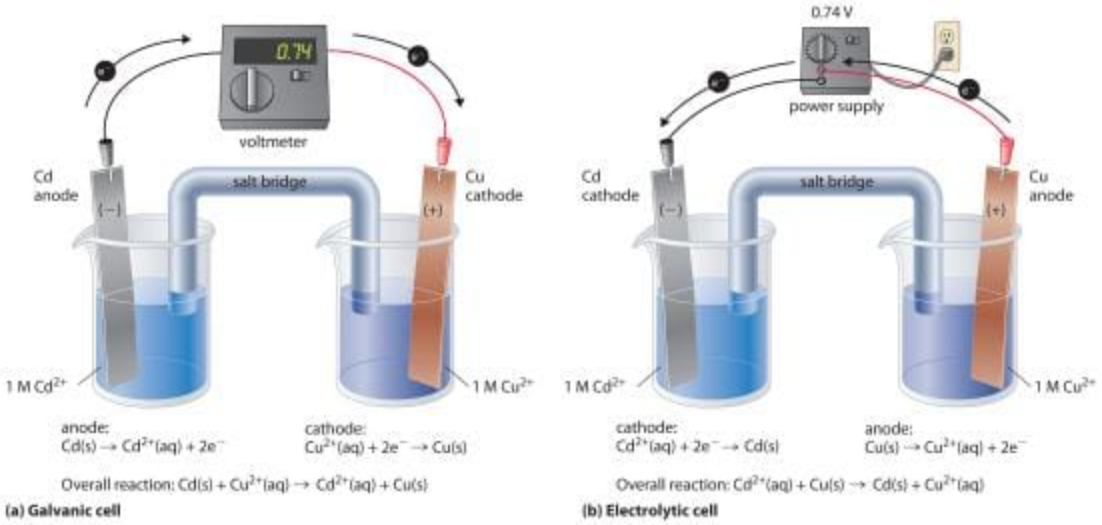


Figure 19.7.1 An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is *positive* because electrons are flowing from it, whereas the cathode is *negative* because electrons are flowing into it.

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an *input* of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (part (b) in Figure 19.21). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

$$cathode: \quad Cd^{2+}(aq) + 2e^- \rightarrow Cd(s) \qquad E^o_{cathode} = -0.40 \ V$$

$$anode: \quad Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \qquad E^o_{anode} = 0.34 \ V$$

$$overall: \quad Cd^{2+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + Cd(s) \qquad E^o_{cell} = -0.74 \ V$$

Because $E°_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly cannot occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table 19.7.1.

Table 19.7.1 Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten NaCl, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

$$2NaCl\,(l) \rightarrow Na\,(l) + Cl_2\,(g)$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is *liquid* sodium because the melting point of sodium metal is 97.8°C, well below that of NaCl (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten NaCl in a *Downs cell* (Figure 19.7.2). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the NaCl to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

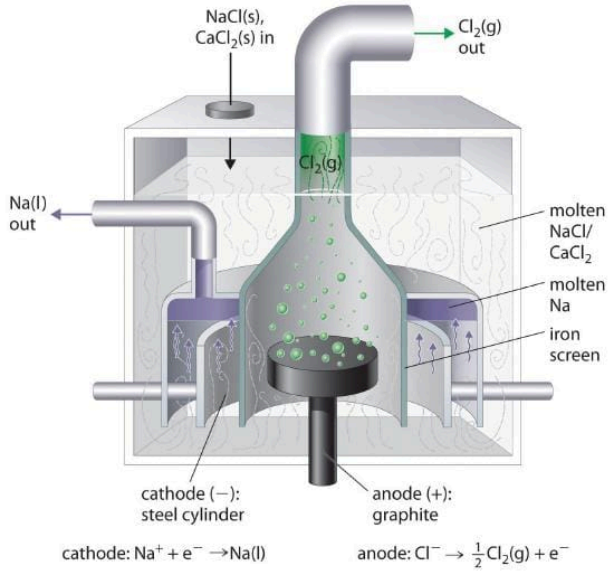


Figure 19.7.2 A Downs Cell for the Electrolysis of Molten NaCl The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact.

Similarly, in the *Hall–Heroult process* used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2Al_2O_3\,(l) + 3C\,(s) \rightarrow 4Al\,(l) + 3CO_2\,(g)$$

Oxide ions react with oxidized carbon at the anode, producing CO_2(g).

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table 19.3.1 and Table P1, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

Example 19.7.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 3.3.9, determine which species will be reduced and which species will be oxidized.

B Identify the products that will form at each electrode.

Solution:

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

Exercise

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

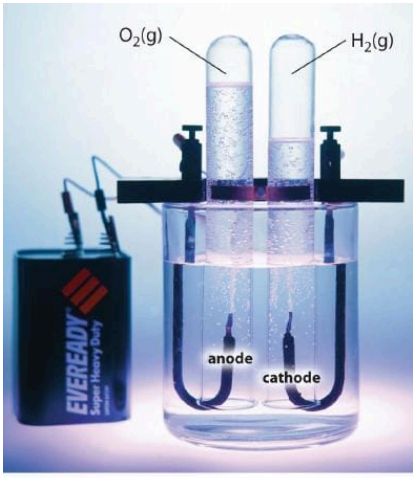
Answer: Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 19.7.3). The reactions that occur are as follows:

$$cathode: \quad 2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^o_{cathode} = 0 \ V$$

$$anode: \quad 2H_2O(l) \rightarrow O_2(g) + 4H^+(g) + 4e^- \qquad E^o_{anode} = 1.23 \ V$$

$$overall: \quad 2H_2O(l) \rightarrow O_2(g) + 2H_2(g) \qquad E^o_{cell} = -1.23 \ V$$



anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

overall: $2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$

Figure 19.7.3 The Electrolysis of Water Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode.

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P(O_2) = P(H_2) = 1$ atm, we can use the standard potentials and Equation 19.4.17 to calculate E for the overall reaction:

$$E_{cell} = E^o_{cell} - \left(\frac{0.0591\ V}{n}\right) log\ \ (P_{O_2} P^2_{H_2})$$

$$E_{cell} = -1.23\ \ V - \left(\frac{0.0591\ V}{4}\right) log\ \ (1) = -1.23\ \ V$$

Thus E_{cell} is –1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an overvoltageThe voltage that must be applied in electrolysis in addition to the calculated (theoretical) value to overcome factors such as a high activation energy and the formation of bubbles on a surface., represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does *not* react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The *p*-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

Note the Pattern

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.

Electroplating

In a process called electroplatingA process in which a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis., a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 19.7.4.

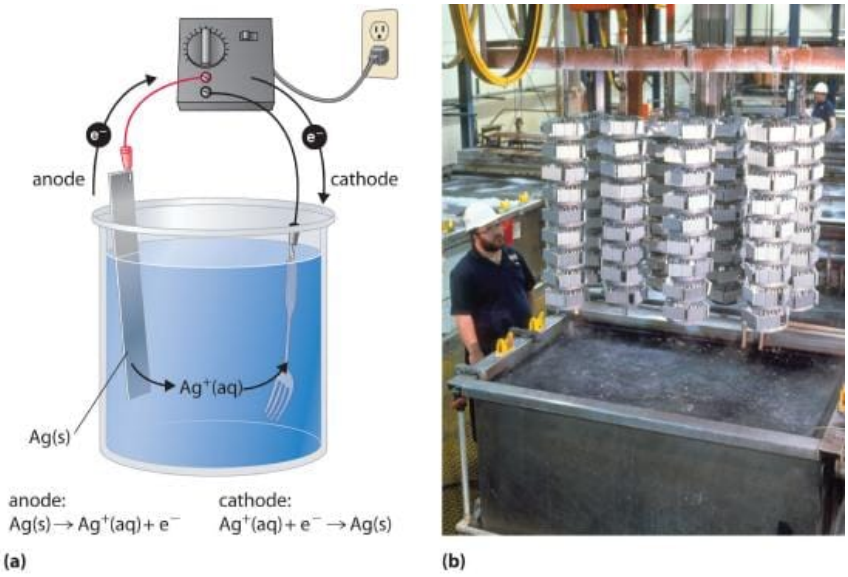


Figure 19.7.4 Electroplating (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag^+ solution and applying the correct potential.

The half-reactions in electroplating a fork, for example, with silver are as follows:

$$cathode\,(fork):\quad Ag^+\,(aq) + e^- \rightarrow Ag\,(s) \qquad E^o_{cathode} = 0.80\ V$$

$$anode\,(silverbar):\quad Ag\,(s) \rightarrow Ag^+\,(aq) + e^- \qquad E^o_{anode} = 0.80\ V$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E°_{cell}$ = 0 V, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction $Ag^+(aq) + e^- \rightarrow Ag(s)$, 1 mol of electrons reduces 1 mol of Ag^+ to Ag metal. In contrast, in the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, 1 mol of electrons reduces only 0.5 mol of Cu^{2+} to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 *F*), which is equal to 96,486 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given

period of time. The total charge (C) transferred is the product of the current (A) and the time (*t*, in seconds):

$$C = A \times t$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $CuSO_4$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$charge = (0.60\ A)\left(6.0\ \cancel{min}\right)\left(60\ s/\cancel{min}\right) = 220 A \cdot s$$

The number of moles of electrons transferred to Cu^{2+} is therefore

$$moles\ \ e^- = \frac{220\ \cancel{C}}{96,486\ \cancel{C}/mol} = 2.3 \times 10^{-3}\ \ mol\ \ e^-$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 *F*/s, and reaction times are on the order of 3–4 weeks.

Example 19.7.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A Calculate the number of moles of metal corresponding to the given mass transferred.

B Write the reaction and determine the number of moles of electrons required for the electroplating process.

C Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution:

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$moles\ \ Ag = \frac{2.0\ \cancel{g}}{107.868\ \cancel{g}/mol} = 1.85 \times 10^{-2}\ \ mol\ \ Ag$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$Coulombs = \left(1.85 \times 10^{-2}\ \cancel{mol}\right)\left(96,486\ C/\cancel{mol}\right) = 1.78 \times 10^3\ \ C$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$amperes = \frac{1.78 \times 10^3\ C}{\left(12.0\ \cancel{h}\right)\left(60\ \cancel{min}/\cancel{h}\right)\left(60\ s/\cancel{min}\right)}$$

$$= 4.12 \times 10^{-2}\ \ C/s = 4.12 \times 10^{-2}\ \ A$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

Exercise

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer: 5.8 h

Summary

In **electrolysis**, an external voltage is applied to drive a nonspontaneous reaction. A Downs cell is used to produce sodium metal from a mixture of salts, and the Hall–Heroult process is used to produce aluminum commercially. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an **overvoltage**, must be applied to overcome factors such as a large activation energy and a junction potential. **Electroplating** is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

Key Takeaways

- In electrolysis, an external voltage is applied to drive a nonspontaneous reaction.
- The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred.

Key Equation

Relationship of charge, current and time

Equation 19.116: $C = A \times t$

Conceptual Problems

1. Why might an electrochemical reaction that is thermodynamically favored require an overvoltage to occur?
2. How could you use an electrolytic cell to make quantitative comparisons of the strengths of various oxidants and reductants?
3. Why are mixtures of molten salts, rather than a pure salt, generally used during electrolysis?
4. Two solutions, one containing $Fe(NO_3)_2{\cdot}6H_2O$ and the other containing the same molar concentration of $Fe(NO_3)_3{\cdot}6H_2O$, were electrolyzed under identical conditions. Which solution produced the most metal? Justify your answer.

Numerical Problems

1. The electrolysis of molten salts is frequently used in industry to obtain pure metals. How many grams of metal are deposited from these salts for each mole of electrons?
    1. $AlCl_3$
    2. $MgCl_2$
    3. $FeCl_3$
2. Electrolysis is the most direct way of recovering a metal from its ores. However, the $Na^+(aq)/Na(s)$, $Mg^{2+}(aq)/Mg(s)$, and $Al^{3+}(aq)/Al(s)$ couples all have standard electrode potentials ($E°$) more negative than the reduction potential of water at pH 7.0 (−0.42 V), indicating that these metals can never be obtained by electrolysis of aqueous solutions of their salts. Why?

What reaction would occur instead?

3. What volume of chlorine gas at standard temperature and pressure is evolved when a solution of $MgCl_2$ is electrolyzed using a current of 12.4 A for 1.0 h?
4. What mass of copper metal is deposited if a 5.12 A current is passed through a $Cu(NO_3)_2$ solution for 1.5 h.
5. What mass of PbO_2 is reduced when a current of 5.0 A is withdrawn over a period of 2.0 h from a lead storage battery?
6. Electrolysis of $Cr^{3+}(aq)$ produces $Cr^{2+}(aq)$. If you had 500 mL of a 0.15 M solution of $Cr^{3+}(aq)$, how long would it take to reduce the Cr^{3+} to Cr^{2+} using a 0.158 A current?
7. Predict the products obtained at each electrode when aqueous solutions of the following are electrolyzed.
    1. $AgNO_3$
    2. RbI
8. Predict the products obtained at each electrode when aqueous solutions of the following are electrolyzed.
    1. $MgBr_2$
    2. $Hg(CH_3CO_2)_2$
    3. $Al_2(SO_4)_3$

Answers

1.
2.
3. 5.2 L
4.
5.
6.
7. 1. cathode: Ag(s); anode: $O_2(g)$;
    2. cathode: $H_2(g)$; anode: $I_2(s)$
8.

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14: ATOMIC NUCLEI CAN CHANGE

14.1: Overview and Objectives
14.2: The Components of the Nucleus
14.3: Nuclear Reactions
14.4: Kinetics of Radioactive Decay

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14.1: Overview and Objectives

> "The energy produced by the breaking down of the atom is a very poor kind of thing. Anyone who looks for a source of power in the transformation of the atoms is talking moonshine." (Ernest Rutherford)

Rutherford may have done seminal experiments to help elucidate the structure of the atom, but he was dead wrong here. As it turns out, the energy associated with changes in the *strong forces* that hold together subatomic particles is so massive that humanity has used it for weapons of mass destruction. In this chapter, we'll look at the principles of nuclear decay.

