MAP: CHEMISTRY (ZUMDAHL AND DECOSTE)

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Map: Chemistry (Zumdahl and Decoste)

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TABLE OF CONTENTS

1: Chemical Foundations

2: Atoms Molecules and Ions

3: Stoichiometry

4: Chemical Reactions

18: The Representative Elements

19: Transition Metals and Coordination Chemistry

20: The Nucleus A Chemists View

21: Organic and Biological Chemistry

6: Chemical Equilibrium

7: Acids and Bases

8: Equilibria in Aqueous Solutions

Index

Glossary

Detailed Licensing

Licensing

A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing****.*

CHAPTER OVERVIEW

1: Chemical Foundations

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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CHAPTER OVERVIEW

Front Matter

1: Chemical Foundations

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1.1: Chemistry: An Overview

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1.2: Chemistry Applications

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1.3: The Scientific Method

Learning Objectives

- To identify the components of the scientific method

Scientists search for answers to questions and solutions to problems by using a procedure called the **scientific method**. This procedure consists of making observations, formulating hypotheses, and designing experiments, which in turn lead to additional observations, hypotheses, and experiments in repeated cycles (Figure $1.3.1$).

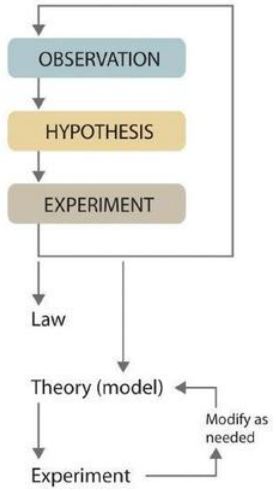


Figure $1.3.1$: The Scientific Method. As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

Observations can be qualitative or quantitative. Qualitative observations describe properties or occurrences in ways that do not rely on numbers. Examples of qualitative observations include the following: the outside air temperature is cooler during the winter season, table salt is a crystalline solid, sulfur crystals are yellow, and dissolving a penny in dilute nitric acid forms a blue solution and a brown gas. Quantitative observations are measurements, which by definition consist of both a number and a unit. Examples of quantitative observations include the following: the melting point of crystalline sulfur is 115.21 °C, and 35.9 grams of table salt—whose chemical name is sodium chloride—dissolve in 100 grams of water at 20 °C. An example of a quantitative observation was the initial observation leading to the modern theory of the dinosaurs' extinction: iridium concentrations in sediments dating to 66 million years ago were found to be 20–160 times higher than normal. The development of this theory is a good exemplar of the scientific method in action (see Figure $1.3.2$ below).

After deciding to learn more about an observation or a set of observations, scientists generally begin an investigation by forming a **hypothesis**, a tentative explanation for the observation(s). The hypothesis may not be correct, but it puts the scientist's understanding of the system being studied into a form that can be tested. For example, the observation that we experience alternating periods of light and darkness corresponding to observed movements of the sun, moon, clouds, and shadows is consistent with either of two hypotheses:

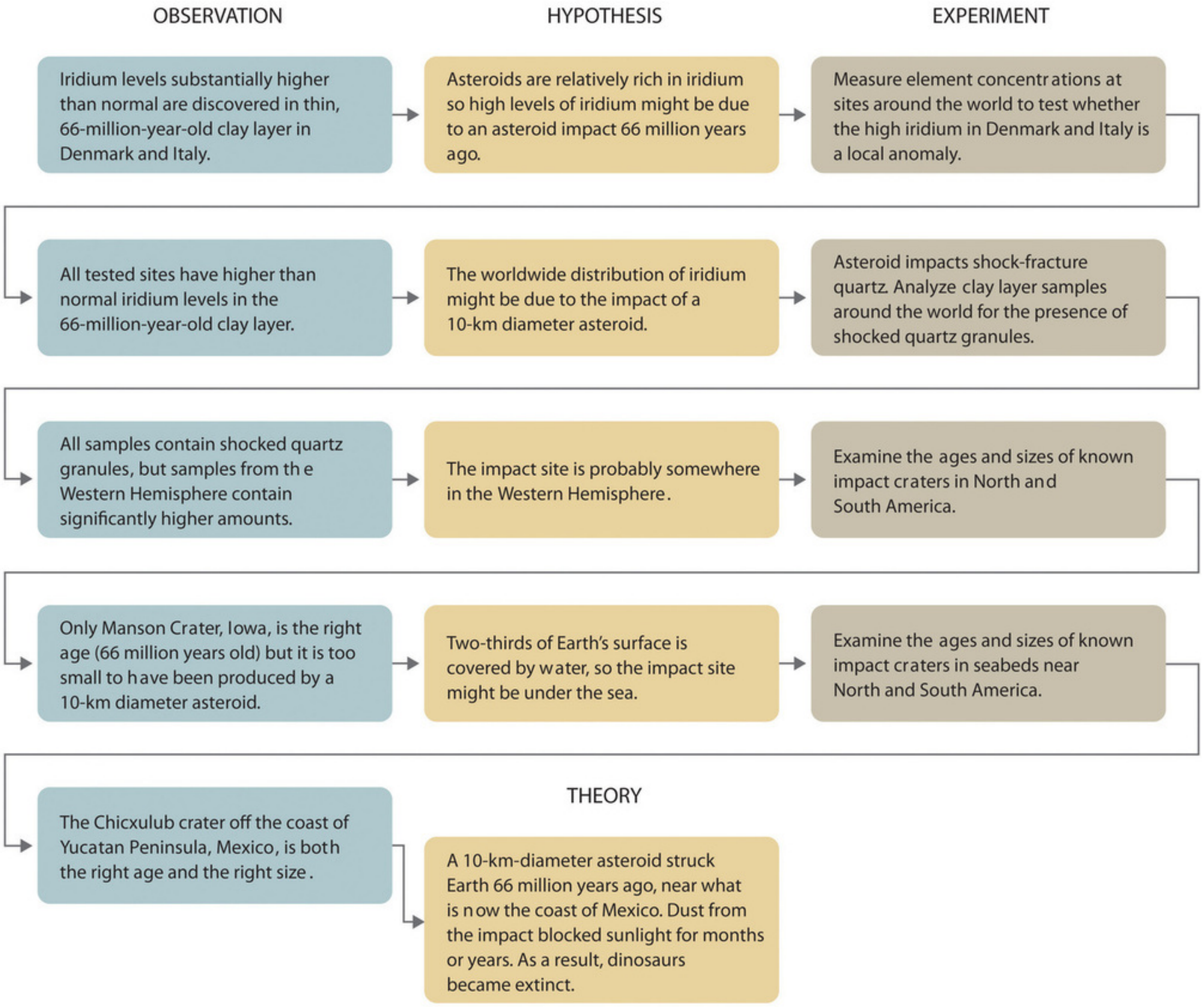
1. Earth rotates on its axis every 24 hours, alternately exposing one side to the sun, or
2. The sun revolves around Earth every 24 hours.

Suitable experiments can be designed to choose between these two alternatives. For the disappearance of the dinosaurs, the hypothesis was that the impact of a large extraterrestrial object caused their extinction. Unfortunately (or perhaps fortunately), this hypothesis does not lend itself to direct testing by any obvious experiment, but scientists collected additional data that either support or refute it.

After a hypothesis has been formed, scientists conduct experiments to test its validity. **Experiments** are systematic observations or measurements, preferably made under controlled conditions—that is, under conditions in which a single variable changes. For example, in the dinosaur extinction scenario, iridium concentrations were measured worldwide and compared. A properly designed and executed experiment enables a scientist to determine whether the original hypothesis is valid. Experiments often demonstrate that the hypothesis is incorrect or that it must be modified. More experimental data are then collected and analyzed, at which point a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in a **law**, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply says what happens; it does not address the question of why.

One example of a law, the Law of Definite Proportions, which was discovered by the French scientist Joseph Proust (1754–1826), states that a chemical substance always contains the same proportions of elements by mass. Thus sodium chloride (table salt) always contains the same proportion by mass of sodium to chlorine, in this case 39.34% sodium and 60.66% chlorine by mass, and sucrose (table sugar) is always 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass. Some solid compounds do not strictly obey the law of definite proportions. The law of definite proportions should seem obvious—we would expect the composition of sodium chloride to be consistent—but the head of the US Patent Office did not accept it as a fact until the early 20th century.

Whereas a law states only what happens, a **theory** attempts to explain why nature behaves as it does. Laws are unlikely to change greatly over time unless a major experimental error is discovered. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered. The theory developed to explain the extinction of the dinosaurs, for example, is that Earth occasionally encounters small- to medium-sized asteroids, and these encounters may have unfortunate implications for the continued existence of most species. This theory is by no means proven, but it is consistent with the bulk of evidence amassed to date. Figure 1.3.2 summarizes the application of the scientific method in this case.



Iridium levels substantially higher than normal are discovered in thin, 66-million-year-old clay layer in Denmark and Italy.

Asteroids are relatively rich in iridium so high levels of iridium might be due to an asteroid impact 66 million years ago.

Measure element concentrations at sites around the world to test whether the high iridium in Denmark and Italy is a local anomaly.

All tested sites have higher than normal iridium levels in the 66-million-year-old clay layer.

The worldwide distribution of iridium might be due to the impact of a 10-km diameter asteroid.

Asteroid impacts shock-fracture quartz. Analyze clay layer samples around the world for the presence of shocked quartz granules.

All samples contain shocked quartz granules, but samples from the Western Hemisphere contain significantly higher amounts.

The impact site is probably somewhere in the Western Hemisphere.

Examine the ages and sizes of known impact craters in North and South America.

Only Manson Crater, Iowa, is the right age (66 million years old) but it is too small to have been produced by a 10-km diameter asteroid.

Two-thirds of Earth's surface is covered by water, so the impact site might be under the sea.

Examine the ages and sizes of known impact craters in seabeds near North and South America.

The Chicxulub crater off the coast of Yucatan Peninsula, Mexico, is both the right age and the right size.

A 10-km-diameter asteroid struck Earth 66 million years ago, near what is now the coast of Mexico. Dust from the impact blocked sunlight for months or years. As a result, dinosaurs became extinct.

Figure 1.3.2: A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth

✓ Example 1.3.1

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Ice always floats on liquid water.
b. Birds evolved from dinosaurs.
c. Hot air is less dense than cold air, probably because the components of hot air are moving more rapidly.
d. When 10 g of ice were added to 100 mL of water at 25 °C, the temperature of the water decreased to 15.5 °C after the ice melted.
e. The ingredients of Ivory soap were analyzed to see whether it really is 99.44% pure, as advertised.

Given: components of the scientific method

Asked for: statement classification

Strategy: Refer to the definitions in this section to determine which category best describes each statement.

Solution

a. This is a general statement of a relationship between the properties of liquid and solid water, so it is a law.
b. This is a possible explanation for the origin of birds, so it is a hypothesis.
c. This is a statement that tries to explain the relationship between the temperature and the density of air based on fundamental principles, so it is a theory.
d. The temperature is measured before and after a change is made in a system, so these are quantitative observations.
e. This is an analysis designed to test a hypothesis (in this case, the manufacturer's claim of purity), so it is an experiment.

? Exercise 1.3.1

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Measured amounts of acid were added to a Rolaids tablet to see whether it really "consumes 47 times its weight in excess stomach acid."
b. Heat always flows from hot objects to cooler ones, not in the opposite direction.
c. The universe was formed by a massive explosion that propelled matter into a vacuum.
d. Michael Jordan is the greatest pure shooter ever to play professional basketball.
e. Limestone is relatively insoluble in water but dissolves readily in dilute acid with the evolution of a gas.
f. Gas mixtures that contain more than 4% hydrogen in air are potentially explosive.

Answer a

experiment

Answer b

law

Answer c

theory

Answer d

hypothesis

Answer e

qualitative observation

Answer f

quantitative observation

Because scientists can enter the cycle shown in Figure 1.3.1 at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

It is important to remember that scientists have a tendency to formulate hypotheses in familiar terms simply because it is difficult to propose something that has never been encountered or imagined before. As a result, scientists sometimes discount or overlook unexpected findings that disagree with the basic assumptions behind the hypothesis or theory being tested. Fortunately, truly important findings are immediately subject to independent verification by scientists in other laboratories, so science is a self-correcting discipline. When the Alvarezes originally suggested that an extraterrestrial impact caused the extinction of the dinosaurs, the response was almost universal skepticism and scorn. In only 20 years, however, the persuasive nature of the evidence overcame the skepticism of many scientists, and their initial hypothesis has now evolved into a theory that has revolutionized paleontology and geology.