Chapter Objectives

- Identify factors that affect nuclear stability.
- Predict the products and write balanced reactions for nuclear decay reactions.
- Calculate kinetic parameters for decay processes, including half-life

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14.2: The Components of the Nucleus

Learning Objectives

By the end of this section, you will have information that will help you to be able to:

- Identify factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or *decay*, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that were the main focus of earlier chapters and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

The Atomic Nucleus

As you learned previously, each element can be represented by the notation http://www.w3.org/1999/xlink">empty mmultiscripts XZA, where *A*, the mass number, is the sum of the number of protons and the number of neutrons, and *Z*, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are called nucleonsThe protons and neutrons that make up the nucleus of an atom., and an atom with a particular number of protons and neutrons is called a nuclideAn atom with a particular number of nucleons.. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

$$\begin{matrix}
_{Z}^{A}X: & _{8}^{16}O & _{8}^{17}O & _{8}^{18}O\\
^{A}X: & ^{16}O &^{17}O & ^{18}O\\
\text{element -A} & \text{oxygen-16} & \text{oxygen-17} & \text{oxygen-18}
\end{matrix} \notag$$

Because the number of neutrons is equal to $A - Z$, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17.

Any nucleus that is unstable and decays spontaneously is said to be radioactiveAny nucleus that is unstable and decays spontaneously, emitting particles and electromagnetic radiation., emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called radioisotopesAn isotope that emits radiation. As you learned in Chapter 14, the rate at which radioactive decay occurs is characteristic of the isotope and is generally reported as a **half-life** ($t_{1/2}$), the amount of time required for half of the initial number of nuclei present to decay in a first-order reaction. (For more information on half-life, see Section 14.5.) An isotope's half-life can range from fractions of a second to billions of years and, among other applications, can be used to measure the age of ancient objects. Example 1 and its corresponding exercise review the calculations involving radioactive decay rates and half-lives.

Example 24.1.1

Fort Rock Cave in Oregon is the site where archaeologists discovered several Indian sandals, the oldest ever found in Oregon. Analysis of the ^{14}C content of the sagebrush used to make the sandals gave an average decay rate of 5.1 disintegrations per minute (dpm) per gram of carbon. The current $^{14}C/^{12}C$ ratio in living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g C. How long ago was the sagebrush in the sandals cut? The half-life of ^{14}C is 5730 yr.

Given: radioisotope, current $^{14}C/^{12}C$ ratio, initial decay rate, final decay rate, and half-life

Asked for: age

Strategy:

A Use Equation 14.5.5 to calculate N_0/N, the ratio of the number of atoms of ^{14}C originally present in the sample to the number of atoms now present.

B Substitute the value for the half-life of ^{14}C into Equation 14.5.3 to obtain the rate constant for the reaction.

C Substitute the calculated values for N_0/N and the rate constant into Equation 14.5.7 to obtain the elapsed time t.

Solution:

We can use the integrated rate law for a first-order nuclear reaction (Equation 14.5.7 to calculate the amount of time that has passed since the sagebrush was cut to make the sandals:

$$\ln \dfrac{N}{N_{o}}=-kt$$

A From Equation 14.5.5, we know that $A = kN$. We can therefore use the initial and final activities (A_0 = 15 and A = 5.1) to calculate N_0/N:

$$\dfrac{A_{o}}{A}=\dfrac{kN_{o}}{kN}=\dfrac{N_{o}}{N}=dfrac{1.5}{5.1}$$

B Now we can calculate the rate constant k from the half-life of the reaction (5730 yr) using Equation 14.5.3:

$$t_{1/2}=\dfrac{0.693}{k}$$

Rearranging this equation to solve for k,

$$k =\dfrac{0.693}{t_{1/2}}=\dfrac{0.693}{5730 \; yr}=1.21\times 10^{-4} \; yr^{-1}$$

C Substituting the calculated values into the equation for t,

$$t =\dfrac{\ln\left (N/N_{o} \right)}{k}=\dfrac{\ln\left (15/5.1 \right)}{1.21\times 10^{-4} \; yr^{-1}} = 8900 \; yr$$

Thus the sagebrush in the sandals is about 8900 yr old.

Exercise

While trying to find a suitable way to protect his own burial chamber, the ancient Egyptian pharaoh Sneferu developed the pyramid, a burial structure that protected desert graves from thieves and exposure to wind. Analysis of the ^{14}C content of several items in pyramids built during his reign gave an average decay rate of 8.6 dpm/g C. When were the objects in the chamber created?

Answer: about 4600 yr ago, or about 2600 BC

Nuclear Stability

The nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the strong nuclear forceAn extremely powerful but very short-range attractive force between nucleons that keeps the nucleus of an atom from flying apart (due to electrostatic repulsions between protons)., an extremely powerful but very short-range attractive force between nucleons (Figure 24.1.1). All stable nuclei except the hydrogen-1 nucleus (^1H) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

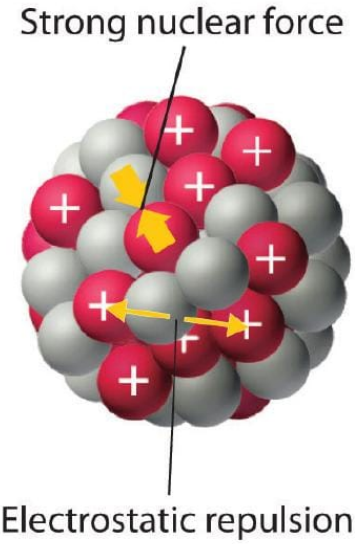


Figure 24.1.1 Competing Interactions within the Atomic **Nucleus** Eectrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure 24.1.2. The stable isotopes form a “peninsula of stability” in a “sea of instability.” Only two stable isotopes, ^{1}H and ^{3}He, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., ^{4}He, ^{10}B, ^{40}Ca. All other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with $Z > 83$ are unstable and radioactive.

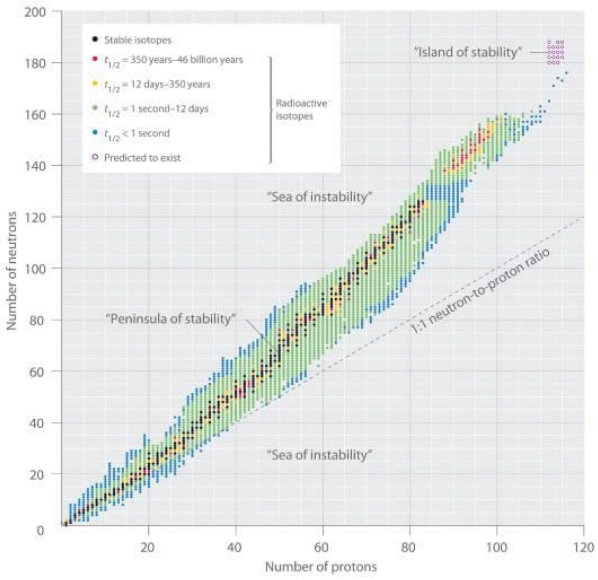


Figure 24.1.2 The Relationship between Nuclear Stability and the Neutron-to-Proton **Ratio** In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized.

Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart

of Nuclides, http://www.nndc.bnl.gov/chart.

As shown in Figure 24.1.3, more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in especially stable nuclei; these are the so-called *magic numbers* 2, 8, 20, 50, 82, and 126. For example, tin (Z = 50) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium (Z = 49) and antimony (Z = 51), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be "doubly magic" and are even more stable. Examples of elements with doubly magic nuclei are ^{4}He with 2 protons and 2 neutrons, and ^{208}Pb with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

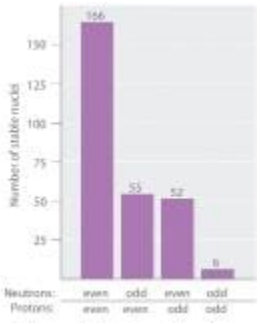


Figure 24.1.3 The Relationship between the Number of Protons and the Number of Neutrons and Nuclear **Stability** Most stable nuclei contain even numbers of both neutrons and protons.

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure 24.1.2, the "peninsula" of stable isotopes is surrounded by a "reef" of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

Example 24.1.2

Classify each nuclide as stable or radioactive.

1. \(_{15}^{30}P \)
2. \(_{43}^{98}Tc \)
3. tin-118
4. \(_{94}^{239}Pu \)

Given: mass number and atomic number

Asked for: predicted nuclear stability

Strategy:

Use the number of protons, the neutron-to-proton ratio, and the presence of even or odd numbers of neutrons and protons to predict the stability or radioactivity of each nuclide.

Solution:

1. This isotope of phosphorus has 15 neutrons and 15 protons, giving a neutron-to-proton ratio of 1.0. Although the atomic number, 15, is much less than the value of 83 above which all nuclides are unstable, the neutron-to-proton ratio is less than that expected for stability for an element with this mass. As shown in Figure 24.1.2, its neutron-to-proton ratio should be greater than 1. Moreover, this isotope has an odd number of both neutrons and protons, which also tends to make a nuclide unstable. Consequently, \(_{15}^{30}P \) is predicted to be radioactive, and it is.
2. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which places \(_{43}^{98}Tc \) near the edge of the band of stability. The atomic number, 55, is much less than the value of 83 above which all isotopes are unstable. These facts suggest that \(_{43}^{98}Tc \) might be stable. However, \(_{43}^{98}Tc \) has an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, \(_{43}^{98}Tc \) is

predicted to be radioactive, and it is.
3. Tin-118 has 68 neutrons and 50 protons, for a neutron-to-proton ratio of 1.36. As in part b, this value and the atomic number both suggest stability. In addition, the isotope has an *even* number of both neutrons and protons, which tends to increase nuclear stability. Most important, the nucleus has 50 protons, and 50 is one of the magic numbers associated with especially stable nuclei. Thus \(_{50}^{118}Sn \) should be particularly stable.
4. This nuclide has an atomic number of 94. Because all nuclei with $Z > 83$ are unstable, \(_{94}^{239}Sn \)must be radioactive.

Exercise

Classify each nuclide as stable or radioactive.

1. \(_{90}^{232}Th \)
2. \(_{20}^{40}Ca \)
3. \(_{8}^{15}O \)
4. \(_{57}^{139}La \)

Answer

1. radioactive
2. stable
3. radioactive
4. stable

Superheavy Elements

In addition to the “peninsula of stability,” Figure 24.1.2 shows a small “island of stability” that is predicted to exist in the upper right corner. This island corresponds to the superheavy elementsAn element with an atomic number near the magic number of 126., with atomic numbers near the magic number 126. Because the next magic number for neutrons should be 184, it was suggested that an element with 114 protons and 184 neutrons might be stable enough to exist in nature. Although these claims were met with skepticism for many years, since 1999 a few atoms of isotopes with $Z = 114$ and $Z = 116$ have been prepared and found to be surprisingly stable. One isotope of element 114 lasts 2.7 seconds before decaying, described as an “eternity” by nuclear chemists. Moreover, there is recent evidence for the existence of a nucleus with $A = 292$ that was found in ^{232}Th. With an estimated half-life greater than 10^8 years, the isotope is particularly stable. Its measured mass is consistent with predictions for the mass of an isotope with $Z = 122$. Thus a number of relatively long-lived nuclei may well be accessible among the superheavy elements.

Summary

Subatomic particles of the nucleus (protons and neutrons) are called **nucleons**. A **nuclide** is an atom with a particular number of protons and neutrons. An unstable nucleus that decays spontaneously is **radioactive**, and its emissions are collectively called *radioactivity*. Isotopes that emit radiation are called **radioisotopes**. Each nucleon is attracted to other nucleons by the **strong nuclear force**. Stable nuclei generally have even numbers of both protons and neutrons and a neutron-to-proton ratio of at least 1. Nuclei that contain *magic numbers* of protons and neutrons are often especially stable. **Superheavy elements**, with atomic numbers near 126, may even be stable enough to exist in nature.

Key Takeaway

- Nuclei with magic numbers of neutrons or protons are especially stable, as are those nuclei that are doubly magic.

Conceptual Problems

1. What distinguishes a nuclear reaction from a chemical reaction? Use an example of each to illustrate the differences.

2. What do chemists mean when they say a substance is *radioactive*?

3. What characterizes an isotope? How is the mass of an isotope of an element related to the atomic mass of the element

shown in the periodic table?

4. In a typical nucleus, why does electrostatic repulsion between protons not destabilize the nucleus? How does the neutron-to-proton ratio affect the stability of an isotope? Why are all isotopes with $Z > 83$ unstable?

5. What is the significance of a *magic number* of protons or neutrons? What is the relationship between the number of stable isotopes of an element and whether the element has a magic number of protons?

6. Do you expect Bi to have a large number of stable isotopes? Ca? Explain your answers.

7. Potassium has three common isotopes, ^{39}K, ^{40}K, and ^{41}K, but only potassium-40 is radioactive (a beta emitter). Suggest a reason for the instability of ^{40}K.

8. Samarium has 11 relatively stable isotopes, but only 4 are nonradioactive. One of these 4 isotopes is ^{144}Sm, which has a lower neutron-to-proton ratio than lighter, radioactive isotopes of samarium. Why is ^{144}Sm more stable?

Answers

1.
2.
3.
4.

5. Isotopes with magic numbers of protons and/or neutrons tend to be especially stable. Elements with magic numbers of protons tend to have more stable isotopes than elements that do not.

6.

7. Potassium-40 has 19 protons and 21 neutrons. Nuclei with odd numbers of both protons and neutrons tend to be unstable. In addition, the neutron-to-proton ratio is very low for an element with this mass, which decreases nuclear stability.

8.

Numerical Problems

1. Write the nuclear symbol for each isotope using notation.

    1. chlorine-39
    2. lithium-8
    3. osmium-183
    4. zinc-71

2. Write the nuclear symbol for each isotope using \(_{Z}^{A}X \) notation.

    1. lead-212
    2. helium-5
    3. oxygen-19
    4. plutonium-242

3. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.