Summary

Chemists expand their knowledge by making observations, carrying out experiments, and testing hypotheses to develop laws to summarize their results and theories to explain them. In doing so, they are using the scientific method.

Fundamental Definitions in Chemistry: https://youtu.be/SBwjbkFNkdw

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1.4: Chemistry in Industry

Learning Objectives

- Recognize the SI base units and explain the system of prefixes used with them.
- Define and calculate density.

People who live in the United States measure weight in pounds, height in feet and inches, and a car's speed in miles per hour. In contrast, chemistry and other branches of science use the International System of Units (also known as **SI** after *Système Internationale d'Unités*), which was established so that scientists around the world could communicate efficiently with each other. Many countries have also adopted SI units for everyday use as well. The United States is one of the few countries that has not.

Base SI Units

Base (or basic) units, are the fundamental units of SI. There are seven base units, which are listed in Table 1.4.1, Chemistry uses five of the base units: the mole for amount, the kilogram for mass, the meter for length, the second for time, and the kelvin for temperature. The degree Celsius (°C) is also commonly used for temperature. The numerical relationship between kelvins and degrees Celsius is as follows:

$$K = {}^{\circ}C + 273 \tag{1.4.1}$$

Table 1.4.1: The Seven Base SI Units

Property	Unit	Abbreviation
length	meter	m
mass	kilogram	kg
time	second	s
amount	mole	mol
temperature	kelvin	K
electrical current	ampere	amp
luminous intensity	candela	cd

> The United States uses the English (sometimes called Imperial) system of units for many quantities. Inches, feet, miles, gallons, pounds, and so forth, are all units connected with the English system of units. There have been many mistakes due to the improper conversion of units between the SI and English systems.

The size of each base unit is defined by international convention. For example, the *kilogram* is defined as the quantity of mass of a special metal cylinder kept in a vault in France (Figure 1.4.1). The other base units have similar definitions and standards. The sizes of the base units are not always convenient for all measurements. For example, a meter is a rather large unit for describing the width of something as narrow as human hair. Instead of reporting the diameter of hair as 0.00012 m or as 1.2×10^{-4} m using scientific notation as discussed in section 1.4, SI also provides a series of **prefixes** that can be attached to the units, creating units that are larger or smaller by powers of 10.

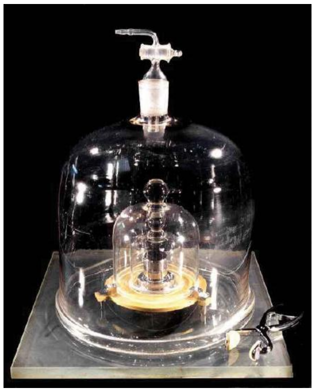

Figure 1.4.1: The Kilogram. The standard for the kilogram is a platinum-iridium cylinder kept in a special vault in France. Source: Photo reproduced by permission of the Bureau International des Poids et Mesures, who retain full internationally protected copyright.

Common prefixes and their multiplicative factors are listed in Table 1.4.2. (Perhaps you have already noticed that the base unit *kilogram* is a combination of a prefix, kilo- meaning 1,000 ×, and a unit of mass, the gram.) Some prefixes create a multiple of the original unit: 1 kilogram equals 1,000 grams, and 1 megameter equals 1,000,000 meters. Other prefixes create a fraction of the original unit. Thus, 1 centimeter equals 1/100 of a meter, 1 millimeter equals 1/1,000 of a meter, 1 microgram equals 1/1,000,000 of a gram, and so forth.

Table 1.4.2: Prefixes Used with SI Units

Prefix	Abbreviation	Multiplicative Factor	Multiplicative Factor in Scientific Notation
giga-	G	1,000,000,000 ×	10^9 ×
mega-	M	1,000,000 ×	10^6 ×
kilo-	k	1,000 ×	10^3 ×
deca-	D	10 ×	10^1 ×
deci-	d	1/10 ×	10^{-1} ×
centi-	c	1/100 ×	10^{-2} ×
milli-	m	1/1,000 ×	10^{-3} ×
micro-	µ*	1/1,000,000 ×	10^{-6} ×
nano-	n	1/1,000,000,000 ×	10^{-9} ×

*The letter µ is the Greek lowercase letter for *m* and is called “mu,” which is pronounced “myoo.”

Both SI units and prefixes have abbreviations, and the combination of a prefix abbreviation with a base unit abbreviation gives the abbreviation for the modified unit. For example, kg is the abbreviation for kilogram. We will be using these abbreviations throughout this book.

The Difference Between Mass and Weight

The mass of a body is a measure of its inertial property or how much matter it contains. The weight of a body is a measure of the force exerted on it by gravity or the force needed to support it. Gravity on earth gives a body a downward acceleration of about 9.8 m/s^2. In common parlance, weight is often used as a synonym for mass in weights and measures. For instance, the verb “to weigh” means “to determine the mass of” or “to have a mass of.” The incorrect use of weight in place of mass should be phased out, and the term mass used when mass is meant. The SI unit of mass is the kilogram (kg). In science and technology, the weight of a body in a particular reference frame is defined as the force that gives the body an acceleration equal to the local acceleration of free fall in that reference frame. Thus, the SI unit of the quantity weight defined in this way (force) is the newton (N).

Derived SI Units

Derived units are combinations of SI base units. Units can be multiplied and divided, just as numbers can be multiplied and divided. For example, the area of a square having a side of 2 cm is 2 cm × 2 cm, or 4 cm^2 (read as "four centimeters squared" or "four square centimeters"). Notice that we have squared a length unit, the centimeter, to get a derived unit for area, the square centimeter.

Volume is an important quantity that uses a derived unit. **Volume** is the amount of space that a given substance occupies and is defined geometrically as length × width × height. Each distance can be expressed using the meter unit, so volume has the derived unit m × m × m, or m^3 (read as "meters cubed" or "cubic meters"). A cubic meter is a rather large volume, so scientists typically express volumes in terms of 1/1,000 of a cubic meter. This unit has its own name—the liter (L). A liter is a little larger than 1 US quart in volume. Below are approximate equivalents for some of the units used in chemistry.

Approximate Equivalents to Some SI Units

- 1 m ≈ 39.36 in. ≈ 3.28 ft ≈ 1.09 yd
- 1 in. ≈ 2.54 cm
- 1 km ≈ 0.62 mi
- 1 kg ≈ 2.20 lb
- 1 lb ≈ 454 g
- 1 L ≈ 1.06 qt
- 1 qt ≈ 0.946 L

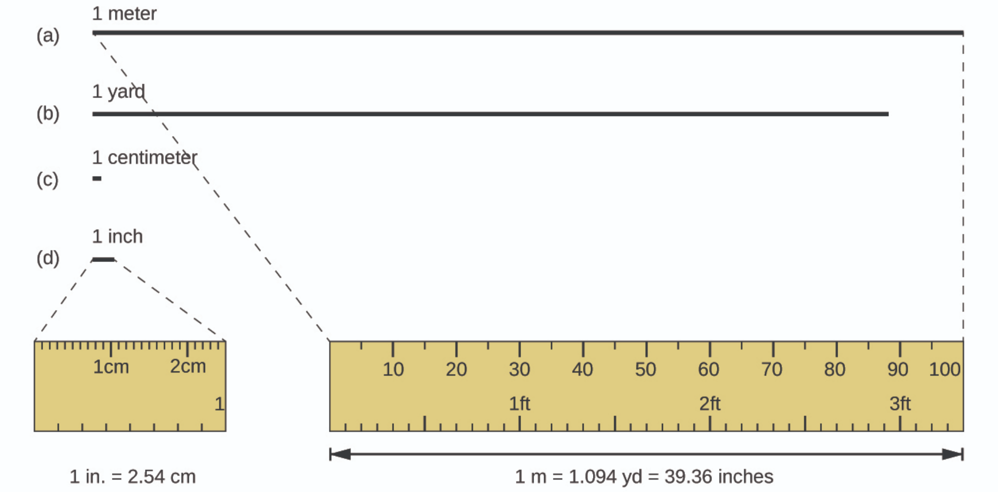

Figure 1.4.2: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd. (CC BY 4.0; OpenStax)

As shown in Figure 1.4.3, a liter is also 1,000 cm^3. By definition, there are 1,000 mL in 1 L, so 1 milliliter and 1 cubic centimeter represent the same volume.

$$1\ mL = 1\ cm^3 \tag{1.4.2}$$

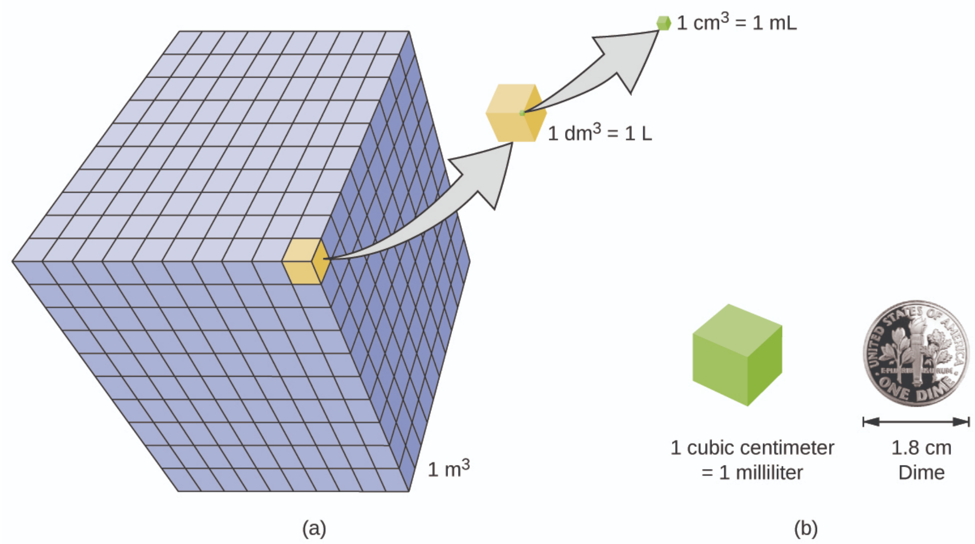

Figure 1.4.3: Units of Volume. (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). A liter (L) is defined as a cube 1 dm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter. (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube. (CC BY 4.0; OpenStax)

✓ Example 1.4.1

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kiloliter
b. microsecond
c. decimeter
d. nanogram

Answer a

The abbreviation for a kiloliter is kL. Because kilo means “1,000 ×,” 1 kL equals 1,000 L.

Answer b

The abbreviation for microsecond is µs. Micro implies 1/1,000,000th of a unit, so 1 µs equals 0.000001 s.

Answer c

The abbreviation for decimeter is dm. Deci means 1/10th, so 1 dm equals 0.1 m.

Answer d

The abbreviation for nanogram is ng and equals 0.000000001 g.

? Exercise 1.4.1

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kilometer
b. milligram
c. nanosecond
d. centiliter

Answer a

km (1,000 m)

Answer b

mg (0.001 g)

Answer c

ns (0.000000001 s)

Answer d

cL (0.01L)

Energy, another important quantity in chemistry, is the ability to perform work, such as moving a box of books from one side of a room to the other side. It has a derived unit of kg•m^2/s^2. (The dot between the kg and m units implies the units are multiplied together.) Because this combination is cumbersome, this collection of units is redefined as a **joule** (J). An older unit of energy, but likely more familiar to you, the calorie (cal), is also widely used. There are 4.184 J in 1 cal. Energy changes occur during all chemical processes and will be discussed in a later chapter.

To Your Health: Energy and Food

The food in our diet provides the energy our bodies need to function properly. The energy contained in food could be expressed in joules or calories, which are the conventional units for energy, but the food industry prefers to use the kilocalorie and refers to it as the Calorie (with a capital C). The average daily energy requirement of an adult is about 2,000–2,500 Calories, which is 2,000,000–2,500,000 calories (with a lowercase c).