    1. iron-57
    2. \(^{185}W \)
    3. potassium-39
    4. \(^{131}Xe \)

4. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.

1. technetium-99*m*
2. \(^{140}La \)
3. radium-227
4. \(^{208}Bi \)

5. Which of these nuclides do you expect to be radioactive? Explain your reasoning.

    1. \(^{20}ne \)
    2. tungsten-184
    3. \(^{106}Ti \)

6. Which of these nuclides do you expect to be radioactive? Explain your reasoning.

    1. \(^{107}Ag \)
    2. \(^{50}V \)
    3. lutetium-176

Answers

1. 1. \(_{17}^{39}Cl \)
   2. \(_{3}^{8}Li \)
   3. \(_{76}^{183}Os \)
   4. \(_{30}^{71}Zn \)
2.
3. 1. 26 protons; 31 neutrons; 1.19
   2. 74 protons; 111 neutrons; 1.50
   3. 19 protons; 20 neutrons; 1.05
   4. 54 protons; 77 neutrons; 1.43
4.
5.
6.

Contributors

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Modified by Joshua B. Halpern

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14.3: Nuclear Reactions

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Predict the products and write balanced reactions for nuclear decay reactions.

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions**.** In a **nuclear decay reaction**, also called radioactive decay, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting daughter nuclei have a lower mass and are lower in energy (more stable) than the parent nucleus that decayed. In contrast, in a **nuclear transmutation reaction**, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

> Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.

Classes of Radioactive Nuclei

The three general classes of radioactive nuclei are characterized by a different decay process or set of processes:

1. **Neutron-rich nuclei.** The nuclei on the upper left side of the band of stable nuclei have a neutron-to-proton ratio that is too high to give a stable nucleus. These nuclei decay by a process that *converts a neutron to a proton*, thereby *decreasing* the neutron-to-proton ratio.
2. **Neutron-poor nuclei.** Nuclei on the lower right side of the band of stable nuclei have a neutron-to-proton ratio that is too low to give a stable nucleus. These nuclei decay by processes that have the net effect of *converting a proton to a neutron*, thereby *increasing* the neutron-to-proton ratio.
3. **Heavy nuclei.** With very few exceptions, heavy nuclei (those with $A \geq 200$) are intrinsically unstable regardless of the neutron-to-proton ratio, and all nuclei with $Z > 83$ are unstable. This is presumably due to the cumulative effects of electrostatic repulsions between the large number of positively charged protons, which cannot be totally overcome by the strong nuclear force, regardless of the number of neutrons present. Such nuclei tend to decay by emitting an α particle (a helium nucleus, $^{4}_{2}\mathrm{He}$, which decreases the number of protons and neutrons in the original nucleus by 2. Because the neutron-to-proton ratio in an α particle is 1, the net result of alpha emission is an increase in the neutron-to-proton ratio.

> Nuclear decay reactions always produce daughter nuclei that have a more favorable neutron-to- proton ratio and hence are more stable than the parent nucleus.

Nuclear Decay Reactions

Just as we use the number and type of atoms present to balance a chemical equation, we can use the number and type of nucleons present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, the total number of nucleons is conserved in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the $^{A}_{Z}\mathrm{X}$ notation for nuclides to include radioactive emissions. Table $14.3.1$ lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

Table 14.3.1: Nuclear Decay Emissions and Their Symbols

Identity	Symbol	Charge	Mass (amu)
helium nucleus	${}^{4}_{2}\alpha$	+2	4.001506
electron	${}^{0}_{-1}\beta$ or β^{-}	–1	0.000549
photon	${}^{0}_{0}\gamma$	—	—
neutron	${}^{1}_{0}\mathrm{n}$	0	1.008665
proton	${}^{1}_{1}\mathrm{p}$	+1	1.007276
positron	${}^{0}_{+1}\beta$ or β^{+}	+1	0.000549

Like the notation used to indicate isotopes, the upper left superscript in the symbol for a particle gives the mass number, which is the total number of protons and neutrons. For a proton or a neutron, $A = 1$. Because neither an electron nor a positron contains protons or neutrons, its mass number is 0. The numbers should not be taken literally, however, as meaning that these particles have zero mass; ejection of a beta particle (an electron) simply has a negligible effect on the mass of a nucleus.

Similarly, the lower left subscript gives the charge of the particle. Because protons carry a positive charge, $Z = +1$ for a proton. In contrast, a neutron contains no protons and is electrically neutral, so $Z = 0$. In the case of an electron, $Z = –1$, and for a positron, $Z = +1$. Because γ rays are high-energy photons, both A and Z are 0. In some cases, two different symbols are used for particles that are identical but produced in different ways. For example, the symbol ${}^{0}_{-1}\mathrm{e}$, which is usually simplified to e^{-}, represents a free electron or an electron associated with an atom, whereas the symbol ${}^{0}_{-1}\beta$, which is often simplified to β^{-}, denotes an electron that originates from within the nucleus, which is a β particle. Similarly, ${}^{4}_{2}\mathrm{He}^{2+}$ refers to the nucleus of a helium atom, and ${}^{4}_{2}\alpha$ denotes an identical particle that has been ejected from a heavier nucleus.

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure 14.3.1. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.

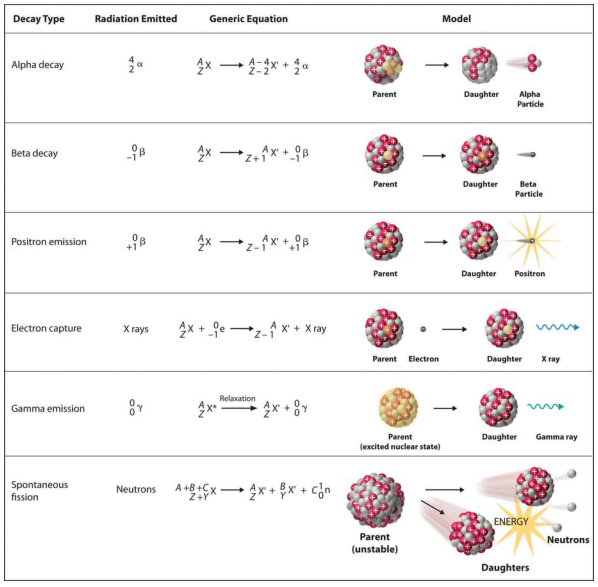


Figure 14.3.1: Common Modes of Nuclear Decay

Alpha Decay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, ${}^{4}_{2}\alpha$. The general reaction is as follows:

$$\underset{\text{parent}}{{}^{A}_{Z}\mathrm{X}} \rightarrow \underset{\text{daughter}}{{}^{A-4}_{Z-2}\mathrm{X}'} + \underset{\substack{\text{alpha}\\ \text{particle}}}{{}^{4}_{2}\alpha} \tag{14.3.1}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$${}^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + {}^{4}_{2}\alpha \tag{14.3.2}$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

> Just as the total number of atoms is conserved in a chemical reaction, the total number of nucleons is conserved in a nuclear reaction.

Beta Decay

Nuclei that contain too many neutrons often undergo **beta (β) decay**, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\substack{\text{unstable}\\ \text{neutron in}\\ \text{nucleus}}}{{}^{1}_{0}\mathrm{n}} \rightarrow \underset{\substack{\text{proton}\\ \text{retained}\\ \text{by nucleus}}}{{}^{1}_{1}\mathrm{p}} + \underset{\substack{\text{beta particle}\\ \text{emitted by}\\ \text{nucleus}}}{{}^{0}_{-1}\beta} \tag{14.3.3}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\mathrm{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\mathrm{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{14.3.4}$$

Although beta decay does not change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$${}^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\beta \tag{14.3.5}$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

Positron Emission

Because a positron has the same mass as an electron but opposite charge, **positron emission** is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

$${}^{1}_{1}\mathrm{p}^{+} \rightarrow {}^{1}_{0}\mathrm{n} + {}^{0}_{+1}\beta^{+} \tag{14.3.6}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\mathrm{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\mathrm{X}'} + \underset{\text{positron}}{{}^{0}_{+1}\beta^{+}} \tag{14.3.7}$$

Like beta decay, positron emission does not change the mass number of the nucleus. In this case, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Thus the neutron-to-proton ratio has increased, again moving the nucleus closer to the band of stable nuclei. For example, carbon-11 undergoes positron emission to form boron-11:

$${}^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta^{+} \tag{14.3.8}$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

Electron Capture

A neutron-poor nucleus can decay by either positron emission or **electron capture (EC)**, in which an electron in an inner shell reacts with a proton to produce a neutron:

$$ {}^{1}_{1}\mathrm{p} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{1}_{0}\mathrm{n} \tag{14.3.9} $$

When a second electron moves from an outer shell to take the place of the lower-energy electron that was absorbed by the nucleus, an x-ray is emitted. The overall reaction for electron capture is thus

$$ \underset{\text{parent}}{{}^{A}_{Z}\mathrm{X}} + \underset{\text{electron}}{{}^{0}_{-1}\mathrm{e}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\mathrm{X}'} + \text{x-ray} \tag{14.3.10} $$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

$$ {}^{55}_{26}\mathrm{Fe} \overset{\mathrm{EC}}{\rightarrow} {}^{55}_{25}\mathrm{Mn} + \text{x-ray} \tag{14.3.11} $$

The atomic numbers of the parent and daughter nuclides differ in Equation 20.2.11, although the mass numbers are the same. To write a balanced nuclear equation for this reaction, we must explicitly include the captured electron in the equation:

$$ {}^{55}_{26}\mathrm{Fe} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{55}_{25}\mathrm{Mn} + \text{x-ray} \tag{14.3.12} $$

Both positron emission and electron capture are usually observed for nuclides with low neutron-to-proton ratios, but the decay rates for the two processes can be very different.

Gamma Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. These high-energy photons are γ rays. **Gamma** (γ) **emission** can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$ {}^{238}_{92}\mathrm{U} \rightarrow \underset{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}}{{}^{234}_{90}\mathrm{Th}^{*}} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\mathrm{Th} + {}^{0}_{0}\gamma \tag{14.3.13} $$

If we disregard the decay event that created the excited nucleus, then

$$ {}^{234}_{88}\mathrm{Th}^{*} \rightarrow {}^{234}_{88}\mathrm{Th} + {}^{0}_{0}\gamma \tag{14.3.14} $$

or more generally,

$$ {}^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma \tag{14.3.15} $$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Spontaneous Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of $^{254}_{98}\mathrm{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$^{254}_{98}\mathrm{Cf} \rightarrow {}^{118}_{46}\mathrm{Pd} + {}^{132}_{52}\mathrm{Te} + 4{}^{1}_{0}\mathrm{n} \tag{14.3.16}$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

Example 14.3.1

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\mathrm{S}$
b. the decay of $^{201}_{80}\mathrm{Hg}$ by electron capture
c. the decay of $^{30}_{15}\mathrm{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of A and Z to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as $^{A}_{Z}\mathrm{X}$:

$$^{35}_{16}\mathrm{S} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta \tag{14.3.17}$$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$$^{35}_{16}\mathrm{S} \rightarrow {}^{35}_{17}\mathrm{Cl} + {}^{0}_{-1}\beta \tag{14.3.18}$$

b.

A We know the identities of both reactants: $^{201}_{80}\mathrm{Hg}$ and an inner electron, $^{0}_{-1}\mathrm{e}$. The reaction is as follows:

$$^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z}\mathrm{X}$$

B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$$^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{201}_{79}\mathrm{Au}$$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$^{30}_{15}\mathrm{P} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{+1}\beta$$

B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}\beta$$

Exercise 14.3.1

Write a balanced nuclear equation to describe each reaction.

a. $^{11}_{6}\mathrm{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from $^{185}_{74}\mathrm{W}$

Answer

a. $^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta$
b. $^{99}_{42}\mathrm{Mo} \rightarrow {}^{99m}_{43}\mathrm{Tc} + {}^{0}_{-1}\beta$
c. $^{185}_{74}\mathrm{W} \rightarrow {}^{181}_{72}\mathrm{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$

Example 14.3.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{45}_{22}\mathrm{Ti}$
b. $^{242}_{94}\mathrm{Pu}$
c. $^{12}_{5}\mathrm{B}$
d. $^{256}_{100}\mathrm{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of Z, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{242}_{94}\mathrm{Pu}$ is expected to decay by alpha emission.

c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}\mathrm{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}\mathrm{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

Exercise 14.3.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{32}_{14}\mathrm{Si}$
b. $^{43}_{21}\mathrm{Sc}$
c. $^{231}_{91}\mathrm{Pa}$

Answer

a. beta decay
b. positron emission or electron capture
c. alpha decay

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases Z by only 2, and positron emission or electron capture decreases Z by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and beta-decay reactions is called a **radioactive decay series**. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure 14.3.2). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of “only” 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

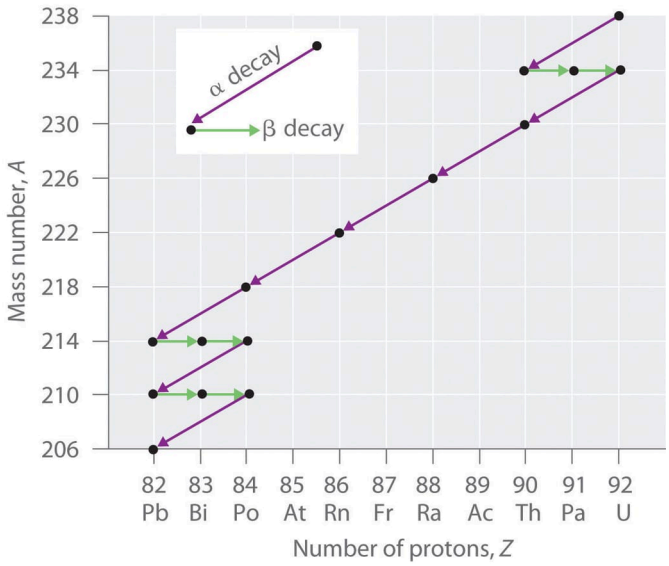


Figure 14.3.1: A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

Due to these radioactive decay series, small amounts of very unstable isotopes are found in ores that contain uranium or thorium. These rare, unstable isotopes should have decayed long ago to stable nuclei with a lower atomic number, and they would no longer be found on Earth. Because they are generated continuously by the decay of uranium or thorium, however, their amounts have reached a steady state, in which their rate of formation is equal to their rate of decay. In some cases, the abundance of the daughter isotopes can be used to date a material or identify its origin.

Induced Nuclear Reactions

The discovery of radioactivity in the late 19th century showed that some nuclei spontaneously transform into nuclei with a different number of protons, thereby producing a different element. When scientists realized that these naturally occurring radioactive isotopes decayed by emitting subatomic particles, they realized that—in principle—it should be possible to carry out the reverse reaction, converting a stable nucleus to another more massive nucleus by bombarding it with subatomic particles in a nuclear transmutation reaction.

The first successful nuclear transmutation reaction was carried out in 1919 by Ernest Rutherford, who showed that α particles emitted by radium could react with nitrogen nuclei to form oxygen nuclei. As shown in the following equation, a proton is emitted in the process:

$$ {}^{4}_{2}\alpha + {}^{14}_{7}\mathrm{N} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p} \tag{14.3.19} $$

Rutherford's nuclear transmutation experiments led to the discovery of the neutron. He found that bombarding the nucleus of a light target element with an α particle usually converted the target nucleus to a product that had an atomic number higher by 1 and a mass number higher by 3 than the target nucleus. Such behavior is consistent with the emission of a proton after reaction with the α particle. Very light targets such as Li, Be, and B reacted differently, however, emitting a new kind of highly penetrating radiation rather than a proton. Because neither a magnetic field nor an electrical field could deflect these high-energy particles, Rutherford concluded that they were electrically neutral. Other observations suggested that the mass of the neutral particle was similar to the mass of the proton. In 1932, James Chadwick (Nobel Prize in Physics, 1935), who was a student of Rutherford's at the time, named these neutral particles neutrons and proposed that they were fundamental building blocks of the atom. The reaction that Chadwick initially used to explain the production of neutrons was as follows:

$$ {}^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{14.3.20} $$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure 14.3.3). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14

with neutrons generated by cosmic rays:

$$^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{14.3.21}$$

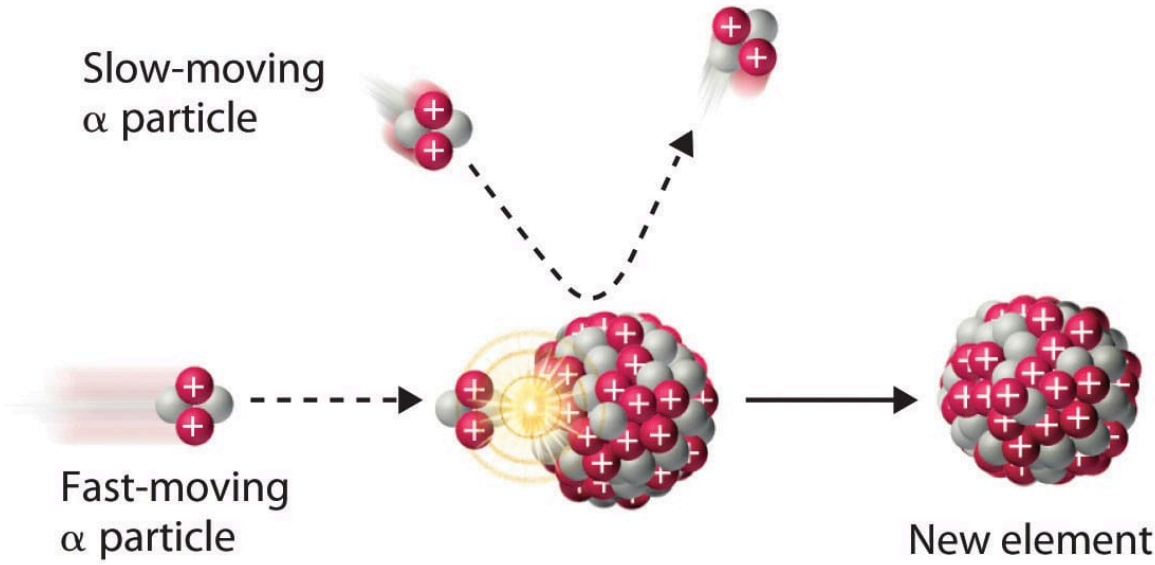


Figure 14.3.3: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.

Example 14.3.3

In 1933, Frédéric Joliot and Iréne Joliot-Curie (daughter of Marie and Pierre Curie) prepared the first artificial radioactive isotope by bombarding aluminum-27 with α particles. For each ^{27}Al that reacted, one neutron was released. Identify the product nuclide and write a balanced nuclear equation for this transmutation reaction.

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

A Based on the reactants and one product, identify the other product of the reaction. Use conservation of mass and charge to determine the values of *Z* and *A* of the product nuclide and thus its identity.

B Write the balanced nuclear equation for the reaction.

Solution

A Bombarding an element with α particles usually produces an element with an atomic number that is 2 greater than the atomic number of the target nucleus. Thus we expect that aluminum (*Z* = 13) will be converted to phosphorus (*Z* = 15). With one neutron released, conservation of mass requires that the mass number of the other product be 3 greater than the mass number of the target. In this case, the mass number of the target is 27, so the mass number of the product will be 30. The second product is therefore phosphorus-30, $^{30}_{15}\mathrm{P}$.

B The balanced nuclear equation for the reaction is as follows:

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\alpha \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n} \tag{14.3.22}$$

Exercise 14.3.1

Because all isotopes of technetium are radioactive and have short half-lives, it does not exist in nature. Technetium can, however, be prepared by nuclear transmutation reactions. For example, bombarding a molybdenum-96 target with deuterium nuclei ($^{2}_{1}\mathrm{H}$) produces technetium-97. Identify the other product of the reaction and write a balanced nuclear equation for this transmutation reaction.

Answer

neutron, $^{1}_{0}\mathrm{n}$; $^{96}_{42}\mathrm{Mo} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{97}_{43}\mathrm{Tc} + {}^{1}_{0}\mathrm{n}$

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of Z, such as the isotopes of uranium ($Z = 92$) and plutonium ($Z = 94$), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as $^{235}_{92}\mathrm{U}$ and $^{239}_{94}\mathrm{Pu}$ undergo induced nuclear fission when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure 14.3.3:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{14.3.23}$$

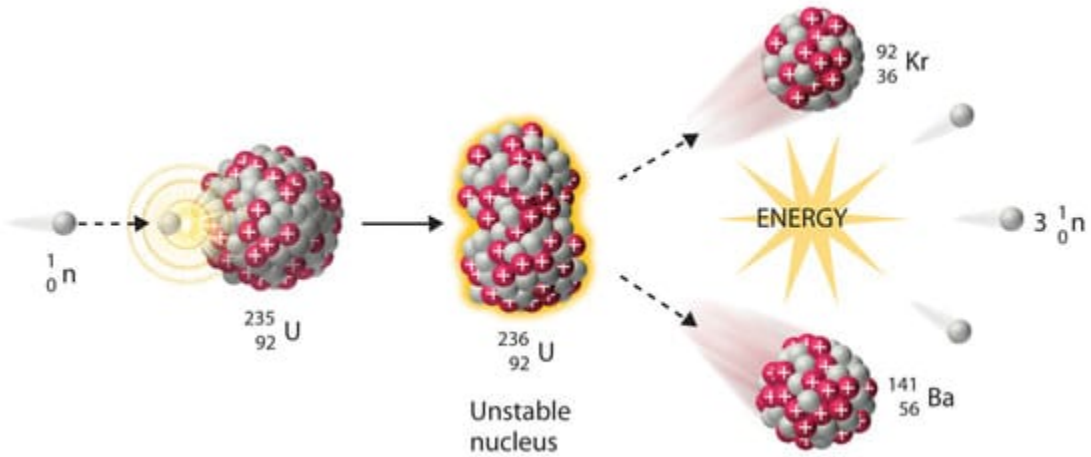


Figure 14.3.4: Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

Any isotope that can undergo a nuclear fission reaction when bombarded with neutrons is called a **fissile isotope**.

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure 14.3.4. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure 14.3.5, a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

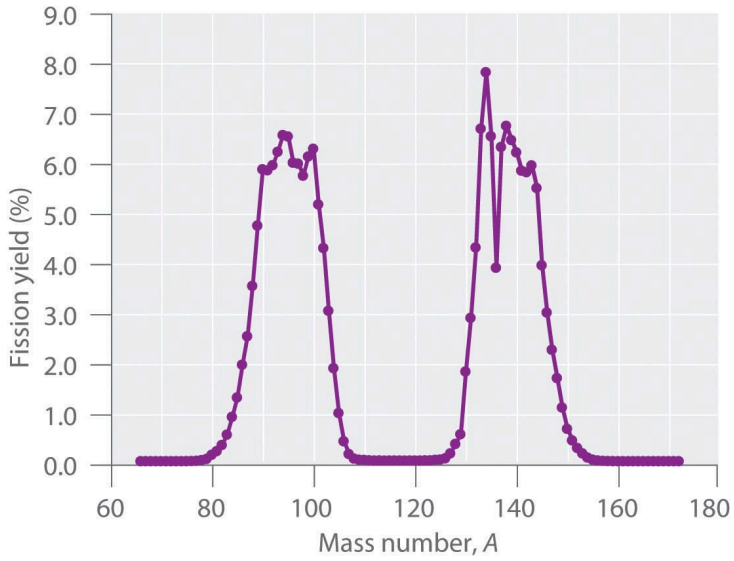


Figure 14.3.5: Mass Distribution of Nuclear Fission Products of ^{235}U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for235U. Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

Synthesis of Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with Z > 92, the **transuranium elements**, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation 20.21, this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta$$

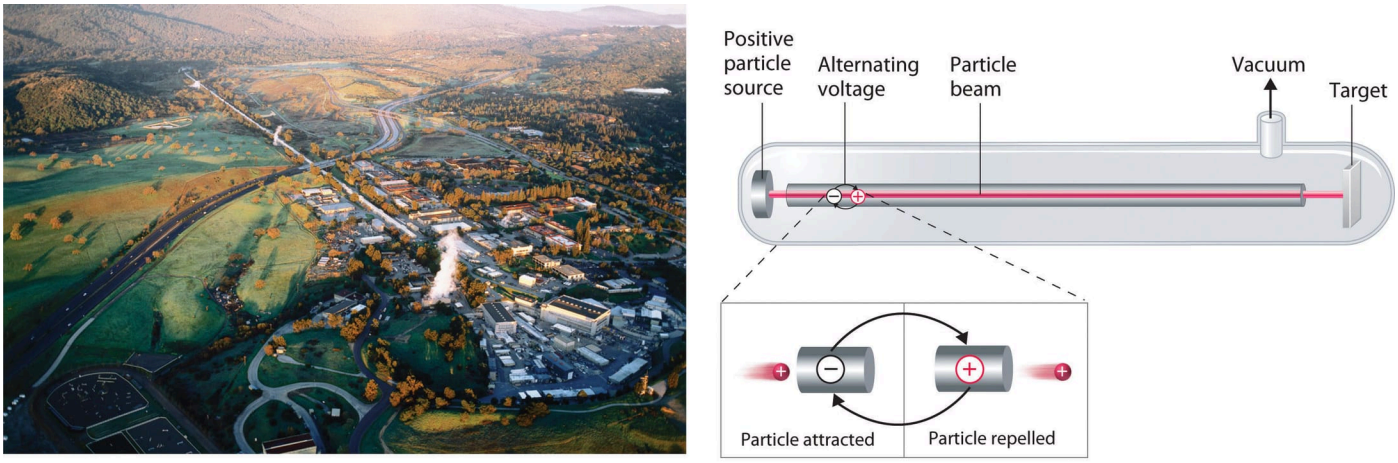
Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 14.3.2). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability."

Table 14.3.2: Some Reactions Used to Synthesize Transuranium Elements

$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{241}_{95}\mathrm{Am} + {}^{1}_{1}\mathrm{p} + {}^{1}_{0}\mathrm{n}$
$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\alpha \rightarrow {}^{243}_{97}\mathrm{Bk} + {}^{1}_{1}\mathrm{p} + 2{}^{1}_{0}\mathrm{n}$
$^{253}_{99}\mathrm{Es} + {}^{4}_{2}\alpha \rightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$
$^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{246}_{98}\mathrm{Cf} + 4{}^{1}_{0}\mathrm{n}$
$^{252}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \rightarrow {}^{256}_{103}\mathrm{Lr} + 6{}^{1}_{0}\mathrm{n}$

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 14.3.6), in which a beam of particles is injected at one end of a long evacuated

tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.



(a) (b)

Figure 14.3.6: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

To achieve the same outcome in less space, a particle accelerator called a cyclotron forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

The length of a linear accelerator and the size of the D-shaped electrodes in a cyclotron severely limit the kinetic energy that particles can attain in these devices. These limitations can be overcome by using a synchrotron, a hybrid of the two designs. A synchrotron contains an evacuated tube similar to that of a linear accelerator, but the tube is circular and can be more than a mile in diameter. Charged particles are accelerated around the circle by a series of magnets whose polarities rapidly alternate.