If we expend the same amount of energy that our food provides, our body weight remains stable. If we ingest more Calories from food than we expend, however, our bodies store the extra energy in high-energy-density compounds, such as fat, and we gain weight. On the other hand, if we expend more energy than we ingest, we lose weight. Other factors affect our weight as well—genetic, metabolic, behavioral, environmental, cultural factors—but dietary habits are among the most important.

In 2008 the US Centers for Disease Control and Prevention issued a report stating that 73% of Americans were either overweight or obese. More alarmingly, the report also noted that 19% of children aged 6–11 and 18% of adolescents aged 12–19 were overweight—numbers that had tripled over the preceding two decades. Two major reasons for this increase are excessive calorie consumption (especially in the form of high-fat foods) and reduced physical activity. Partly because of that report, many restaurants and food companies are working to reduce the amounts of fat in foods and provide consumers with more healthy food options.

Density is defined as the mass of an object divided by its volume; it describes the amount of matter contained in a given amount of space.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.4.3}$$

Thus, the units of density are the units of mass divided by the units of volume: g/cm^3 or g/mL (for solids and liquids), g/L (for gases), kg/m^3, and so forth. For example, the density of water is about 1.00 g/cm^3, while the density of mercury is 13.6 g/mL. (Remember that 1 mL equals 1 cm^3.) Mercury is over 13 times as dense as water, meaning that it contains over 13 times the amount of matter in the same amount of space. The density of air at room temperature is about 1.3 g/L. Table 1.6.3 shows the densities of some common substances.

Table 1.4.2: 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
oak (wood) 0.60–0.90 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
iron 7.9 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L
copper 9.0 g/cm^3	glycerin 1.26 g/cm^3	carbon dioxide 1.80 g/L
lead 11.3 g/cm^3	olive oil 0.92 g/cm^3	helium 0.16 g/L
silver 10.5 g/cm^3	gasoline 0.70–0.77 g/cm^3	neon 0.83 g/L
gold 19.3 g/cm^3	mercury 13.6 g/cm^3	radon 9.1 g/L

✓ Example 1.4.2: Density of Bone

What is the density of a section of bone if a 25.3 cm^3 sample has a mass of 27.8 g?

Solution

Because density is defined as the mass of an object divided by its volume, we can set up the following relationship:

$$\begin{aligned}\text{density} &= \frac{mass}{volume} \\ &= \frac{27.8\ g}{25.3\ cm^3} \\ &= 1.10\ g/cm^3\end{aligned}$$

Note that we have limited our final answer to three significant figures.

? Exercise 1.4.2: Density of Oxygen

What is the density of oxygen gas if a 15.0 L sample has a mass of 21.7 g?

Answer

1.45 g/L

Density can be used to convert between the mass and the volume of a substance. This will be discussed in the next section.

Concept Review Exercises

1. What is the difference between a base unit and a derived unit? Give two examples of each type of unit.

2. Do units follow the same mathematical rules as numbers do? Give an example to support your answer.

3. What is density?

Answers

1. Base units are the seven fundamental units of SI; derived units are constructed by making combinations of the base units; Two examples of base units: kilograms and meters (answers will vary); Two examples of derived units: grams per milliliter and joules (answers will vary).

2. yes; $\text{mL} \times \frac{\text{g}}{\text{mL}} = \text{g}$ (answers will vary)

3. Density is defined as the mass of an object divided by its volume

Key Takeaways

- Recognize the SI base units and derived units.
- Combining prefixes with base units creates new units of larger or smaller sizes.

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1.5: Polymer Chemistry

All measurements have a degree of uncertainty regardless of precision and accuracy. This is caused by two factors, the limitation of the measuring instrument (systematic error) and the skill of the experimenter making the measurements (random error).

Introduction

The graduated buret in Figure 1 contains a certain amount of water (with yellow dye) to be measured. The amount of water is somewhere between 19 ml and 20 ml according to the marked lines. By checking to see where the bottom of the meniscus lies, referencing the ten smaller lines, the amount of water lies between 19.8 ml and 20 ml. The next step is to estimate the uncertainty between 19.8 ml and 20 ml. Making an approximate guess, the level is less than 20 ml, but greater than 19.8 ml. We then report that the measured amount is approximately 19.9 ml. The graduated cylinder itself may be distorted such that the graduation marks contain inaccuracies providing readings slightly different from the actual volume of liquid present.

Figure 1: *A meniscus as seen in a burette of colored water. '20.00 mL' is the correct depth measurement. Click here for a more complete description on buret use, including proper reading. Figure used with permission from Wikipedia.*

Systematic vs. Random Error

The diagram below illustrates the distinction between **systematic** and **random** errors.

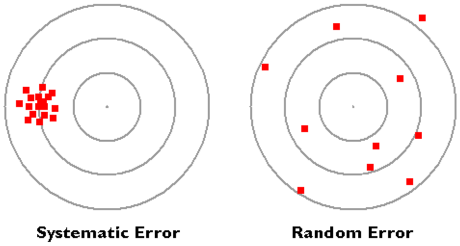
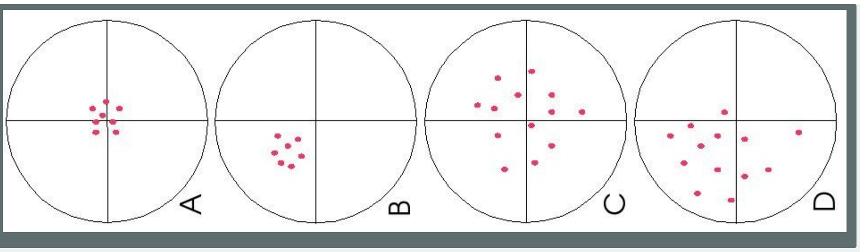


Figure 2: *Systematic and random errors. Figure used with permission from David DiBiase (Penn State U).*

Systematic errors: When we use tools meant for measurement, we assume that they are correct and accurate, however measuring tools are not always right. In fact, they have errors that naturally occur called **systematic errors**. Systematic errors tend to be consistent in magnitude and/or direction. If the magnitude and direction of the error is known, accuracy can be improved by additive or proportional corrections. **Additive correction** involves adding or subtracting a constant adjustment factor to each measurement; **proportional correction** involves multiplying the measurement(s) by a constant.

Random errors: Sometimes called human error, random error is determined by the experimenter's skill or ability to perform the experiment and read scientific measurements. These errors are random since the results yielded may be too high or low. Often random error determines the precision of the experiment or limits the precision. For example, if we were to time a revolution of a steadily rotating turnable, the random error would be the reaction time. Our reaction time would vary due to a delay in starting (an underestimate of the actual result) or a delay in stopping (an overestimate of the actual result). Unlike systematic errors, random errors vary in magnitude and direction. It is possible to calculate the average of a set of measured positions, however, and that average is likely to be more accurate than most of the measurements.



5. Since Tom must rely on the machine for an absorbance reading and it provides consistently different measurements, this is an example of systematic error.
6. The majority of Claire's variation in time can likely be attributed to random error such as fatigue after multiple laps, inconsistency in swimming form, slightly off timing in starting and stopping the stop watch, or countless other small factors that alter lap times. To a much smaller extent, the stop watch itself may have errors in keeping time resulting in systematic error.
7. The researcher's percent error is about 0.62%.
8. This is known as multiplier or scale factor error.
9. This is called an offset or zero setting error.
10. Susan's percent error is -7.62%. This percent error is negative because the measured value falls *below* the accepted value. In problem 7, the percent error was positive because it was *higher* than the accepted value.
11. You would first weigh the beaker itself. After obtaining the weight, then you add the graphite in the beaker and weigh it. After obtaining this weight, you then subtract the weight of the graphite plus the beaker minus the weight of the beaker.

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- **Uncertainties in Measurements** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

Back Matter

Index

CHAPTER OVERVIEW

2: Atoms Molecules and Ions

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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2.1 The Early History of Chemistry

Timeline of Chemistry

- Wikipedia Link: Timeline of Chemistry

the-mole-and-avogadro-s-number

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2.2 Fundamental Chemical Laws

Learning Objectives

- Explain how all matter is composed of atoms.
- Describe the modern atomic theory.

Take some aluminum foil. Cut it in half. Now there are two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil. It should be obvious that the pieces are still aluminum foil; they are just becoming smaller and smaller. But how far can this exercise be taken, at least in theory? Can one continue cutting the aluminum foil into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of aluminum foil? Thought experiments like this—and the conclusions based on them—were debated as far back as the fifth century BC.

John Dalton (1766-1844) is the scientist credited for proposing the atomic theory. The theory explains several concepts that are relevant in the observable world: the composition of a pure gold necklace, what makes the pure gold necklace different than a pure silver necklace, and what occurs when pure gold is mixed with pure copper. This section explains the theories that Dalton used as a basis for his theory: (1) Law of Conservation of Mass, (2) Law of Definite Proportions, and (3) Law of Multiple Proportions

Law 1: The Conservation of Mass

"Nothing comes from nothing" is an important idea in ancient Greek philosophy that argues that what exists **now** has always **existed**, since no new matter can come into existence where there was none before. Antoine Lavoisier (1743-1794) restated this principle for chemistry with the law of conservation of mass, which "means that the atoms of an object cannot be created or destroyed, but can be moved around and be changed into different particles." This law says that when a chemical reaction rearranges atoms into a new product, the mass of the reactants (chemicals before the chemical reaction) is the same as the mass of the products (the new chemicals made). More simply, whatever you do, you will still have the same amount of stuff (however, certain nuclear reactions like fusion and fission can convert a small part of the mass into energy.

The law of conservation of mass states that the total mass present before a chemical reaction is the same as the total mass present after the chemical reaction; in other words, **mass is conserved**. The law of conservation of mass was formulated by Lavoisier as a result of his combustion experiment, in which he observed that the mass of his original substance—a glass vessel, tin, and air—was equal to the mass of the produced substance—the glass vessel, “tin calx”, and the remaining air.

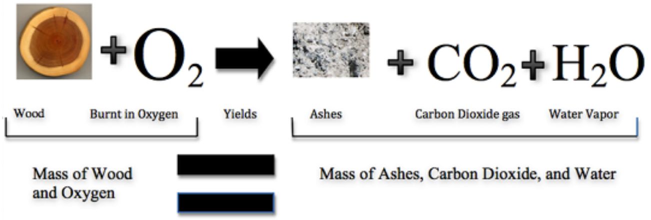

Figure 1: Image of the wood courtesy of Ehamberg and Stannered on Wikimedia Commons, available under Creative Commons Attribution 2.5 Generic license. Image of ashes courtesy of Walter Siegmund. Image as a whole constructed by Jessica Thornton (UCD).
Chemical equation; wood + oxygen yields ashes + carbon dioxide gas + water vapor. The mass of wood and oxygen equals the mass of ashes, carbon dioxide, and water.

Historically, this was a difficult concept for scientists to grasp. If this law was true, then how could a large piece of wood be reduced to a small pile of ashes? The wood clearly has a greater mass than the ashes. From this observation scientists concluded that mass had been lost. However, Figure 1 shows that the burning of word does follow the law of conservation of mass. Scientists did not account for the gases that play a critical role in this reaction.

> *The law of conservation of mass states that the total mass present before a chemical reaction is the same as the total mass present after the chemical reaction.*

Law 2: Definite Proportions

Joseph Proust (1754-1826) formulated the *law of definite proportions* (also called the **Law of Constant *Composition*** or **Proust's Law**). This law states that if a compound is broken down into its constituent elements, the masses of the constituents will always have the same proportions, regardless of the quantity or source of the original substance. Joseph Proust based this law primarily on his experiments with basic copper carbonate. The illustration below depicts this law in action.