Summary

In **nuclear decay reactions (or radioactive decay)**, the parent nucleus is converted to a more stable daughter nucleus. Nuclei with too many neutrons decay by converting a neutron to a proton, whereas nuclei with too few neutrons decay by converting a proton to a neutron. Very heavy nuclei (with $A \geq 200$ and $Z > 83$) are unstable and tend to decay by emitting an **α particle**. When an unstable nuclide undergoes radioactive decay, the total number of nucleons is conserved, as is the total positive charge. Six different kinds of nuclear decay reactions are known. *Alpha decay* results in the emission of an α particle, ${}^{4}_{2}\alpha$, and produces a daughter nucleus with a mass number that is lower by 4 and an atomic number that is lower by 2 than the parent nucleus. **Beta decay** converts a neutron to a proton and emits a high-energy electron, producing a daughter nucleus with the same mass number as the parent and an atomic number that is higher by 1. **Positron emission** is the opposite of beta decay and converts a proton to a neutron plus a positron. Positron emission does not change the mass number of the nucleus, but the atomic number of the daughter nucleus is lower by 1 than the parent. In **electron capture (EC)**, an electron in an inner shell reacts with a proton to produce a neutron, with emission of an x-ray. The mass number does not change, but the atomic number of the daughter is lower by 1 than the parent. In **gamma emission**, a daughter nucleus in a nuclear excited state undergoes a transition to a lower-energy state by emitting a γ ray. Very heavy nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that can have different atomic numbers and atomic masses with the release of neutrons. Many very heavy nuclei decay via a **radioactive decay series**—a succession of some combination of alpha- and beta-decay reactions. In **nuclear transmutation reactions**, a target nucleus is bombarded with energetic subatomic particles to give a product nucleus that is more massive than the original. All **transuranium elements**—elements with $Z > 92$—are artificial and must be prepared by nuclear transmutation reactions. These reactions are carried out in particle accelerators such as linear accelerators, cyclotrons, and synchrotrons.

Key Takeaway

Nuclear decay reactions occur spontaneously under all conditions and produce more stable daughter nuclei, whereas nuclear transmutation reactions are induced and form a product nucleus that is more massive than the starting material.

Key Equations

alpha decay

Equation 20.1: ${}^{A}_{Z}\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^{4}_{2}\alpha$

beta decay

Equation 20.4: ${}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z+1}\mathrm{X}' + {}^{0}_{-1}\beta$

positron emission

Equation 20.7: ${}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + {}^{0}_{+1}\beta$

electron capture

Equation 20.10: ${}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + \text{x-ray}$

gamma emission

Equation 20.15: ${}^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma$

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14.4: Kinetics of Radioactive Decay

Learning Objectives

By the end of this section, you will have background information that will help you to be able to:

- Calculate kinetic parameters for decay processes, including half-life

Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant **half-life** ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, coba source, since half of the nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

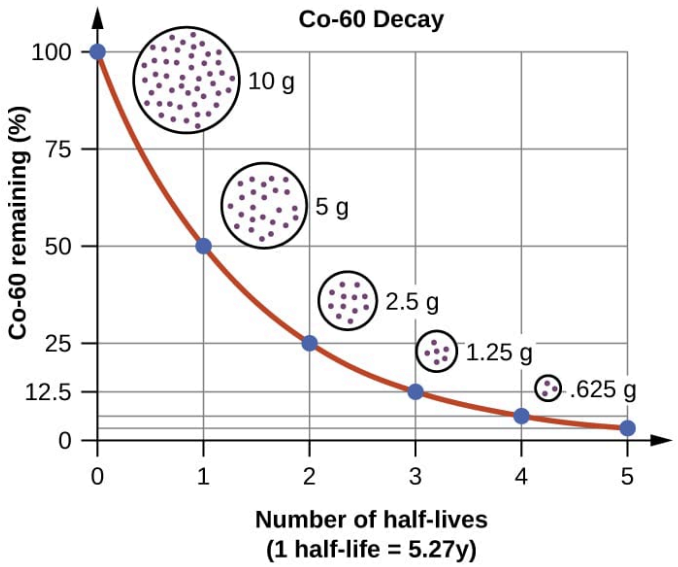


Figure 14.4.6: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions. We generally substitute the number of nuclei, N, for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the **activity** of the radioactive sample. The rate for radioactive decay is:

$$\text{decay rate} = \lambda N$$

with λ = the decay constant for the particular radioisotope.

The decay constant, λ, which is the same as a rate constant discussed in the kinetics chapter. It is possible to express the decay constant in terms of the half-life, $t_{1/2}$:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

or

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

The first-order equations relating amount, N, and time are:

$$N_t = N_0 e^{-\lambda t} \tag{14.4.1}$$

or

$$t = -\frac{1}{\lambda} \ln \left(\frac{N_t}{N_0} \right)$$

Example 14.4.1: Rates of Radioactive Decay

$^{60}_{27}\text{Co}$ decays with a half-life of 5.27 years to produce $^{60}_{28}\text{Co}$

a. What is the decay constant for the radioactive disintegration of cobalt-60?
b. Calculate the fraction of a sample of the $^{60}_{27}\text{Co}$ isotope that will remain after 15 years.
c. How long does it take for a sample of $^{60}_{27}\text{Co}$ to disintegrate to the extent that only 2.0% of the original amount remains?

Solution a

The value of the rate constant is given by:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5.27y} = 0.132y^{-1}$$

Solution b

The fraction of $^{60}_{27}\text{Co}$ that is left after time t is given by $\frac{N_t}{N_0}$. Rearranging the first-order relationship in Equation 14.4.1 ($N_t = N_0 e^{-\lambda t}$ to solve for this ratio yields:

$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-(0.132/\text{y})(15\,\text{y})} = 0.138$$

The fraction of $^{60}_{27}\text{Co}$ that will remain after 15.0 years is 0.138. Or put another way, 13.8% of the original $^{60}_{27}\text{Co}$ present will remain after 15 years.

Solution c

2.00% of the original amount of $^{60}_{27}\text{Co}$ is equal to 0.0200 N_0. Substituting this into the equation for time for first-order kinetics, we have:

$$t = -\frac{1}{\lambda} \ln \left(\frac{N_t}{N_0} \right) = -\frac{1}{0.132\,\text{y}^{-1}} \ln \left(\frac{0.0200 \times N_0}{N_0} \right) = 29.6y$$

Exercise 14.4.1

Radon-222, $^{222}_{86}\text{Rn}$ has a half-life of 3.823 days. How long will it take a sample of radon-222 with a mass of 0.750 g to decay into other elements, leaving only 0.100 g of radon-222?

Answer available at the end of this section.

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of $^{209}_{83}\mathrm{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\mathrm{Ra}$ is 24,000 years; $^{222}_{86}\mathrm{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in Table 14.4.1, and others are listed in Appendix M.

Table 14.4.1: Half-lives of Radioactive Isotopes Important to Medicine

Type[1]	Decay Mode	Half-Life	Uses
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m	γ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of "dating" the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is **radiometric dating** and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: $^{12}_{6}\mathrm{C}$ which constitutes about 99% of the carbon on earth; $^{13}_{6}\mathrm{C}$, about 1% of the total; and trace amounts of $^{14}_{6}\mathrm{C}$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H}$$

All isotopes of carbon react with oxygen to produce $\mathrm{CO_2}$ molecules. The ratio of $^{14}_{6}\mathrm{CO_2}$ to $^{12}_{6}\mathrm{CO_2}$ depends on the ratio of $^{14}_{6}\mathrm{CO}$ to $^{12}_{6}\mathrm{CO}$ in the atmosphere. The natural abundance of $^{14}_{6}\mathrm{CO}$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of $^{14}_{6}\mathrm{CO_2}$ and $^{14}_{6}\mathrm{CO_2}$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio found in a living plant is the **same** as the $^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}\mathrm{C}$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}_{-1}{}^{0}\,\mathrm{e}$$

Thus, the ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure 14.4.7: visually depicts this process.

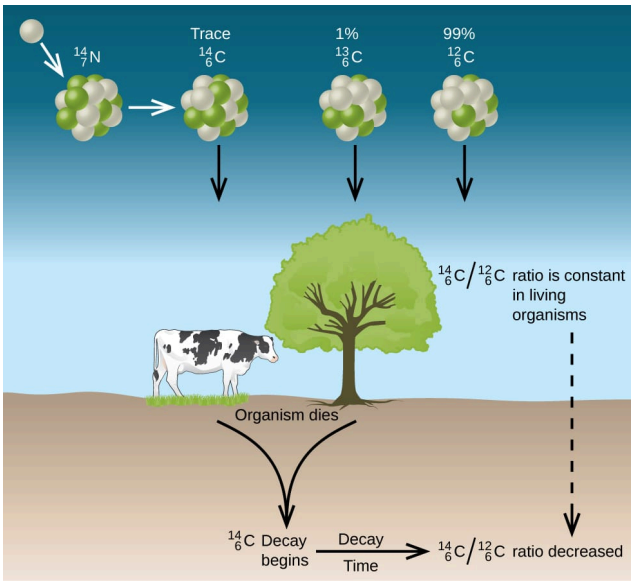


Figure 14.4.7: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

For example, with the half-life of being 5730 years, if the ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Link to Learning

Visit this website to perform simulations of radiometric dating.

Example 14.4.2: Radiocarbon Dating

A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls has an activity of 10.8 disintegrations per minute per gram of carbon. If the initial C-14 activity was 13.6 disintegrations/min/g of C, estimate the age of the Dead Sea Scrolls.

Solution

The rate of decay (number of disintegrations/minute/gram of carbon) is proportional to the amount of radioactive C-14 left in the paper, so we can substitute the rates for the amounts, N, in the relationship:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) \longrightarrow t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_{\,t}}{\text{Rate}_{\,0}}\right)$$

where the subscript 0 represents the time when the plants were cut to make the paper, and the subscript t represents the current time.

The decay constant can be determined from the half-life of C-14, 5730 years:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730\,\text{y}} = 1.21 \times 10^{-4}\,\text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_{\,t}}{\text{Rate}_{\,0}}\right) = -\frac{1}{1.21\times10^{-4}\,\text{y}^{-1}}\ln\left(\frac{10.8\ \cancel{\text{dis/min/g C}}}{13.6\ \cancel{\text{dis/min/g C}}}\right) = 1910\,\text{y}$$

Therefore, the Dead Sea Scrolls are approximately 1900 years old (Figure 14.4.8).



Figure 14.4.8: Carbon-14 dating has shown that these pages from the Dead Sea Scrolls were written or copied on paper made from plants that died between 100 BC and AD 50.

Exercise 14.4.1

More accurate dates of the reigns of ancient Egyptian pharaohs have been determined recently using plants that were preserved in their tombs. Samples of seeds and plant matter from King Tutankhamun's tomb have a C-14 decay rate of 9.07 disintegrations/min/g of C. How long ago did King Tut's reign come to an end?

Answer available at the end of this section.

There have been some significant, well-documented changes to the $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio. The accuracy of a straightforward application of this technique depends on the $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely $^{12}_{6}\text{C}$) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the $^{14}_{6}\text{C}$ has decayed), the ratio of $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ in the atmosphere may be changing. This manmade increase in $^{12}_{6}\text{C}$ in the atmosphere causes the $^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there is additional lead-206 present, which is indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Example 14.4.3: Radioactive Dating of Rocks

An igneous rock contains 9.58×10^{-5} g of U-238 and 2.51×10^{-5} g of Pb-206, and much, much smaller amounts of Pb-208. Determine the approximate time at which the rock formed.

Solution

The sample of rock contains very little Pb-208, the most common isotope of lead, so we can safely assume that all the Pb-206 in the rock was produced by the radioactive decay of U-238. When the rock formed, it contained all of the U-238 currently in it, plus some U-238 that has since undergone radioactive decay.

The amount of U-238 currently in the rock is:

$$9.58 \times 10^{-5} \cancel{\text{g U}} \times \left(\frac{1 \text{ mol U}}{238 \cancel{\text{g U}}} \right) = 4.03 \times 10^{-7} \text{ mol U}$$

Because when one mole of U-238 decays, it produces one mole of Pb-206, the amount of U-238 that has undergone radioactive decay since the rock was formed is:

$$2.51 \times 10^{-5} \cancel{\text{g Pb}} \times \left(\frac{1 \cancel{\text{ mol Pb}}}{206 \cancel{\text{ g Pb}}} \right) \times \left(\frac{1 \text{ mol U}}{1 \cancel{\text{ mol Pb}}} \right) = 1.22 \times 10^{-7} \text{ mol U}$$

The total amount of U-238 originally present in the rock is therefore:

$$4.03 \times 10^{-7} \text{ mol U} + 1.22 \times 10^{-7} \text{ mol U} = 5.25 \times 10^{-7} \text{ mol U}$$

The amount of time that has passed since the formation of the rock is given by:

$$t = -\frac{1}{\lambda} \ln \left(\frac{N_t}{N_0} \right)$$

with N_0 representing the original amount of U-238 and N_t representing the present amount of U-238.

U-238 decays into Pb-206 with a half-life of 4.5×10^9 y, so the decay constant λ is:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \text{ y}} = 1.54 \times 10^{-10} \text{ y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{1.54 \times 10^{-10} \text{ y}^{-1}} \ln \left(\frac{4.03 \times 10^{-7} \cancel{\text{ mol U}}}{5.25 \times 10^{-7} \cancel{\text{ mol U}}} \right) = 1.7 \times 10^9 \text{ y}$$

Therefore, the rock is approximately 1.7 billion years old.

Exercise 14.4.1

A sample of rock contains 6.14×10^{-4} g of Rb-87 and $3.51 \times 10^{-5} g$ of Sr-87. Calculate the age of the rock. (The half-life of the β decay of Rb-87 is 4.7×10^{10} y.)

Answer available at the end of this section.

Footnotes

- 1The “m” in Tc-99m stands for “metastable,” indicating that this is an unstable, high-energy state of Tc-99. Metastable

isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

Answers

Exercise 14.4.1

11.1 days

Exercise 14.4.1

about 3350 years ago, or approximately 1340 BC

Exercise 14.4.1

3.7×10^{9} y

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INDEX

A

absolute zero
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

accuracy
1.4: Significant Figures for Measurements and Calculations
1.5: Accuracy and Precision of Experimental Results (lab topic)

actinide
2.3: The Periodic Table

activated complex
9.7: Collision Theory

activation energy
9.7: Collision Theory

actual yield
3.8: Reaction Yields

alkali metal
2.3: The Periodic Table

alkaline earth metal
2.3: The Periodic Table

alloy
6.6: The Dissolution Process

alpha decay
14.4: Kinetics of Radioactive Decay

Amonton's law
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

amorphous solid
5.3: Metallic Bonding

amplitude
4.2: Electromagnetic Energy

angular momentum quantum number
4.5: Development of Quantum Theory

anion
2.2: Atomic Structure and Symbolism

aqueous solution
3.4: Molarity

Arrhenius equation
9.7: Collision Theory

atmosphere
7.2: Gas Pressure

atomic mass
2.2: Atomic Structure and Symbolism

atomic mass unit
2.2: Atomic Structure and Symbolism

atomic number
2.2: Atomic Structure and Symbolism

atomic orbital
4.5: Development of Quantum Theory

Aufbau principle
4.6: Electronic Structure of Atoms (Electron Configurations)

Author tag:OpenStax
1.2: Measurements
1.3: Dimensional Analysis for Calculations
1.4: Significant Figures for Measurements and Calculations
1.5: Accuracy and Precision of Experimental Results (lab topic)
13.3: Balancing Redox Reactions
14.4: Kinetics of Radioactive Decay
2.2: Atomic Structure and Symbolism
2.3: The Periodic Table
2.4: Molecular and Ionic Compounds
2.5: Chemical Nomenclature
3.3: Determining Empirical and Molecular Formulas
3.4: Molarity
3.5: Writing and Balancing Chemical Equations
3.7: Reaction Stoichiometry
3.8: Reaction Yields
4.2: Electromagnetic Energy
4.4: The Bohr Model
4.5: Development of Quantum Theory
4.6: Electronic Structure of Atoms (Electron Configurations)
4.7: Periodic Variations in Element Properties
5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals
5.13: Coordinate Covalent Bonding is Different
5.14: Spectroscopic and Magnetic Properties of Coordination Compounds
5.2: Ionic Bonding
5.3: Metallic Bonding
5.4: Covalent Bonding
5.5: Lewis Symbols and Structures
5.6: Strengths of Ionic and Covalent Bonds
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity
5.9: Valence Bond Theory Describes Bonds as Overlapping Atomic Orbitals
6.3: Intermolecular Forces
6.4: Phase Transitions
6.5: Phase Diagrams
6.6: The Dissolution Process
6.7: Dissolution of Electrolytes
6.8: Solubility
6.9: Colligative Properties
7.2: Gas Pressure
7.5: The Kinetic-Molecular Theory
7.7: Non-Ideal Gas Behavior
8.12: Spontaneity is Related to Entropy
9.3: Rate Laws
9.4: Integrated Rate Laws
9.5: Factors Affecting Reaction Rates
9.6: Catalysis
9.7: Collision Theory
9.8: Reaction Mechanisms

avogadro's law
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

Avogadro's number
3.2: Formula Mass and the Mole Concept

axial position
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity

B

balanced equation
3.5: Writing and Balancing Chemical Equations

bar
7.2: Gas Pressure

barometer
7.2: Gas Pressure

beta decay
14.4: Kinetics of Radioactive Decay

bidentate ligand
5.13: Coordinate Covalent Bonding is Different

bimolecular reaction
9.8: Reaction Mechanisms

binary acid
2.5: Chemical Nomenclature

binary compound
2.5: Chemical Nomenclature

blackbody
4.2: Electromagnetic Energy

Bohr's model of the hydrogen atom
4.4: The Bohr Model

boiling point
6.4: Phase Transitions

boiling point elevation
6.9: Colligative Properties

boiling point elevation constant
6.9: Colligative Properties

bond angle
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity

bond dipole moment
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity

bond distance
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity

bond energy
5.6: Strengths of Ionic and Covalent Bonds

bond length
5.4: Covalent Bonding

Boyle's law
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

C

catalyst
9.5: Factors Affecting Reaction Rates

cation
2.2: Atomic Structure and Symbolism

Celsius
1.2: Measurements

central metal
5.13: Coordinate Covalent Bonding is Different

chalcogen
2.3: The Periodic Table

Charles's Law
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

chelate
5.13: Coordinate Covalent Bonding is Different

chelating ligand
5.13: Coordinate Covalent Bonding is Different

chemical equation
3.5: Writing and Balancing Chemical Equations

chemical symbol
2.2: Atomic Structure and Symbolism

circuit
13.3: Balancing Redox Reactions

cis configuration
5.13: Coordinate Covalent Bonding is Different

coefficient
3.5: Writing and Balancing Chemical Equations

colligative property
6.9: Colligative Properties

collision theory
9.7: Collision Theory

combustion reaction
3.6: Classifying Chemical Reactions

complete ionic equation
3.5: Writing and Balancing Chemical Equations

compressibility factor
7.7: Non-Ideal Gas Behavior

concentrated
3.4: Molarity

concentration
3.4: Molarity

condensation
6.4: Phase Transitions

condensed formula
6.2: Skeletal Structures For Representing Organic Compounds

continuous spectrum
4.2: Electromagnetic Energy

conversion factors
1.3: Dimensional Analysis for Calculations

coordination compound
5.13: Coordinate Covalent Bonding is Different

coordination number
5.13: Coordinate Covalent Bonding is Different

coordination sphere
5.13: Coordinate Covalent Bonding is Different

core electron
4.6: Electronic Structure of Atoms (Electron Configurations)

covalent bond
2.4: Molecular and Ionic Compounds
5.4: Covalent Bonding

covalent compound
2.4: Molecular and Ionic Compounds

covalent network solid
5.3: Metallic Bonding

covalent radius
4.7: Periodic Variations in Element Properties

crenation
6.9: Colligative Properties

critical point
6.5: Phase Diagrams

crystal field splitting
5.14: Spectroscopic and Magnetic Properties of Coordination Compounds

crystal field theory
5.14: Spectroscopic and Magnetic Properties of Coordination Compounds

crystalline solid
5.3: Metallic Bonding

cubic centimeter
1.2: Measurements

cubic meter
1.2: Measurements

current
13.3: Balancing Redox Reactions

D

d orbital
4.5: Development of Quantum Theory

Dalton unit
2.2: Atomic Structure and Symbolism

Dalton's Law of Partial Pressure
7.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

daughter nuclide
14.4: Kinetics of Radioactive Decay

density
1.2: Measurements

deposition
6.4: Phase Transitions

diffusion
7.6: Effusion and Diffusion of Gases

dilution
3.4: Molarity

dimensional analysis
1.3: Dimensional Analysis for Calculations

dipole moment
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity

Dispersion
6.3: Intermolecular Forces

dissociation
6.7: Dissolution of Electrolytes

dissolved
3.4: Molarity

donor atom
5.13: Coordinate Covalent Bonding is Different

double bond
5.5: Lewis Symbols and Structures

dynamic equilibrium
6.4: Phase Transitions

E

effective nuclear charge
4.7: Periodic Variations in Element Properties

effusion
7.6: Effusion and Diffusion of Gases

eg orbitals
5.14: Spectroscopic and Magnetic Properties of Coordination Compounds

electrical potential
13.3: Balancing Redox Reactions

electrolyte
6.7: Dissolution of Electrolytes

electromagnetic radiation
4.2: Electromagnetic Energy

electromagnetic spectrum
4.2: Electromagnetic Energy

electron affinity
4.7: Periodic Variations in Element Properties

electron capture
14.4: Kinetics of Radioactive Decay

electron configuration
4.6: Electronic Structure of Atoms (Electron Configurations)

electron density
4.5: Development of Quantum Theory

electronegativity
5.4: Covalent Bonding

elementary reaction
9.8: Reaction Mechanisms

empirical formula mass
3.3: Determining Empirical and Molecular Formulas

entropy
8.13: Entropy

equatorial position
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity

exact number
1.4: Significant Figures for Measurements and Calculations
1.5: Accuracy and Precision of Experimental Results (lab topic)

excess reactant
3.8: Reaction Yields

excited state
4.4: The Bohr Model

F

f orbital
4.5: Development of Quantum Theory

Fahrenheit
1.3: Dimensional Analysis for Calculations

formula mass
3.2: Formula Mass and the Mole Concept

free radical
5.5: Lewis Symbols and Structures

freezing
6.4: Phase Transitions

freezing point
6.4: Phase Transitions

freezing point depression
6.9: Colligative Properties

freezing point depression constant
6.9: Colligative Properties

frequency
4.2: Electromagnetic Energy

frequency factor
9.7: Collision Theory

fundamental unit of charge
2.2: Atomic Structure and Symbolism

G

gamma emission
14.4: Kinetics of Radioactive Decay

geometric isomers
5.14: Spectroscopic and Magnetic Properties of Coordination Compounds

Gibbs Free Energy
8.15: Temperature Dependence of Free Energy

goiter
2.2: Atomic Structure and Symbolism

Gouy balance
5.12: Molecular Orbital Theory Resolves Issues in Other Bonding Theories

Graham's law
7.6: Effusion and Diffusion of Gases

ground state
4.4: The Bohr Model

group
2.3: The Periodic Table

H

halogen
2.3: The Periodic Table

Heisenberg uncertainty principle
4.5: Development of Quantum Theory

hemolysis
6.9: Colligative Properties

Henry's law
6.8: Solubility

hertz
4.2: Electromagnetic Energy

heterogeneous catalyst
9.6: Catalysis

homogeneous catalyst
9.6: Catalysis

Hund's rule
4.6: Electronic Structure of Atoms (Electron Configurations)

hybrid orbital
5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals

hybridization
5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals

hydrogen bonding
6.3: Intermolecular Forces

hydrostatic pressure
7.2: Gas Pressure

hypertonic
6.9: Colligative Properties

hypervalent molecule
5.5: Lewis Symbols and Structures

hypothesis:yes
10.2: The Concept of Chemical Equilibrium
10.3: The Equilibrium Constant
10.5: Non-equilibrium Conditions
10.6: Factors That Affect Equilibrium
10.7: Spontaneity and Equilibrium
11.2: Definitions of Acids and Bases
11.3: Acid-Base Reactions
11.4: The Autoionization of Water and Solution pH
11.5: Equilibria and pH of Weak Acid and Salt Solutions
11.6: Buffers
11.7: Acid-Base Titrations
12.3: Determining the Solubility of Ionic Compounds
12.4: Solubility and pH
12.5: Qualitative Analysis Using Selective Precipitation
13.4: Describing Electrochemical Cells
13.5: Standard Potentials
13.6: Comparing Strengths of Oxidants and Reductants
13.7: Electrochemical Cells and Thermodynamics
13.8: Electrolysis
14.2: The Components of the Nucleus
8.2: Energy Changes in Chemical Reactions
8.3: Enthalpy and Reactions
8.4: Thermodynamics and Work
8.5: The First Law of Thermodynamics
8.6: Direction of Heat Flow and Enthalpy of Reaction
8.7: Calorimetry
8.8: Hess's Law
8.9: Heats of Formation

hypotonic
6.9: Colligative Properties

I

ideal gas
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

ideal gas constant
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

ideal gas law
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

ideal solution
6.6: The Dissolution Process

immiscible
6.8: Solubility

induced dipole
6.3: Intermolecular Forces

inert gas
2.3: The Periodic Table

inert pair effect
5.2: Ionic Bonding

initial rate
9.2: Chemical Reaction Rates

inner transition metal
2.3: The Periodic Table

instantaneous dipole
6.3: Intermolecular Forces

instantaneous rate
9.2: Chemical Reaction Rates

integrated rate law
9.4: Integrated Rate Laws

Intensity
4.2: Electromagnetic Energy

interference pattern
4.2: Electromagnetic Energy

intermediate
9.8: Reaction Mechanisms

intermolecular force
6.3: Intermolecular Forces

international system of units
1.2: Measurements

interstitial sites
5.3: Metallic Bonding

ion
2.2: Atomic Structure and Symbolism

ion pair
6.9: Colligative Properties

ionic bond
2.4: Molecular and Ionic Compounds
5.2: Ionic Bonding

ionic compound
2.4: Molecular and Ionic Compounds

ionic solid
5.3: Metallic Bonding

ionization energy
4.7: Periodic Variations in Element Properties

ionization isomer
5.13: Coordinate Covalent Bonding is Different

isoelectronic
4.7: Periodic Variations in Element Properties

isotonic
6.9: Colligative Properties

K

Kelvin
1.2: Measurements

kilogram
1.2: Measurements

kinetic molecular theory
7.5: The Kinetic-Molecular Theory

L

lanthanide
2.3: The Periodic Table

Lattice Energy
5.6: Strengths of Ionic and Covalent Bonds

length
1.2: Measurements

Lewis formula
6.2: Skeletal Structures For Representing Organic Compounds

Lewis structure
5.5: Lewis Symbols and Structures

Lewis symbol
5.5: Lewis Symbols and Structures

ligand
5.13: Coordinate Covalent Bonding is Different

limiting reactant
3.8: Reaction Yields

line spectrum
4.2: Electromagnetic Energy

linear
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity

linkage isomer
5.13: Coordinate Covalent Bonding is Different

liter
1.2: Measurements
lone pair
5.5: Lewis Symbols and Structures

M

magnetic quantum number
4.5: Development of Quantum Theory
manometer
7.2: Gas Pressure
mass number
2.2: Atomic Structure and Symbolism
mean free path
7.6: Effusion and Diffusion of Gases
melting
6.4: Phase Transitions
melting point
6.4: Phase Transitions
metal
2.3: The Periodic Table
metallic solid
5.3: Metallic Bonding
metalloid
2.3: The Periodic Table
meter
1.2: Measurements
Method of Initial Rates
9.3: Rate Laws
microstates
8.13: Entropy
milliliter
1.2: Measurements
miscible
6.8: Solubility
molality
6.9: Colligative Properties
molar mass
3.2: Formula Mass and the Mole Concept
molarity
3.4: Molarity
mole
3.2: Formula Mass and the Mole Concept
mole fraction
7.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions
molecular compound
2.4: Molecular and Ionic Compounds
molecular equation
3.5: Writing and Balancing Chemical Equations
molecular formula
6.2: Skeletal Structures For Representing Organic Compounds
molecular orbital theory
5.12: Molecular Orbital Theory Resolves Issues in Other Bonding Theories
molecular solid
5.3: Metallic Bonding
molecular structure
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity
molecularity
9.8: Reaction Mechanisms
monatomic ion
2.4: Molecular and Ionic Compounds
monodentate
5.13: Coordinate Covalent Bonding is Different