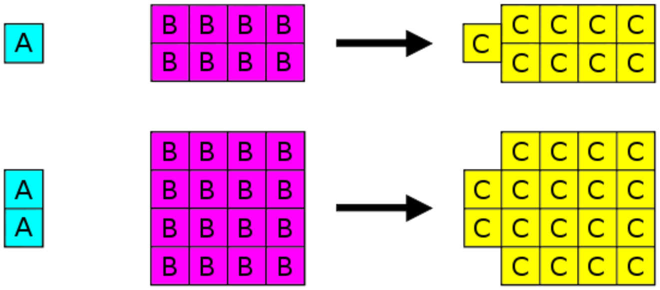

Figure 2: If 1 gram of A reacts with 8 grams of B, then by the Law of Definite Proportions, 2 grams of A must react with 16 grams of B. If 1 gram of A reacts with 8 grams of B, then by the Law of Conservation of Mass, they must produce 9 grams of C. Similarly, when 2 grams of A react with 16 grams of B, they must produce 18 grams of C.

Top: Single block labelled A. Eight blocks labelled B with arrow pointing to nine blocks labelled C. Bottom: Two blocks labelled A. Sixteen blocks labelled B with arrow pointing to eighteen blocks labelled C.

> *Law of Definite Proportions states that in a given type of chemical substance, the elements are always combined in the same proportions by mass.*

The Law of Definite Proportions applies when elements are reacted together to form *the same* product. Therefore, while the Law of Definite Proportions can be used to compare two experiments in which hydrogen and oxygen react to form water, the Law of Definite Proportions can *not* be used to compare one experiment in which hydrogen and oxygen react to form water, and another experiment in which hydrogen and oxygen react to form hydrogen peroxide (peroxide is another material that can be made from hydrogen and oxygen).

✓ Example 1: water

Oxygen makes up 88.8% of the mass of any sample of pure water, while hydrogen makes up the remaining 11.2% of the mass. You can get water by melting ice or snow, by condensing steam, from river, sea, pond, etc. It can be from different places: USA, UK, Australia, or anywhere. It can be made by chemical reactions like burning hydrogen in oxygen.

However, if the water is **pure**, it will **always** consist of 88.8 % oxygen by mass and 11.2 % hydrogen by mass, irrespective of its source or method of preparation.

Law 3: Multiple Proportions

Many combinations of elements can react to form more than one compound. In such cases, this law states that the weights of one element that combine with a fixed weight of another of these elements are integer multiples of one another. It's easy to say this, but please make sure that you understand how it works. Nitrogen forms a very large number of oxides, five of which are shown here.

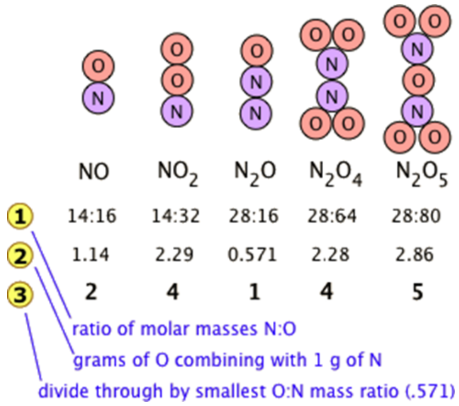

Figure 3: Law of Multiple Proportions applied to nitrogen oxides (NO_x) compounds. Table of several nitrogen-oxygen compounds. Column headings, left to right: N O, N O 2, N 2 O, N 2 O 4, N 2 O 5. Second row heading: ratio of molar masses N:O. Values, left to right: 14:16, 14:32, 28:16, 28:64, 28:80. Second row heading: grams of O combining with 1 gram of N. Values: 1.14, 2.29, 0.571, 2.28, 2.86. Third row heading: divide through by smallest O:N mass ratio (.571). Values: 2, 4, 1, 4, 5. (CC-BY; Stephen Lower)

- Line ① shows the ratio of the relative weights of the two elements in each compound. These ratios were calculated by simply taking the molar mass of each element, and multiplying by the number of atoms of that element per mole of the compound. Thus for NO_2, we have (1 × 14) : (2 × 16) = 14:32. (These numbers were not known in the early days of Chemistry because atomic weights (i.e., molar masses) of most elements were not reliably known.)
- The numbers in Line ② are just the mass ratios of O:N, found by dividing the corresponding ratios in line 1. But someone who depends solely on experiment would work these out by finding the mass of O that combines with unit mass (1 g) of nitrogen.
- Line is obtained by dividing the figures the previous line by the smallest O:N ratio in the line above, which is the one for N_2O. Note that just as the law of multiple proportions says, the weight of oxygen that combines with unit weight of nitrogen work out to small integers.
- Of course we just as easily could have illustrated the law by considering the mass of nitrogen that combines with one gram of oxygen; it works both ways!

> *The law of multiple proportions states that if two elements form more than one compound between them, the masses of one element combined with a fixed mass of the second element form in ratios of small integers.*

✓ Example 2: Oxides of Carbon

Consider two separate compounds are formed by only carbon and oxygen. The first compound contains 42.9% carbon and 57.1% oxygen (by mass) and the second compound contains 27.3% carbon and 72.7% oxygen (again by mass). Is this consistent with the law of multiple proportions?

Solution

The *Law of Multiple Proportions* states that the masses of one element which combine with a fixed mass of the second element are in a ratio of **whole** numbers. Hence, the masses of oxygen in the two compounds that combine with a fixed mass of carbon should be in a whole-number ratio.

Thus for every 1 g of the first compound there are 0.57 g of oxygen and 0.429 g of carbon. The mass of oxygen per gram carbon is:

$$\frac{0.571 \text{ g oxygen}}{0.429 \text{ g carbon}} = 1.33 \frac{\text{g oxygen}}{\text{g carbon}}$$

Similarly, for 1 g of the second compound, there are 0.727 g oxygen and 0.273 g of carbon. The ration of mass of oxygen per gram of carbon is

$$\frac{0.727 \text{ g oxygen}}{0.273 \text{ g carbon}} = 2.66 \frac{\text{g oxygen}}{\text{g carbon}}$$

Dividing the mass of oxygen per g of carbon of the second compound:

$$\frac{2.66}{1.33} = 2$$

Hence the masses of oxygen combine with carbon in a 2:1 ratio which s consistent with the Law of Multiple Proportions since they are whole numbers.

Dalton's Atomic Theory

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 4), is a fundamental concept that states that all elements are composed of atoms. Previously, an atom was defined as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4 × 10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of the human pinkie (about 1 cm).

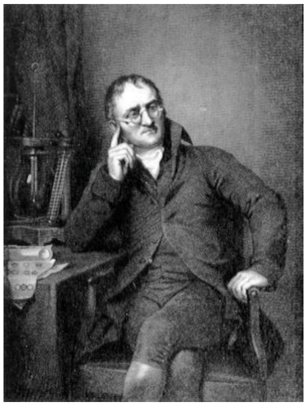

Figure 4: John Dalton was an English scientist who enunciated the modern atomic theory.

Dalton's ideas are called the *modern* atomic theory because the concept of atoms is very old. The Greek philosophers Leucippus and Democritus originally introduced atomic concepts in the fifth century BC. (The word *atom* comes from the Greek word *atomos*, which means "indivisible" or "uncuttable.") Dalton had something that the ancient Greek philosophers didn't have, however; he had experimental evidence, such as the formulas of simple chemicals and the behavior of gases. In the 150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was being used to study nature. When Dalton announced a modern atomic theory, he was proposing a fundamental theory to describe many previous observations of the natural world; he was not just participating in a philosophical discussion.

Dalton's Theory was a powerful development as it explained the three laws of chemical combination (above) and recognized a workable distinction between the fundamental particle of an element (atom) and that of a compound (molecule). Six postulates are involved in Dalton's Atomic Theory:

1. All matter consists of indivisible particles called atoms.
2. Atoms of the same element are similar in shape and mass, but differ from the atoms of other elements.
3. Atoms cannot be created or destroyed.
4. Atoms of different elements may combine with each other in a fixed, simple, whole number ratios to form compound atoms.
5. Atoms of same element can combine in more than one ratio to form two or more compounds.
6. The atom is the smallest unit of matter that can take part in a chemical reaction.

In light of the current state of knowledge in the field of Chemistry, Dalton's theory had a few drawbacks. According to Dalton's postulates,

1. The indivisibility of an atom was proved wrong: an atom can be further subdivided into protons, neutrons and electrons. However an atom is the smallest particle that takes part in chemical reactions.
2. According to Dalton, the atoms of same element are similar in all respects. However, atoms of some elements vary in their masses and densities. These atoms of different masses are called isotopes. For example, chlorine has two isotopes with mass

numbers 35 and 37.

3. Dalton also claimed that atoms of different elements are different in all respects. This has been proven wrong in certain cases: argon and calcium atoms each have an same atomic mass (40 amu).
4. According to Dalton, atoms of different elements combine in simple whole number ratios to form compounds. This is not observed in complex organic compounds like sugar ($C_{12}H_{22}O_{11}$).
5. The theory fails to explain the existence of allotropes (different forms of pure elements); it does not account for differences in properties of charcoal, graphite, diamond.

Despite these drawbacks, the importance of Dalton's theory should not be underestimated. He displayed exceptional insight into the nature of matter. and his ideas provided a framework that was later modified and expanded by other. Consequentiually, John Dalton is often considered to be the father of modern atomic theory.

Fundamental Experiments in Chemistry: Fundamental Experiments in Chemistry, YouTube(opens in new window) [youtu.be]

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Summary

This article explains the theories that Dalton used as a basis for his theory: (1) the Law of Conservation of Mass, (2) the Law of Constant Composition, (3) the Law of Multiple Proportions.

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SECTION OVERVIEW

2.3 Dalton's Atomic Theory

John Dalton, a British school teacher, published his theory about atoms in 1808. His findings were based on experiments and the laws of chemical combination.

Topic hierarchy

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2.4: Cannizzaro's Interpretation

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2.5: Early Experiments to Characterize the Atom

Learning Objectives

- To become familiar with the components and structure of the atom.

Long before the end of the 19th century, it was well known that applying a high voltage to a gas contained at low pressure in a sealed tube (called a gas discharge tube) caused electricity to flow through the gas, which then emitted light (Figure $2.5.1$). Researchers trying to understand this phenomenon found that an unusual form of energy was also emitted from the cathode, or negatively charged electrode; this form of energy was called a cathode ray.

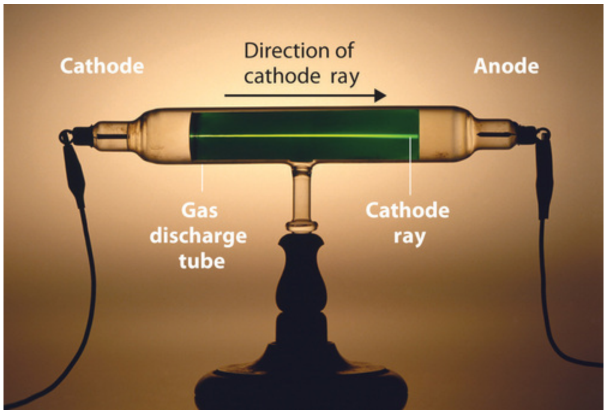

Figure $2.5.1$: A Gas Discharge Tube Producing Cathode Rays. When a high voltage is applied to a gas contained at low pressure in a gas discharge tube, electricity flows through the gas, and energy is emitted in the form of light. Image used with Permission (CC BY-SA-NC).

In 1897, the British physicist J. J. Thomson (1856–1940) proved that atoms were not the most basic form of matter. He demonstrated that cathode rays could be deflected, or bent, by magnetic or electric fields, which indicated that cathode rays consist of charged particles (Figure $2.5.2$). More important, by measuring the extent of the deflection of the cathode rays in magnetic or electric fields of various strengths, Thomson was able to calculate the mass-to-charge ratio of the particles. These particles were emitted by the negatively charged cathode and repelled by the negative terminal of an electric field. Because like charges repel each other and opposite charges attract, Thomson concluded that the particles had a net negative charge; these particles are now called electrons. Most relevant to the field of chemistry, Thomson found that the mass-to-charge ratio of cathode rays is independent of the nature of the metal electrodes or the gas, which suggested that electrons were fundamental components of all atoms.

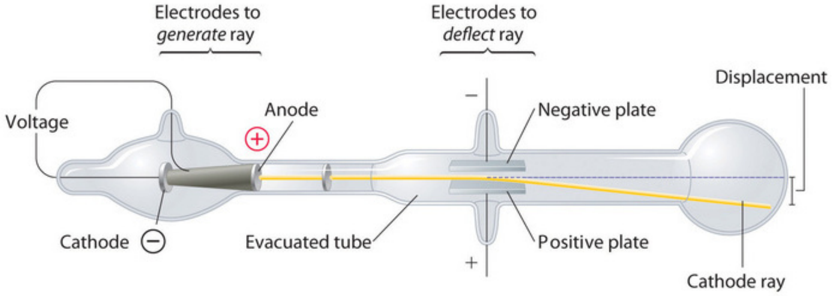

Figure $2.5.2$: Deflection of Cathode Rays by an Electric Field. As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged. Image used with Permission (CC BY-SA-NC).

Schematic of cathode ray tube with deflection. Electrodes generate the ray. Another set of electrode plates deflect the ray, with the ray bending towards the positive plate.

Subsequently, the American scientist Robert Millikan (1868–1953) carried out a series of experiments using electrically charged oil droplets, which allowed him to calculate the charge on a single electron. With this information and Thomson's mass-to-charge ratio, Millikan determined the mass of an electron:

$$\frac{mass}{charge} \times charge = mass$$

It was at this point that two separate lines of investigation began to converge, both aimed at determining how and why matter emits energy. The video below shows how JJ Thompson used such a tube to measure the ratio of charge over mass of an electron

Measuring e/m For an Electron. Video from Davidson College demonstrating Thompson's e/m experiment.

Radioactivity

The second line of investigation began in 1896, when the French physicist Henri Becquerel (1852–1908) discovered that certain minerals, such as uranium salts, emitted a new form of energy. Becquerel's work was greatly extended by Marie Curie (1867–1934) and her husband, Pierre (1854–1906); all three shared the Nobel Prize in Physics in 1903. Marie Curie coined the term radioactivity (from the Latin *radius*, meaning "ray") to describe the emission of energy rays by matter. She found that one particular uranium ore, pitchblende, was substantially more radioactive than most, which suggested that it contained one or more highly radioactive impurities. Starting with several tons of pitchblende, the Curies isolated two new radioactive elements after months of work: polonium, which was named for Marie's native Poland, and radium, which was named for its intense radioactivity. Pierre Curie carried a vial of radium in his coat pocket to demonstrate its greenish glow, a habit that caused him to become ill from radiation poisoning well before he was run over by a horse-drawn wagon and killed instantly in 1906. Marie Curie, in turn, died of what was almost certainly radiation poisoning.

Figure 2.5.3: Radium bromide illuminated by its own radioactive glow. This 1922 photo was taken in the dark in the Curie laboratory.

Building on the Curies' work, the British physicist Ernest Rutherford (1871–1937) performed decisive experiments that led to the modern view of the structure of the atom. While working in Thomson's laboratory shortly after Thomson discovered the electron, Rutherford showed that compounds of uranium and other elements emitted at least two distinct types of radiation. One was readily absorbed by matter and seemed to consist of particles that had a positive charge and were massive compared to electrons. Because it was the first kind of radiation to be discovered, Rutherford called these substances α particles. Rutherford also showed that the particles in the second type of radiation, β particles, had the same charge and mass-to-charge ratio as Thomson's electrons; they are now known to be high-speed electrons. A third type of radiation, γ rays, was discovered somewhat later and found to be similar to the lower-energy form of radiation called x-rays, now used to produce images of bones and teeth.

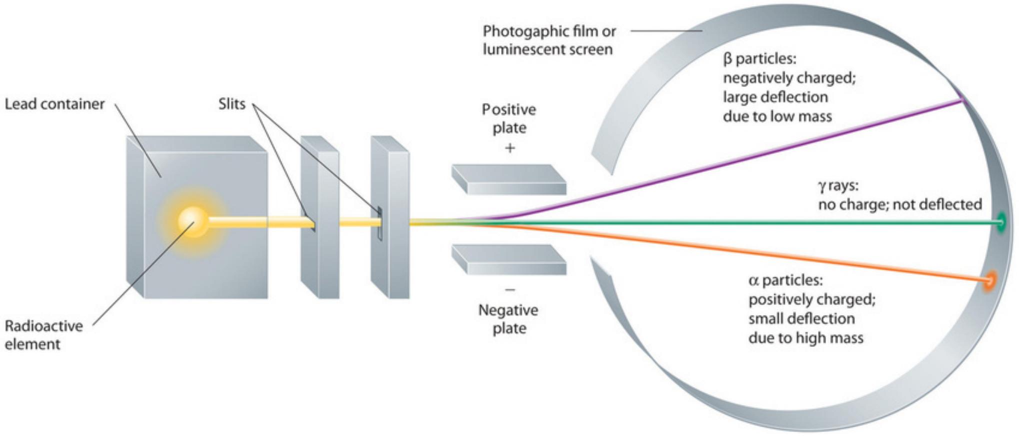

Figure 2.5.4: Effect of an Electric Field on α Particles, β Particles, and γ Rays. A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown to scale.) Image used with Permission (CC BY-SA-NC).

Schematic of a radioactive element in a lead container projected through slits to produce a narrow beam that impacts a photographic film. Two plates, one positive and one negative, deflect the beam depending on whether it is beta, gamma, or alpha. Beta particles deflect towards the positive plate and have a large deflection due to small mass. Alpha particles deflect towards the negative plate and have a small deflection due to high mass. Gamma rays do not deflect.

These three kinds of radiation—α particles, β particles, and γ rays—are readily distinguished by the way they are deflected by an electric field and by the degree to which they penetrate matter. As Figure 2.5.3 illustrates, α particles and β particles are deflected in opposite directions; α particles are deflected to a much lesser extent because of their higher mass-to-charge ratio. In contrast, γ rays have no charge, so they are not deflected by electric or magnetic fields. Figure 2.5.5 shows that α particles have the least penetrating power and are stopped by a sheet of paper, whereas β particles can pass through thin sheets of metal but are absorbed by lead foil or even thick glass. In contrast, γ-rays can readily penetrate matter; thick blocks of lead or concrete are needed to stop them.

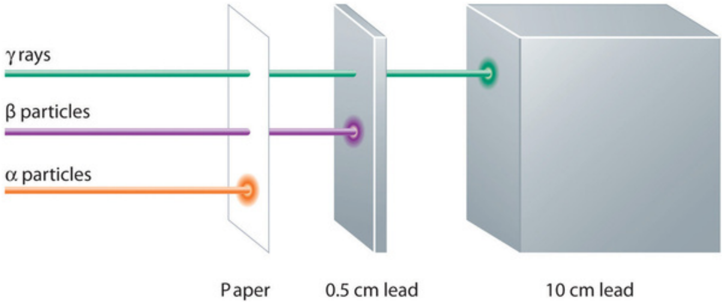

Figure 2.5.5: Relative Penetrating Power of the Three Types of Radiation. A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead or concrete is needed to absorb them. Image used with Permission (CC BY-SA-NC).

Cartoon of gamma, alpha, and beta rays. The beta ray is stopped by paper. The alpha ray is stopped by .5 centimeter lead. The gamma ray is stopped by 10 centimeter lead.

The Atomic Model

Once scientists concluded that all matter contains negatively charged electrons, it became clear that atoms, which are electrically neutral, must also contain positive charges to balance the negative ones. Thomson proposed that the electrons were embedded in a uniform sphere that contained both the positive charge and most of the mass of the atom, much like raisins in plum pudding or chocolate chips in a cookie (Figure 2.5.6).

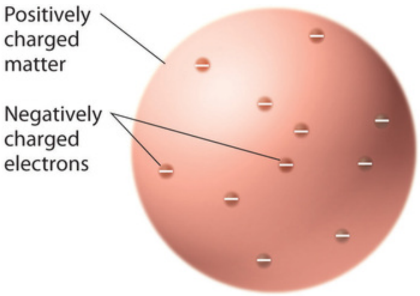

Figure 2.5.6: Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom. In this model, the electrons are embedded in a uniform sphere of positive charge. Image used with Permission (CC BY-SA-NC).

Diagram of the plum-pudding model, with spheres of negatively charged electrons in a larger sphere of positively charged matter.

In a single famous experiment, however, Rutherford showed unambiguously that Thomson's model of the atom was incorrect. Rutherford aimed a stream of α particles at a very thin gold foil target (Figure 2.5.7*a*) and examined how the α particles were scattered by the foil. Gold was chosen because it could be easily hammered into extremely thin sheets, minimizing the number of atoms in the target. If Thomson's model of the atom were correct, the positively-charged α particles should crash through the uniformly distributed mass of the gold target like cannonballs through the side of a wooden house. They might be moving a little slower when they emerged, but they should pass essentially straight through the target (Figure 2.5.7*b*). To Rutherford's amazement, a small fraction of the α particles were deflected at large angles, and some were reflected directly back at the source (Figure 2.5.7*c*). According to Rutherford, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

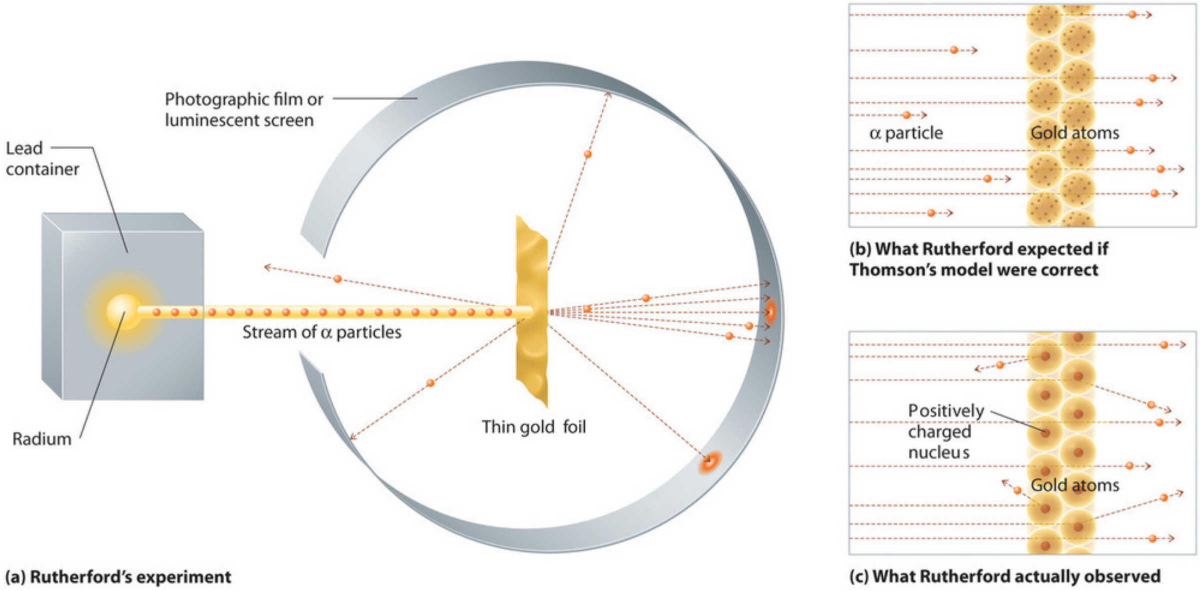

Figure 2.5.7: A Summary of Rutherford's Experiments. (a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles should have passed straight through the gold foil. (c) However, a small number of α particles were deflected in various directions, including right back at the source. This could be true only if the positive charge were much more massive than the α particle. It suggested that the mass of the gold atom is concentrated in a very small region of space, which he called the nucleus. Image used with Permission (CC BY-SA-NC).

Schematic of Rutherford's gold foil experiment. Inset A: Radium fires a stream of alpha particles onto thin gold foil, showing particle deflection onto surrounding photographic film. Inset B: What Rutherford would have expected if Thomas' model were correct: alpha particles continuing through gold foil with no deflection. Inset C: What Rutherford actually observed: alpha particles deflected by nuclei of gold atoms.

The Nuclear Atom: The Nuclear Atom, YouTube(opens in new window) [youtu.be]

Rutherford’s results were not consistent with a model in which the mass and positive charge are distributed uniformly throughout the volume of an atom. Instead, they strongly suggested that both the mass and positive charge are concentrated in a tiny fraction of the volume of an atom, which Rutherford called the nucleus. It made sense that a small fraction of the α particles collided with the dense, positively charged nuclei in either a glancing fashion, resulting in large deflections, or almost head-on, causing them to be reflected straight back at the source.