N

net ionic equation
3.5: Writing and Balancing Chemical Equations
noble gas
2.3: The Periodic Table
node
4.2: Electromagnetic Energy
5.9: Valence Bond Theory Describes Bonds as Overlapping Atomic Orbitals
nomenclature
2.5: Chemical Nomenclature
nonelectrolyte
6.7: Dissolution of Electrolytes
nonmetal
2.3: The Periodic Table
nonpolar covalent bond
5.4: Covalent Bonding
nonspontaneous process
8.12: Spontaneity is Related to Entropy
normal boiling point
6.4: Phase Transitions

O

octahedral
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity
octet rule
5.5: Lewis Symbols and Structures
optical isomer
5.13: Coordinate Covalent Bonding is Different
orbital diagram
4.6: Electronic Structure of Atoms (Electron Configurations)
osmosis
6.9: Colligative Properties
osmotic pressure
6.9: Colligative Properties
overall reaction order
9.3: Rate Laws
overlap
5.9: Valence Bond Theory Describes Bonds as Overlapping Atomic Orbitals
oxidation
3.6: Classifying Chemical Reactions
oxidizing agent
3.6: Classifying Chemical Reactions
oxyacid
2.5: Chemical Nomenclature
oxyanion
2.4: Molecular and Ionic Compounds

P

p orbital
4.5: Development of Quantum Theory
pairing energy
5.14: Spectroscopic and Magnetic Properties of Coordination Compounds
paramagnetism
5.12: Molecular Orbital Theory Resolves Issues in Other Bonding Theories
parent nuclide
14.4: Kinetics of Radioactive Decay
partial pressure
7.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions
partially miscible
6.8: Solubility
Pascal
7.2: Gas Pressure
Pauli exclusion principle
4.5: Development of Quantum Theory
percent composition
3.3: Determining Empirical and Molecular Formulas
percent yield
3.8: Reaction Yields
period
2.3: The Periodic Table
periodic law
2.3: The Periodic Table
periodic table
2.3: The Periodic Table
phase diagram
6.5: Phase Diagrams
photon
4.2: Electromagnetic Energy
pi bond
5.9: Valence Bond Theory Describes Bonds as Overlapping Atomic Orbitals
pnictogen
2.3: The Periodic Table
polar covalent bond
5.4: Covalent Bonding
polar molecule
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity
Polarizability
6.3: Intermolecular Forces
polyatomic ion
2.4: Molecular and Ionic Compounds
polydentate ligand
5.13: Coordinate Covalent Bonding is Different
positron emission
14.4: Kinetics of Radioactive Decay
pounds per square inch
7.2: Gas Pressure
precipitate
3.6: Classifying Chemical Reactions
precipitation reaction
3.6: Classifying Chemical Reactions
precision
1.4: Significant Figures for Measurements and Calculations
1.5: Accuracy and Precision of Experimental Results (lab topic)
pressure
7.2: Gas Pressure
principal quantum number
4.5: Development of Quantum Theory
product
3.5: Writing and Balancing Chemical Equations

PSI (Unit)
7.2: Gas Pressure
pure covalent bond
5.4: Covalent Bonding

Q

quantization
4.2: Electromagnetic Energy
quantum mechanics
4.5: Development of Quantum Theory
quantum number
4.4: The Bohr Model

R

radioactive decay
14.4: Kinetics of Radioactive Decay
radioactive decay series
14.4: Kinetics of Radioactive Decay
radiocarbon dating
14.4: Kinetics of Radioactive Decay
radiometric dating
14.4: Kinetics of Radioactive Decay
Raoult's law
6.9: Colligative Properties
rate constant
9.3: Rate Laws
rate expression
9.2: Chemical Reaction Rates
rate law
9.3: Rate Laws
rate of diffusion
7.6: Effusion and Diffusion of Gases
rate of reaction
9.2: Chemical Reaction Rates
reactant
3.5: Writing and Balancing Chemical Equations
reaction mechanism
9.8: Reaction Mechanisms
reaction order
9.3: Rate Laws
reduction
3.6: Classifying Chemical Reactions
representative element
2.3: The Periodic Table
resonance
5.11: Valence Bond Treatment of Multiple Bonds
reversible process
8.13: Entropy
root mean square velocity
7.5: The Kinetic-Molecular Theory
rounding
1.4: Significant Figures for Measurements and Calculations
1.5: Accuracy and Precision of Experimental Results (lab topic)

S

s orbital
4.5: Development of Quantum Theory
saturated
6.8: Solubility
second
1.2: Measurements
semipermeable membrane
6.9: Colligative Properties
series
2.3: The Periodic Table
shell
4.5: Development of Quantum Theory
SI units
1.2: Measurements
sigma bond
5.9: Valence Bond Theory Describes Bonds as Overlapping Atomic Orbitals
significant figures
1.4: Significant Figures for Measurements and Calculations
1.5: Accuracy and Precision of Experimental Results (lab topic)
single bond
5.5: Lewis Symbols and Structures
skeletal formula
6.2: Skeletal Structures For Representing Organic Compounds
solubility
6.8: Solubility
solute
3.4: Molarity
solvation
6.6: The Dissolution Process
solvent
3.4: Molarity
sp hybrid orbital
5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals
sp2 hybrid orbital
5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals
sp3 hybrid orbital
5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals
sp3d hybrid orbital
5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals
sp3d2 hybrid orbital
5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals
spectator ion
3.5: Writing and Balancing Chemical Equations
spectrochemical series
5.14: Spectroscopic and Magnetic Properties of Coordination Compounds
spin quantum number
4.5: Development of Quantum Theory
spontaneous change
8.12: Spontaneity is Related to Entropy
spontaneous process
6.6: The Dissolution Process
standard conditions of temperature and pressure
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
standard free energy change
8.15: Temperature Dependence of Free Energy
standard free energy of formation
8.15: Temperature Dependence of Free Energy
standard molar volume
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
standing wave
4.2: Electromagnetic Energy
stoichiometric factor
3.7: Reaction Stoichiometry
stoichiometry
3.7: Reaction Stoichiometry
STP
7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
strong electrolyte
6.7: Dissolution of Electrolytes
sublimation
6.4: Phase Transitions
subshell
4.5: Development of Quantum Theory
supercritical fluid
6.5: Phase Diagrams
supersaturated
6.8: Solubility

T

t2g orbitals
5.14: Spectroscopic and Magnetic Properties of Coordination Compounds
termolecular reaction
9.8: Reaction Mechanisms
tetrahedral
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity
theoretical yield
3.8: Reaction Yields
Torr
7.2: Gas Pressure
trans configuration
5.13: Coordinate Covalent Bonding is Different
transition metal
2.3: The Periodic Table
trigonal bipyramidal
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity
trigonal planar
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity
triple bond
5.5: Lewis Symbols and Structures
triple point
6.5: Phase Diagrams

U

uncertainty
1.4: Significant Figures for Measurements and Calculations
1.5: Accuracy and Precision of Experimental Results (lab topic)
unified atomic mass unit
2.2: Atomic Structure and Symbolism
unimolecular reaction
9.8: Reaction Mechanisms
unit
1.2: Measurements

unsaturated
6.8: Solubility

V

vacancy
5.3: Metallic Bonding
valence bond theory
5.9: Valence Bond Theory Describes Bonds as Overlapping Atomic Orbitals
valence electrons
4.6: Electronic Structure of Atoms (Electron Configurations)
valence shell
4.6: Electronic Structure of Atoms (Electron Configurations)
valence shell electron pair repulsion theory
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity
van der Waals equation
7.7: Non-Ideal Gas Behavior
van der Waals force
6.3: Intermolecular Forces
van't Hoff factor
6.9: Colligative Properties
vapor pressure
6.4: Phase Transitions
vapor pressure of water
7.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions
vaporization
6.4: Phase Transitions
volume
1.2: Measurements
VSEPR
5.7: VSEPR Theory Predicts Molecular Structure and Shape
5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity

W

wave
4.2: Electromagnetic Energy
Wavefunction
4.5: Development of Quantum Theory
wavelength
4.2: Electromagnetic Energy
weak electrolyte
6.7: Dissolution of Electrolytes

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S

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    - 1.5: Accuracy and Precision of Experimental Results (lab topic) - *CC BY 4.0*
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    - 2.2: Atomic Structure and Symbolism - *CC BY 4.0*
    - 2.3: The Periodic Table - *CC BY 4.0*
    - 2.4: Molecular and Ionic Compounds - *CC BY 4.0*
    - 2.5: Chemical Nomenclature - *CC BY 4.0*
  - 3: Chemical Composition Involves Fixed Atomic Ratios - *CC BY 4.0*
    - 3.1: Overview and Objectives - *CC BY 4.0*
    - 3.2: Formula Mass and the Mole Concept - *CC BY 4.0*
    - 3.3: Determining Empirical and Molecular Formulas - *CC BY 4.0*
    - 3.4: Molarity - *CC BY 4.0*
    - 3.5: Writing and Balancing Chemical Equations - *CC BY 4.0*
    - 3.6: Classifying Chemical Reactions - *CC BY 4.0*
    - 3.7: Reaction Stoichiometry - *CC BY 4.0*
    - 3.8: Reaction Yields - *CC BY 4.0*
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    - 4.1: Overview and Objectives - *Undeclared*
    - 4.2: Electromagnetic Energy - *CC BY 4.0*
    - 4.3: Coulomb's Law and the Electrostatic Potential - *CC BY 4.0*
      - 4.3.1: Coulomb's Law and the Electrostatic Potential (Problems) - *CC BY 4.0*
    - 4.4: The Bohr Model - *CC BY 4.0*
    - 4.5: Development of Quantum Theory - *CC BY 4.0*
    - 4.6: Electronic Structure of Atoms (Electron Configurations) - *CC BY 4.0*
    - 4.7: Periodic Variations in Element Properties - *CC BY 4.0*
  - 5: Models for Chemical Bonding and Shape - *CC BY 4.0*
    - 5.1: Overview and Objectives - *CC BY 4.0*
    - 5.2: Ionic Bonding - *CC BY 4.0*
    - 5.3: Metallic Bonding - *CC BY 4.0*
    - 5.4: Covalent Bonding - *CC BY 4.0*
    - 5.5: Lewis Symbols and Structures - *CC BY 4.0*
    - 5.6: Strengths of Ionic and Covalent Bonds - *CC BY 4.0*
    - 5.7: VSEPR Theory Predicts Molecular Structure and Shape - *CC BY 4.0*
    - 5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity - *CC BY 4.0*
    - 5.9: Valence Bond Theory Describes Bonds as

Overlapping Atomic Orbitals - *CC BY 4.0*
- 5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals - *CC BY 4.0*
- 5.11: Valence Bond Treatment of Multiple Bonds - *CC BY 4.0*
- 5.12: Molecular Orbital Theory Resolves Issues in Other Bonding Theories - *CC BY 4.0*
- 5.13: Coordinate Covalent Bonding is Different - *CC BY 4.0*
- 5.14: Spectroscopic and Magnetic Properties of Coordination Compounds - *CC BY 4.0*

◦ 6: Intermolecular Interactions Drive Physical Properties - *CC BY 4.0*
- 6.1: Overview and Objectives - *CC BY 4.0*
- 6.2: Skeletal Structures For Representing Organic Compounds - *CC BY 4.0*
- 6.3: Intermolecular Forces - *CC BY 4.0*
- 6.4: Phase Transitions - *CC BY 4.0*
- 6.5: Phase Diagrams - *CC BY 4.0*
- 6.6: The Dissolution Process - *CC BY 4.0*
- 6.7: Dissolution of Electrolytes - *CC BY 4.0*
- 6.8: Solubility - *CC BY 4.0*
- 6.9: Colligative Properties - *CC BY 4.0*

◦ 7: The Gas Phase is Different - *CC BY 4.0*
- 7.1: Overview and Objectives - *CC BY 4.0*
- 7.2: Gas Pressure - *CC BY-NC-SA 3.0*
- 7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law - *CC BY-NC-SA 3.0*
- 7.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions - *CC BY-NC-SA 3.0*
- 7.5: The Kinetic-Molecular Theory - *CC BY-NC-SA 3.0*
- 7.6: Effusion and Diffusion of Gases - *CC BY-NC-SA 3.0*
- 7.7: Non-Ideal Gas Behavior - *CC BY-NC-SA 3.0*

◦ 8: Thermodynamics Describes the Flow of Energy - *Undeclared*
- 8.1: Overview and Objectives - *Undeclared*
- 8.2: Energy Changes in Chemical Reactions - *CC BY-NC-SA 3.0*
- 8.3: Enthalpy and Reactions - *CC BY-NC-SA 3.0*
- 8.4: Thermodynamics and Work - *CC BY-NC-SA 3.0*
- 8.5: The First Law of Thermodynamics - *CC BY-NC-SA 3.0*
- 8.6: Direction of Heat Flow and Enthalpy of Reaction - *CC BY-NC-SA 3.0*
- 8.7: Calorimetry - *CC BY-NC-SA 3.0*
- 8.8: Hess's Law - *CC BY-NC-SA 3.0*
- 8.9: Heats of Formation - *CC BY-NC-SA 3.0*
- 8.10: The Second Law of Thermodynamics - *CC BY-NC-SA 3.0*
- 8.11: Entropy Changes and the Third Law of Thermodynamics - *CC BY-NC-SA 3.0*
- 8.12: Spontaneity is Related to Entropy - *CC BY 4.0*
- 8.13: Entropy - *CC BY 4.0*
- 8.14: Free Energy is a Good Predictor of Spontaneity - *CC BY-NC-SA 3.0*
- 8.15: Temperature Dependence of Free Energy - *CC BY 4.0*
- 8.16: Free Energy - *CC BY-NC-SA 3.0*