Although Rutherford could not explain why repulsions between the positive charges in nuclei that contained more than one positive charge did not cause the nucleus to disintegrate, he reasoned that repulsions between negatively charged electrons would cause the electrons to be uniformly distributed throughout the atom’s volume.Today it is known that strong nuclear forces, which are much stronger than electrostatic interactions, hold the protons and the neutrons together in the nucleus. For this and other insights, Rutherford was awarded the Nobel Prize in Chemistry in 1908. Unfortunately, Rutherford would have preferred to receive the Nobel Prize in Physics because he considered physics superior to chemistry. In his opinion, “All science is either physics or stamp collecting.”

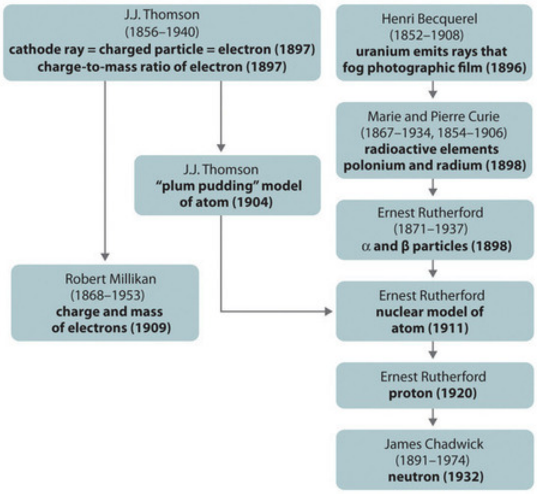

Figure 2.5.8: A Summary of the Historical Development of Models of the Components and Structure of the Atom. The dates in parentheses are the years in which the key experiments were performed. Image used with Permission (CC BY-SA-NC).

The historical development of the different models of the atom’s structure is summarized in Figure 2.5.8. Rutherford established that the nucleus of the hydrogen atom was a positively charged particle, for which he coined the name proton in 1920. He also suggested that the nuclei of elements other than hydrogen must contain electrically neutral particles with approximately the same mass as the proton. The neutron, however, was not discovered until 1932, when James Chadwick (1891–1974, a student of Rutherford; Nobel Prize in Physics, 1935) discovered it. As a result of Rutherford’s work, it became clear that an α particle contains two protons and neutrons, and is therefore the nucleus of a helium atom.

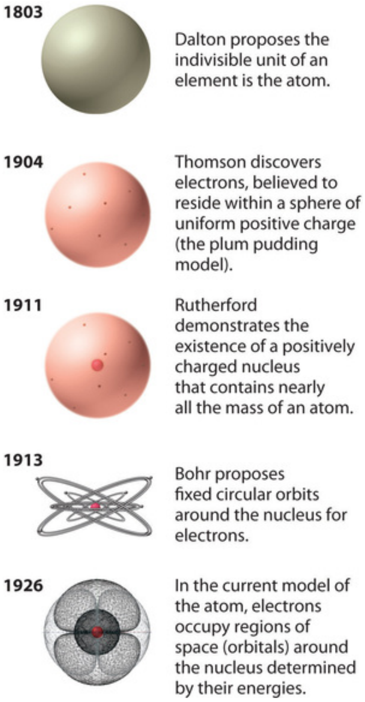

Figure $2.5.9$: The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom. Bohr’s model and the current model are described in Chapter 6, "The Structure of Atoms." Image used with Permission (CC BY-SA-NC).

Summary timeline of the evolution of atomic theory. Shows events at 1803 with Dalton's original proposal, 1904 with Thomson's model, 1911 with Rutherford's experiment, 1913 with Bohr's model, and 1926 with the current orbital model of the atom.

Rutherford’s model of the atom is essentially the same as the modern model, except that it is now known that electrons are not uniformly distributed throughout an atom’s volume. Instead, they are distributed according to a set of principles described by Quantum Mechanics. Figure $2.5.9$ shows how the model of the atom has evolved over time from the indivisible unit of Dalton to the modern view taught today.

Summary

Atoms are the ultimate building blocks of all matter. The modern atomic theory establishes the concepts of atoms and how they compose matter. Atoms, the smallest particles of an element that exhibit the properties of that element, consist of negatively charged electrons around a central nucleus composed of more massive positively charged protons and electrically neutral neutrons. Radioactivity is the emission of energetic particles and rays (radiation) by some substances. Three important kinds of radiation are α particles (helium nuclei), β particles (electrons traveling at high speed), and γ rays (similar to x-rays but higher in energy).

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2.6: Modern Perspective of Atomic Structure

Learning Objectives

- To know the meaning of isotopes and atomic masses.

The precise physical nature of atoms finally emerged from a series of elegant experiments carried out between 1895 and 1915. The most notable of these achievements was Ernest Rutherford's famous 1911 alpha-ray scattering experiment, which established that

- Almost all of the *mass* of an atom is contained within a tiny (and therefore extremely dense) *nucleus* which carries a positive electric charge whose value identifies each element and is known as the *atomic number* of the element.
- Almost all of the *volume* of an atom consists of empty space in which electrons, the fundamental carriers of negative electric charge, reside. The extremely small mass of the electron (1/1840 the mass of the hydrogen nucleus) causes it to behave as a quantum particle, which means that its location at any moment cannot be specified; the best we can do is describe its behavior in terms of the probability of its manifesting itself at any point in space. It is common (but somewhat misleading) to describe the volume of space in which the electrons of an atom have a significant probability of being found as the *electron cloud*. The latter has no definite outer boundary, so neither does the atom. The radius of an atom must be defined arbitrarily, such as the boundary in which the electron can be found with 95% probability. Atomic radii are typically 30-300 pm.

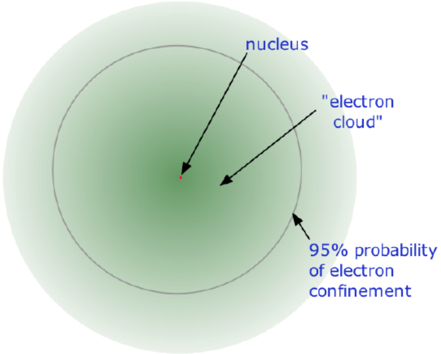


Figure 2.6.1: The structure of the nuclear atom with a central nucleus and surrounding electrons.

The nucleus is itself composed of two kinds of particles. *Protons* are the carriers of positive electric charge in the nucleus; the proton charge is exactly the same as the electron charge, but of opposite sign. This means that in any [electrically neutral] atom, the number of protons in the nucleus (often referred to as the *nuclear charge*) is balanced by the *same* number of electrons outside the nucleus. The other nuclear particle is the *neutron*. As its name implies, this particle carries no electrical charge. Its mass is almost the same as that of the proton. Most nuclei contain roughly equal numbers of neutrons and protons, so we can say that these two particles together account for almost all the mass of the atom.

> *Because the electrons of an atom are in contact with the outside world, it is possible for one or more electrons to be lost, or some new ones to be added. The resulting electrically-charged atom is called an ion.*

Elements

To date, about 115 different elements have been discovered; by definition, each is chemically unique. To understand why they are unique, you need to understand the structure of the atom (the fundamental, individual particle of an element) and the characteristics of its components. Atoms consist of electrons, protons, and neutrons. Although this is an oversimplification that ignores the other subatomic particles that have been discovered, it is sufficient for discussion of chemical principles. Some properties of these subatomic particles are summarized in Table 2.6.1, which illustrates three important points:

1. Electrons and protons have electrical charges that are identical in magnitude but opposite in sign. Relative charges of −1 and +1 are assigned to the electron and proton, respectively.
2. Neutrons have approximately the same mass as protons but no charge. They are electrically neutral.
3. The mass of a proton or a neutron is about 1836 times greater than the mass of an electron. Protons and neutrons constitute the bulk of the mass of atoms.

The discovery of the electron and the proton was crucial to the development of the modern model of the atom and provides an excellent case study in the application of the scientific method. In fact, the elucidation of the atom's structure is one of the greatest detective stories in the history of science.

Table $2.6.1$: Properties of Subatomic Particles*

Particle	Mass (g)	Atomic Mass (amu)	Electrical Charge (coulombs)	Relative Charge
electron	9.109×10^{-28}	0.0005486	-1.602×10^{-19}	−1
proton	1.673×10^{-24}	1.007276	$+1.602 \times 10^{-19}$	+1
neutron	1.675×10^{-24}	1.008665	0	0

In most cases, the symbols for the elements are derived directly from each element's name, such as C for carbon, U for uranium, Ca for calcium, and Po for polonium. Elements have also been named for their properties [such as radium (Ra) for its radioactivity], for the native country of the scientist(s) who discovered them [polonium (Po) for Poland], for eminent scientists [curium (Cm) for the Curies], for gods and goddesses [selenium (Se) for the Greek goddess of the moon, Selene], and for other poetic or historical reasons. Some of the symbols used for elements that have been known since antiquity are derived from historical names that are no longer in use; only the symbols remain to indicate their origin. Examples are Fe for iron, from the Latin *ferrum*; Na for sodium, from the Latin *natrium*; and W for tungsten, from the German *wolfram*. Examples are in Table $2.6.2$.

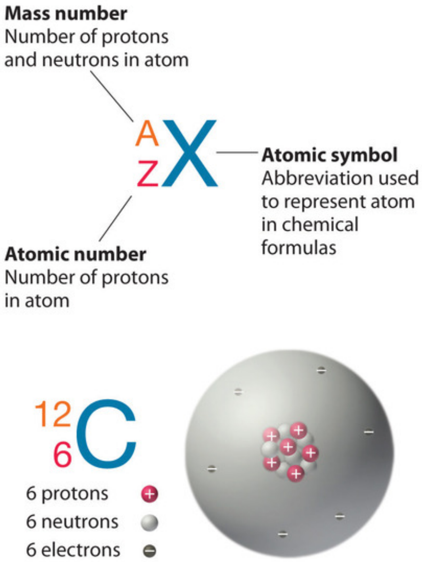
Table $2.6.2$: Element Symbols Based on Names No Longer in Use

Element	Symbol	Derivation	Meaning
antimony	Sb	stibium	Latin for "mark"
copper	Cu	cuprum	from Cyprium, Latin name for the island of Cyprus, the major source of copper ore in the Roman Empire
gold	Au	aurum	Latin for "gold"
iron	Fe	ferrum	Latin for "iron"
lead	Pb	plumbum	Latin for "heavy"
mercury	Hg	hydrargyrum	Latin for "liquid silver"
potassium	K	kalium	from the Arabic al-qili, "alkali"
silver	Ag	argentum	Latin for "silver"
sodium	Na	natrium	Latin for "sodium"
tin	Sn	stannum	Latin for "tin"
tungsten	W	wolfram	German for "wolf stone" because it interfered with the smelting of tin and was thought to devour the tin

Recall that the nuclei of most atoms contain neutrons as well as protons. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called isotopes. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemistry. The isotopes of an element differ only in their atomic mass, which is given by the mass number (A), the sum of the numbers of protons and neutrons.

The element carbon (C) has an atomic number of 6, which means that all neutral carbon atoms contain 6 protons and 6 electrons. In a typical sample of carbon-containing material, 98.89% of the carbon atoms also contain 6 neutrons, so each has a mass number of

12. An isotope of any element can be uniquely represented as ${}^{A}_{Z}X$, where X is the atomic symbol of the element. The isotope of carbon that has 6 neutrons is therefore ${}^{12}_{6}C$. The subscript indicating the atomic number is actually redundant because the atomic symbol already uniquely specifies Z. Consequently, ${}^{12}_{6}C$ is more often written as ^{12}C, which is read as “carbon-12.” Nevertheless, the value of Z is commonly included in the notation for nuclear reactions because these reactions involve changes in Z.



Elaboration of atomic symbol, showing mass and atomic number next to symbol. Carbon-12 is shown as an example.

***Figure 2.6.2**: Formalism used for identifying specific nuclide (any particular kind of nucleus)*

In addition to ${}^{12}C$, a typical sample of carbon contains 1.11% ${}^{13}_{6}C$ (^{13}C), with 7 neutrons and 6 protons, and a trace of ${}^{14}_{6}C$ (^{14}C), with 8 neutrons and 6 protons. The nucleus of ^{14}C is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archaeology. Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. The properties of some common isotopes are in Table 2.6.3.

Table 2.6.3: Properties of Selected Isotopes

Element	Symbol	Atomic Mass (amu)	Isotope Mass Number	Isotope Masses (amu)	Percent Abundances (%)
hydrogen	H	1.0079	1	1.007825	99.9855
			2	2.014102	0.0115
boron	B	10.81	10	10.012937	19.91
			11	11.009305	80.09
carbon	C	12.011	12	12 (defined)	99.89
			13	13.003355	1.11
oxygen	O	15.9994	16	15.994915	99.757
			17	16.999132	0.0378
			18	17.999161	0.205
iron	Fe	55.845	54	53.939611	5.82
			56	55.934938	91.66
			57	56.935394	2.19
			58	57.933276	0.33
uranium	U	238.03	234	234.040952	0.0054

Element	Symbol	Atomic Mass (amu)	Isotope Mass Number	Isotope Masses (amu)	Percent Abundances (%)
			235	235.043930	0.7204
			238	238.050788	99.274

Sources of isotope data: G. Audi et al., Nuclear Physics A 729 (2003): 337–676; J. C. Kotz and K. F. Purcell, Chemistry and Chemical Reactivity, 2nd ed., 1991.

How Elements Are Represented on the Periodic Table: How Elements Are Represented on the Periodic Table, YouTube(opens in new window) [youtu.be]

✓ Example 2.6.1

An element with three stable isotopes has 82 protons. The separate isotopes contain 124, 125, and 126 neutrons. Identify the element and write symbols for the isotopes.

Given: number of protons and neutrons

Asked for: element and atomic symbol

Strategy:

A. Refer to the periodic table and use the number of protons to identify the element.
B. Calculate the mass number of each isotope by adding together the numbers of protons and neutrons.
C. Give the symbol of each isotope with the mass number as the superscript and the number of protons as the subscript, both written to the left of the symbol of the element.

Solution:

A The element with 82 protons (atomic number of 82) is lead: Pb.

B For the first isotope, A = 82 protons + 124 neutrons = 206. Similarly, A = 82 + 125 = 207 and A = 82 + 126 = 208 for the second and third isotopes, respectively. The symbols for these isotopes are ${}^{206}_{82}Pb$, ${}^{207}_{82}Pb$, and ${}^{208}_{82}Pb$, which are usually abbreviated as ${}^{206}Pb$, ${}^{207}Pb$, and ${}^{208}Pb$.

? Exercise 2.6.1

Identify the element with 35 protons and write the symbols for its isotopes with 44 and 46 neutrons.

Answer

${}^{79}_{35}\text{Br}$ and ${}^{81}_{35}\text{Br}$ or, more commonly, ${}^{79}\text{Br}$ and ${}^{81}\text{Br}$.

Summary

The atom consists of discrete particles that govern its chemical and physical behavior. Each atom of an element contains the same number of protons, which is the **atomic number** (Z). Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number** (A), which is the sum of the numbers of protons and neutrons. The relative masses of atoms are reported using the **atomic mass unit** (**amu**), which is defined as one-twelfth of the mass of one atom of carbon-12, with 6 protons, 6 neutrons, and 6 electrons.

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2.7: Molecules and Ions

Chemical compounds can generally be classified into two broad groups: molecular compounds and ionic compounds. Molecular compounds involve atoms joined by covalent bonds and can be represented by a variety of formulas. Ionic compounds are composed of ions joined by ionic bonding, and their formulas are generally written using oxidation states.

Molecular compounds are composed of atoms that are held together by covalent bonds. These bonds are formed when electrons are shared between two atoms. The concept of chemical formulas was created to describe many characteristics of molecular compounds in a simple manner. A normal chemical formula encompasses factors such as which elements are in the molecule and how many atoms of each element there are. The number of atoms of each element is denoted by a subscript, a small number that is written to the left of the element.

$$CH_3COOH$$

In the preceding formula, the subscript “3” denotes the fact that there are three hydrogen atoms present in the molecule.

Other types of formulas are used to display more detailed characteristics of molecules.

An empirical formula represents the proportions of atoms in a molecule. It gives important information about a molecule, because it displays the ratios of atoms that are present within the molecule. However, its limitations exist in the sense that it does not represent the exact number of atoms present in the molecule as the molecular formula does. In certain situations, the molecular and the empirical formula can be the same, but in other situations, the molecular formula is a multiple of the ratios of atoms indicated in the empirical formula. Since empirical formulas can be derived from molecular formulas, molecular formulas are generally more useful than empirical formulas.

Empirical vs. molecular compounds

C_5H_7O is a possible empirical formula, because a ratio of 5:7:1 cannot be simplified any further. In this particular case, the empirical formula could also be the molecular formula, if there are exactly 5 carbon atoms, 7 hydrogen atoms, and 1 oxygen atom per molecule. However, another possible molecular formula for this same molecule is $C_{10}H_{14}O_2$, because while there are 10 carbon atoms, 14 hydrogen atoms, and 2 oxygen atoms present, the ratio 10:14:2 can be simplified to 5:7:1, giving way to the same empirical formula. Additionally, $C_{10}H_{14}O_2$ is not the only possibility of a molecular formula for this molecule; any formula with the same relative proportions of these atoms that can be simplified to a 5:7:1 ratios is a possible molecular formula for this molecule. When given adequate information, the empirical formula and molecular formula can be quantitatively ascertained.

A **structural formula** is written to denote the details of individual atoms’ bonding. More specifically, it clarifies what types of bonds exist, between which atoms these bonds exist, and the order of the atoms’ bonding within the molecule. Covalent bonds are denoted by lines. A single line represents a single bond, two lines represent a double bond, three lines represent a triple bond, and onwards. A single covalent bond occurs when two electrons are shared between atoms, a double occurs when four electrons are shared between two atoms, etc. In this sense, the higher the number of bonds, the stronger the bond between the two atoms.

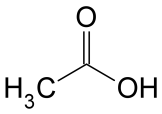


Figure 1: The structural formula of acetic acid, whose molecular formula is CH_3COOH.

A **condensed structural formula** is a less graphical way of representing the same characteristics displayed by a structural formula. In this type of formula, the molecule is written as a molecular formula with the exception that it indicates where the bonding occurs.

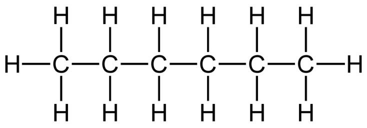
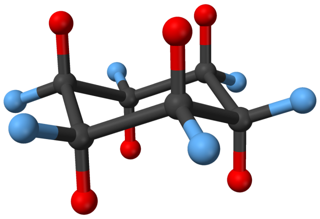
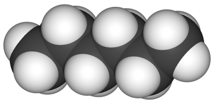


Figure 2: The structural formula of hexane. By referring to the structural formula and emphasizing where bonding occurs, one can ascertain a condensed structural formula of $CH_3CH_2CH_2CH_2CH_2CH_3$.

All the representations discussed thus far have not addressed how to show a molecule's three-dimensional structure. The two ways to illustrate a spatial structure are through the use of the ball-and-stick model as well as the space-filling model.



The ball-and-stick model uses balls to spatially represent a molecule. The balls are the atoms in a molecule and sticks are the bonds between specific atoms.



The space-filling model is also a method of spatially displaying a molecule and its characteristics. A space-filling model shows atoms' sizes relative sizes to one another.

Ionic Compounds

Ionic compounds are composed of positive and negative ions that are joined by ionic bonds. Ionic bonds are generally formed when electrons are transferred from one atom to another, causing individual atoms to become charged particles, or ions. Ions can be referred to as either monatomic or polyatomic. Monatomic ions such as Cl^- are composed of only one ion, while polyatomic ions such as NO_3^- are defined as polyatomic ions. A combination of these ions that forms a compound whose charge is equal to zero is known as a formula unit of an ionic compound. Ionic compounds generally tend to form crystallized salts. They generally have high boiling/melting points, and are good conductors of electricity. The formulas of ionic compounds are always written with the cation first, followed by the anion. The formula can then be completed with reference to the oxidation states of the elements present.

References

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2. Suchocki, J. Conceptual Chemistry: Understanding Our World of Atoms and Molecules. 2nd ed. United Kingdom: Benjamin/Cummings, 2003.

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2.8: An Introduction to the Periodic Table

Learning Objectives

- To become familiar with the organization of the periodic table.

Rutherford's nuclear model of the atom helped explain why atoms of different elements exhibit different chemical behavior. The identity of an element is defined by its *atomic number (Z)*, the number of protons in the nucleus of an atom of the element. The atomic number is therefore different for each element. The known elements are arranged in order of increasing Z in the *periodic table* (Figure 2.8.1). The rationale for the peculiar format of the periodic table is explained later. Each element is assigned a unique one-, two-, or three-letter symbol. The names of the elements are listed in the periodic table, along with their symbols, atomic numbers, and atomic masses. The chemistry of each element is determined by its number of protons and electrons. In a neutral atom, the number of electrons equals the number of protons.

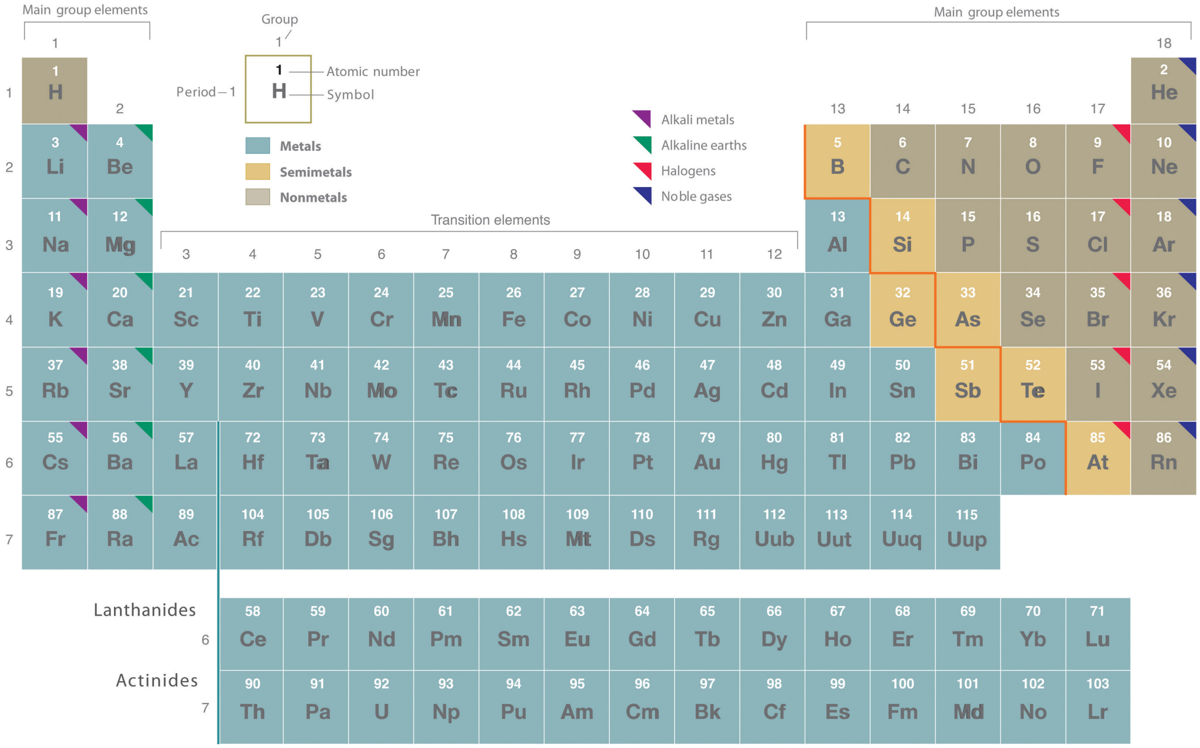

Figure 2.8.1: The Periodic Table Showing the Elements in Order of Increasing Z. The metals are on the bottom left in the periodic table, and the nonmetals are at the top right. The semimetals lie along a diagonal line separating the metals and nonmetals. An interactive Periodic table can be found Periodic Table of the Elements, LibreTexts. (CC-BY-SA-NC 3.0; Anonymous via LibreTexts)

The elements are arranged in a periodic table, which is probably the single most important learning aid in chemistry. It summarizes huge amounts of information about the elements in a way that facilitates the prediction of many of their properties and chemical reactions. The elements are arranged in seven horizontal rows, in order of increasing atomic number from left to right and top to bottom. The rows are called periods, and they are numbered from 1 to 7. The elements are stacked in such a way that elements with similar chemical properties form vertical columns, called groups, numbered from 1 to 18 (older periodic tables use a system based on roman numerals). Groups 1, 2, and 13–18 are the main group elements, listed as A in older tables. Groups 3–12 are in the middle of the periodic table and are the transition elements, listed as B in older tables. The two rows of 14 elements at the bottom of the periodic table are the lanthanides and the actinides, whose positions in the periodic table are indicated in group 3.