◦ 9: Processes Start Out Under Kinetic Control - *CC BY 4.0*
- 9.1: Overview and Objectives - *CC BY 4.0*
- 9.2: Chemical Reaction Rates - *CC BY 4.0*
- 9.3: Rate Laws - *CC BY 4.0*
- 9.4: Integrated Rate Laws - *CC BY 4.0*
- 9.5: Factors Affecting Reaction Rates - *CC BY 4.0*
- 9.6: Catalysis - *CC BY 4.0*
- 9.7: Collision Theory - *CC BY 4.0*
- 9.8: Reaction Mechanisms - *CC BY 4.0*

◦ 10: Processes End Up At Equilibrium - *CC BY 4.0*
- 10.1: Overview and Objectives - *CC BY 4.0*
- 10.2: The Concept of Chemical Equilibrium - *CC BY-NC-SA 3.0*
- 10.3: The Equilibrium Constant - *CC BY-NC-SA 3.0*
- 10.4: Solving Equilibrium Problems - *CC BY-NC-SA 3.0*
- 10.5: Non-equilibrium Conditions - *CC BY-NC-SA 3.0*
- 10.6: Factors That Affect Equilibrium - *CC BY-NC-SA 3.0*
- 10.7: Spontaneity and Equilibrium - *CC BY-NC-SA 3.0*
- 10.8: Comparing Thermodynamics and Kinetics - *CC BY-NC-SA 4.0*

◦ 11: Acids and Bases Have Common Properties and Reactions - *CC BY 4.0*
- 11.1: Overview and Objectives - *CC BY 4.0*
- 11.2: Definitions of Acids and Bases - *CC BY-NC-SA 3.0*
- 11.3: Acid-Base Reactions - *CC BY-NC-SA 3.0*
- 11.4: The Autoionization of Water and Solution pH - *CC BY-NC-SA 3.0*
- 11.5: Equilibria and pH of Weak Acid and Salt Solutions - *CC BY-NC-SA 3.0*
- 11.6: Buffers - *CC BY-NC-SA 3.0*
- 11.7: Acid-Base Titrations - *CC BY-NC-SA 3.0*

◦ 12: Ionic Compounds Have Common Properties and Reactions - *CC BY 4.0*
- 12.1: Overview and Objectives - *CC BY 4.0*
- 12.2: Solubility and Molecular Structure - *CC BY-NC-SA 4.0*
- 12.3: Determining the Solubility of Ionic Compounds - *CC BY-NC-SA 3.0*
- 12.4: Solubility and pH - *CC BY-NC-SA 3.0*
- 12.5: Qualitative Analysis Using Selective Precipitation - *CC BY-NC-SA 3.0*

◦ 13: Redox Reactions Describe The Movement of Electrons - *CC BY 4.0*
- 13.1: Overview and Objectives - *CC BY 4.0*
- 13.2: Oxidation-Reduction Reactions - *CC BY-*

NC-SA 3.0
- 13.3: Balancing Redox Reactions - *CC BY 4.0*
- 13.4: Describing Electrochemical Cells - *CC BY-NC-SA 3.0*
- 13.5: Standard Potentials - *CC BY-NC-SA 3.0*
- 13.6: Comparing Strengths of Oxidants and Reductants - *CC BY-NC-SA 3.0*
- 13.7: Electrochemical Cells and Thermodynamics - *CC BY-NC-SA 3.0*
- 13.8: Electrolysis - *CC BY-NC-SA 3.0*

◦ 14: Atomic Nuclei Can Change - *CC BY 4.0*
- 14.1: Overview and Objectives - *CC BY 4.0*
- 14.2: The Components of the Nucleus - *CC BY-NC-SA 3.0*
- 14.3: Nuclear Reactions - *CC BY-NC-SA 3.0*
- 14.4: Kinetics of Radioactive Decay - *CC BY 4.0*

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    - 1.1: Overview and Objectives - *CC BY 4.0*
    - 1.2: Measurements - *CC BY 4.0*
    - 1.3: Dimensional Analysis for Calculations - *CC BY 4.0*
    - 1.4: Significant Figures for Measurements and Calculations - *CC BY 4.0*
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  - 2: Atoms Make Up Ionic and Covalent Compounds - *CC BY 4.0*
    - 2.1: Overview and Objectives - *CC BY 4.0*
    - 2.2: Atomic Structure and Symbolism - *CC BY 4.0*
    - 2.3: The Periodic Table - *CC BY 4.0*
    - 2.4: Molecular and Ionic Compounds - *CC BY 4.0*
    - 2.5: Chemical Nomenclature - *CC BY 4.0*
  - 3: Chemical Composition Involves Fixed Atomic Ratios - *CC BY 4.0*
    - 3.1: Overview and Objectives - *CC BY 4.0*
    - 3.2: Formula Mass and the Mole Concept - *CC BY 4.0*
    - 3.3: Determining Empirical and Molecular Formulas - *CC BY 4.0*
    - 3.4: Molarity - *CC BY 4.0*
    - 3.5: Writing and Balancing Chemical Equations - *CC BY 4.0*
    - 3.6: Classifying Chemical Reactions - *CC BY 4.0*
    - 3.7: Reaction Stoichiometry - *CC BY 4.0*
    - 3.8: Reaction Yields - *CC BY 4.0*
  - 4: Quantum Mechanics Describes Atomic Structure - *Undeclared*
    - 4.1: Overview and Objectives - *Undeclared*
    - 4.2: Electromagnetic Energy - *CC BY 4.0*
    - 4.3: Coulomb's Law and the Electrostatic Potential - *CC BY 4.0*
      - 4.3.1: Coulomb's Law and the Electrostatic Potential (Problems) - *CC BY 4.0*
    - 4.4: The Bohr Model - *CC BY 4.0*
    - 4.5: Development of Quantum Theory - *CC BY 4.0*
    - 4.6: Electronic Structure of Atoms (Electron Configurations) - *CC BY 4.0*
    - 4.7: Periodic Variations in Element Properties - *CC BY 4.0*
  - 5: Models for Chemical Bonding and Shape - *CC BY 4.0*
    - 5.1: Overview and Objectives - *CC BY 4.0*
    - 5.2: Ionic Bonding - *CC BY 4.0*
    - 5.3: Metallic Bonding - *CC BY 4.0*
    - 5.4: Covalent Bonding - *CC BY 4.0*
    - 5.5: Lewis Symbols and Structures - *CC BY 4.0*
    - 5.6: Strengths of Ionic and Covalent Bonds - *CC BY 4.0*
    - 5.7: VSEPR Theory Predicts Molecular Structure and Shape - *CC BY 4.0*
    - 5.8: Unequal Electron Distributions Produce Bond and Molecular Polarity - *CC BY 4.0*
    - 5.9: Valence Bond Theory Describes Bonds as

Overlapping Atomic Orbitals - *CC BY 4.0*
- 5.10: Valence Bond Theory Needs Hybrid Atomic Orbitals - *CC BY 4.0*
- 5.11: Valence Bond Treatment of Multiple Bonds - *CC BY 4.0*
- 5.12: Molecular Orbital Theory Resolves Issues in Other Bonding Theories - *CC BY 4.0*
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- 5.14: Spectroscopic and Magnetic Properties of Coordination Compounds - *CC BY 4.0*

◦ 6: Intermolecular Interactions Drive Physical Properties - *CC BY 4.0*
- 6.1: Overview and Objectives - *CC BY 4.0*
- 6.2: Skeletal Structures For Representing Organic Compounds - *CC BY 4.0*
- 6.3: Intermolecular Forces - *CC BY 4.0*
- 6.4: Phase Transitions - *CC BY 4.0*
- 6.5: Phase Diagrams - *CC BY 4.0*
- 6.6: The Dissolution Process - *CC BY 4.0*
- 6.7: Dissolution of Electrolytes - *CC BY 4.0*
- 6.8: Solubility - *CC BY 4.0*
- 6.9: Colligative Properties - *CC BY 4.0*

◦ 7: The Gas Phase is Different - *CC BY 4.0*
- 7.1: Overview and Objectives - *CC BY 4.0*
- 7.2: Gas Pressure - *CC BY-NC-SA 3.0*
- 7.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law - *CC BY-NC-SA 3.0*
- 7.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions - *CC BY-NC-SA 3.0*
- 7.5: The Kinetic-Molecular Theory - *CC BY-NC-SA 3.0*
- 7.6: Effusion and Diffusion of Gases - *CC BY-NC-SA 3.0*
- 7.7: Non-Ideal Gas Behavior - *CC BY-NC-SA 3.0*

◦ 8: Thermodynamics Describes the Flow of Energy - *Undeclared*
- 8.1: Overview and Objectives - *Undeclared*
- 8.2: Energy Changes in Chemical Reactions - *CC BY-NC-SA 3.0*
- 8.3: Enthalpy and Reactions - *CC BY-NC-SA 3.0*
- 8.4: Thermodynamics and Work - *CC BY-NC-SA 3.0*
- 8.5: The First Law of Thermodynamics - *CC BY-NC-SA 3.0*
- 8.6: Direction of Heat Flow and Enthalpy of Reaction - *CC BY-NC-SA 3.0*
- 8.7: Calorimetry - *CC BY-NC-SA 3.0*
- 8.8: Hess's Law - *CC BY-NC-SA 3.0*
- 8.9: Heats of Formation - *CC BY-NC-SA 3.0*
- 8.10: The Second Law of Thermodynamics - *CC BY-NC-SA 3.0*
- 8.11: Entropy Changes and the Third Law of Thermodynamics - *CC BY-NC-SA 3.0*
- 8.12: Spontaneity is Related to Entropy - *CC BY 4.0*
- 8.13: Entropy - *CC BY 4.0*
- 8.14: Free Energy is a Good Predictor of Spontaneity - *CC BY-NC-SA 3.0*
- 8.15: Temperature Dependence of Free Energy - *CC BY 4.0*
- 8.16: Free Energy - *CC BY-NC-SA 3.0*

◦ 9: Processes Start Out Under Kinetic Control - *CC BY 4.0*
- 9.1: Overview and Objectives - *CC BY 4.0*
- 9.2: Chemical Reaction Rates - *CC BY 4.0*
- 9.3: Rate Laws - *CC BY 4.0*
- 9.4: Integrated Rate Laws - *CC BY 4.0*
- 9.5: Factors Affecting Reaction Rates - *CC BY 4.0*
- 9.6: Catalysis - *CC BY 4.0*
- 9.7: Collision Theory - *CC BY 4.0*
- 9.8: Reaction Mechanisms - *CC BY 4.0*

◦ 10: Processes End Up At Equilibrium - *CC BY 4.0*
- 10.1: Overview and Objectives - *CC BY 4.0*
- 10.2: The Concept of Chemical Equilibrium - *CC BY-NC-SA 3.0*
- 10.3: The Equilibrium Constant - *CC BY-NC-SA 3.0*
- 10.4: Solving Equilibrium Problems - *CC BY-NC-SA 3.0*
- 10.5: Non-equilibrium Conditions - *CC BY-NC-SA 3.0*
- 10.6: Factors That Affect Equilibrium - *CC BY-NC-SA 3.0*
- 10.7: Spontaneity and Equilibrium - *CC BY-NC-SA 3.0*
- 10.8: Comparing Thermodynamics and Kinetics - *CC BY-NC-SA 4.0*

◦ 11: Acids and Bases Have Common Properties and Reactions - *CC BY 4.0*
- 11.1: Overview and Objectives - *CC BY 4.0*
- 11.2: Definitions of Acids and Bases - *CC BY-NC-SA 3.0*
- 11.3: Acid-Base Reactions - *CC BY-NC-SA 3.0*
- 11.4: The Autoionization of Water and Solution pH - *CC BY-NC-SA 3.0*
- 11.5: Equilibria and pH of Weak Acid and Salt Solutions - *CC BY-NC-SA 3.0*
- 11.6: Buffers - *CC BY-NC-SA 3.0*
- 11.7: Acid-Base Titrations - *CC BY-NC-SA 3.0*

◦ 12: Ionic Compounds Have Common Properties and Reactions - *CC BY 4.0*
- 12.1: Overview and Objectives - *CC BY 4.0*
- 12.2: Solubility and Molecular Structure - *CC BY-NC-SA 4.0*
- 12.3: Determining the Solubility of Ionic Compounds - *CC BY-NC-SA 3.0*
- 12.4: Solubility and pH - *CC BY-NC-SA 3.0*
- 12.5: Qualitative Analysis Using Selective Precipitation - *CC BY-NC-SA 3.0*

◦ 13: Redox Reactions Describe The Movement of Electrons - *CC BY 4.0*
- 13.1: Overview and Objectives - *CC BY 4.0*
- 13.2: Oxidation-Reduction Reactions - *CC BY-*

NC-SA 3.0
- 13.3: Balancing Redox Reactions - *CC BY 4.0*
- 13.4: Describing Electrochemical Cells - *CC BY-NC-SA 3.0*
- 13.5: Standard Potentials - *CC BY-NC-SA 3.0*
- 13.6: Comparing Strengths of Oxidants and Reductants - *CC BY-NC-SA 3.0*
- 13.7: Electrochemical Cells and Thermodynamics - *CC BY-NC-SA 3.0*
- 13.8: Electrolysis - *CC BY-NC-SA 3.0*

◦ 14: Atomic Nuclei Can Change - *CC BY 4.0*
- 14.1: Overview and Objectives - *CC BY 4.0*
- 14.2: The Components of the Nucleus - *CC BY-NC-SA 3.0*
- 14.3: Nuclear Reactions - *CC BY-NC-SA 3.0*
- 14.4: Kinetics of Radioactive Decay - *CC BY 4.0*

◦ Back Matter - *Undeclared*
- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*

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