Metals, Nonmetals, and Semimetals

The heavy orange zigzag line running diagonally from the upper left to the lower right through groups 13–16 in Figure 2.8.1 divides the elements into metals (in blue, below and to the left of the line) and nonmetals (in bronze, above and to the right of the line). Gold-colored lements that lie along the diagonal line exhibit properties intermediate between metals and nonmetals; they are called semimetals.

The distinction between metals and nonmetals is one of the most fundamental in chemistry. Metals—such as copper or gold—are good conductors of electricity and heat; they can be pulled into wires because they are ductile; they can be hammered or pressed into thin sheets or foils because they are malleable; and most have a shiny appearance, so they are lustrous. The vast majority of the known elements are metals. Of the metals, only mercury is a liquid at room temperature and pressure; all the rest are solids.

Nonmetals, in contrast, are generally poor conductors of heat and electricity and are not lustrous. Nonmetals can be gases (such as chlorine), liquids (such as bromine), or solids (such as iodine) at room temperature and pressure. Most solid nonmetals are brittle, so they break into small pieces when hit with a hammer or pulled into a wire. As expected, semimetals exhibit properties intermediate between metals and nonmetals.

✓ Example $2.8.1$: Classifying Elements

Based on its position in the periodic table, do you expect selenium to be a metal, a nonmetal, or a semimetal?

Given: element

Asked for: classification

Strategy:

Find selenium in the periodic table shown in Figure $2.8.1$ and then classify the element according to its location.

Solution:

The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure $2.8.1$, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

? Exercise $2.8.1$

Based on its location in the periodic table, do you expect indium to be a nonmetal, a metal, or a semimetal?

Answer

metal

As previously noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins. For example, the elements of Group 1 are known as the alkali metals, Group 2 are the alkaline earth metals, Group 17 are the halogens, and Group 18 are the noble gases.

Group 1: The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal. The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth’s crust, respectively.

Group 2: The Alkaline Earth Metals

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium, strontium, and barium are rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.

Group 17: The Halogens

The halogens are fluorine, chlorine, bromine, iodine, and astatine. The name halogen is derived from the Greek words for “salt forming,” which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt).

Compounds that contain the fluoride ion are added to toothpaste and the water supply to prevent dental cavities. Fluorine is also found in Teflon coatings on kitchen utensils. Although chlorofluorocarbon propellants and refrigerants are believed to lead to the depletion of Earth’s ozone layer and contain both fluorine and chlorine, the latter is responsible for the adverse effect on the ozone layer. Bromine and iodine are less abundant than chlorine, and astatine is so radioactive that it exists in only negligible amounts in nature.

Group 18: The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, and radon. Because the noble gases are composed of only single atoms, they are called monatomic. At room temperature and pressure, they are unreactive gases. Because of their lack of reactivity, for many years they were called inert gases or rare gases. However, the first chemical compounds containing the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

> *The noble gases are unreactive at room temperature and pressure.*

Summary

The periodic table is used as a predictive tool. It arranges of the elements in order of increasing atomic number. Elements that exhibit similar chemistry appear in vertical columns called groups (numbered 1–18 from left to right); the seven horizontal rows are called periods. Some of the groups have widely-used common names, including the alkali metals (Group 1) and the alkaline earth metals (Group 2) on the far left, and the halogens (Group 17) and the noble gases (Group 18) on the far right. The elements can be broadly divided into metals, nonmetals, and semimetals. Semimetals exhibit properties intermediate between those of metals and nonmetals. Metals are located on the left of the periodic table, and nonmetals are located on the upper right. They are separated by a diagonal band of semimetals. Metals are lustrous, good conductors of electricity, and readily shaped (they are ductile and malleable), whereas solid nonmetals are generally brittle and poor electrical conductors. Other important groupings of elements in the periodic table are the main group elements, the transition metals, the lanthanides, and the actinides.

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2.9: Nomenclature of Simple Compounds

Generally, there are two types of inorganic compounds that can be formed: ionic compounds and molecular compounds. Nomenclature is the process of naming chemical compounds with different names so that they can be easily identified as separate chemicals. Inorganic compounds are compounds that do not deal with the formation of carbohydrates, or simply all other compounds that do not fit into the description of an organic compound. For example, organic compounds include molecules with carbon rings and/or chains with hydrogen atoms (see picture below). Inorganic compounds, the topic of this section, are every other molecule that does not include these distinctive carbon and hydrogen structures.

Compounds between Metals and Nonmetals (Cation and Anion)

Compounds made of a metal and nonmetal are commonly known as Ionic Compounds, where the compound name has an ending of ***–ide***. Cations have positive charges while anions have negative charges. The net charge of any ionic compound must be zero which also means it must be electrically neutral. For example, one Na^+ is paired with one Cl^-; one Ca^{2+} is paired with two Br^-. There are two rules that must be followed through:

- The **cation** (metal) is always named first with its name unchanged
- The **anion** (nonmetal) is written after the cation, modified to end in ***–ide***

Table 1: Cations and Anions:

+1 Charge	+2 Charge	-1 Charge	-2 Charge	-3 Charge	-4 Charge
Group 1A elements	**Group 2A elements**	**Group 7A elements**	**Group 6A elements**	**Group 5A elements**	**Group 4A elements**
Hydrogen: H^+	Beryllium: Be^{2+}	Hydride: H^-	Oxide: O^{2-}	Nitride: N^{3-}	Carbide: C^{4-}
Lithium: Li^+	Magnesium: Mg^{2+}	Fluoride: F^-	Sulfide: S^{2-}	Phosphide: P^{3-}	
Soduim: Na^+	Calcium: Ca^{2+}	Chloride: Cl^-			
Potassium: K^+	Strontium: Sr^{2+}	Bromide: Br^-			
Rubidium: Rb^+	Barium: Ba^{2+}	Iodide: I^-			
Cesium: Cs^+					

Example 1

$Na^+ + Cl^- = NaCl$; $Ca^{2+} + 2Br^- = CaBr_2$

Sodium + Chlorine = Sodium Chlor**ide; **Calcium + Bromine = Calcium Brom**ide**

The transition metals may form more than one ion, thus it is needed to be specified which particular ion we are talking about. This is indicated by assigning a Roman numeral after the metal. The Roman numeral denotes the charge and the oxidation state of the transition metal ion. For example, iron can form two common ions, Fe^{2+} and Fe^{3+}. To distinguish the difference, Fe^{2+} would be named iron (II) and Fe^{3+} would be named iron (III).

Table of Transition Metal and Metal Cations:

+1 Charge	+2 Charge	+3 Charge	+4 Charge
Copper(I): Cu^+	Copper(II): Cu^{2+}	Aluminum: Al^{3+}	Lead(IV): Pb^{4+}
Silver: Ag^+	Iron(II): Fe^{2+}	Iron(III): Fe^{3+}	Tin(IV): Sn^{4+}
	Cobalt(II): Co^{2+}	Cobalt(III): Co^{3+}	
	Tin(II): Sn^{2+}		
	Lead(II): Pb^{2+}		
	Nickel: Ni^{2+}		

+1 Charge	+2 Charge	+3 Charge	+4 Charge
	Zinc: Zn^{2+}		

✓ Example 2

Ions:	Fe^{2+}+ $2Cl^-$	Fe^{3+}+ $3Cl^-$
Compound:	$FeCl_2$	$FeCl_3$
Nomenclature	Iron (II) Chloride	Iron (III) Chloride

However, some of the transition metals' charges have specific Latin names. Just like the other nomenclature rules, the ion of the transition metal that has the lower charge has the Latin name ending with **-ous** and the one with the the higher charge has a Latin name ending with **-ic**. The most common ones are shown in the table below:

Transition Metal Ion with Roman Numeral	Latin name
Copper (I): Cu^+	Cuprous
Copper (II): Cu^{2+}	Cupric
Iron (II): Fe^{2+}	Ferrous
Iron (III): Fe^{3+}	Ferric
Lead (II): Pb^{2+}	Plumbous
Lead (IV): Pb^{4+}	Plumbic
Mercury (I): Hg_2^{2+}	Mercurous
Mercury (II): Hg^{2+}	Mercuric
Tin (II): Sn^{2+}	Stannous
Tin (IV): Sn^{4+}	Stannic

Several exceptions apply to the Roman numeral assignment: Aluminum, Zinc, and Silver. Although they belong to the transition metal category, these metals do not have Roman numerals written after their names because these metals only exist in one ion. Instead of using Roman numerals, the different ions can also be presented in plain words. The metal is changed to end in ***–ous*** or ***–ic***.

- ***-ous*** ending is used for the **lower** oxidation state
- ***-ic*** ending is used for the **higher** oxidation state

✓ Example 3

Compound	Cu_2O	CuO	$FeCl_2$	$FeCl_3$
Charge	Charge of copper is +1	Charge of copper is +2	Charge of iron is +2	Charge of iron is +3
Nomenclature	Cuprous Oxide	Cupric Oxide	Ferrous Chloride	Ferric Chloride

However, this **-ous/-ic** system is inadequate in some cases, so the Roman numeral system is preferred. This system is used commonly in naming acids, where H_2SO_4 is commonly known as Sulfuric Acid, and H_2SO_3 is known as Sulfurous Acid.

Compounds between Nonmetals and Nonmetals

Compounds that consist of a nonmetal bonded to a nonmetal are commonly known as **Molecular Compounds**, where the element with the positive oxidation state is written first. In many cases, nonmetals form more than one binary compound, so **prefixes** are used to distinguish them.

# of Atoms	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Prefixes	Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	Deca-

✓ Example 4

CO = carbon ***mon***oxide BCl$_3$ = boron***tri***chloride

CO$_2$ = carbon ***di***oxide N$_2$O$_5$ =***di***nitrogen ***pent***oxide

The prefix ***mono-*** is not used for the first element. If there is not a prefix before the first element, it is assumed that there is only one atom of that element.

Binary Acids

Although HF can be named hydrogen fluoride, it is given a different name for emphasis that it is an acid. An acid is a substance that dissociates into hydrogen ions (H$^+$) and anions in water. A quick way to identify acids is to see if there is an H (denoting hydrogen) in front of the molecular formula of the compound. To name acids, the prefix ***hydro-*** is placed in front of the nonmetal modified to end with ***–ic***. The state of acids is aqueous (aq) because acids are found in water.

Some common binary acids include:

HF (g) = hydrogen fluor**ide** -> HF (aq) = ***hydro***fluor***ic*** acid

HBr (g) = hydrogen brom**ide** -> HBr (aq) = ***hydro***brom***ic*** acid

HCl (g) = hydrogen chlor**ide** -> HCl (aq) = ***hydro***chlor***ic*** acid

H$_2$S (g) = hydrogen sulf**ide** -> H$_2$S (aq) = ***hydro***sulfur***ic***acid

It is important to include (aq) after the acids because the same compounds can be written in gas phase with hydrogen named first followed by the anion ending with ***–ide***.

✓ Example 5

hypo____ite ____ite ____ate per____ate

ClO$^-$ ClO$_2^-$ ClO$_3^-$ ClO$_4^-$

hypo*chlor*ite *chlor*ite *chlor*ate per*chlor*ate

---------------->

As indicated by the arrow, moving to the right, the following trends occur:

Increasing number of oxygen atoms

Increasing oxidation state of the nonmetal

(Usage of this example can be seen from the set of compounds containing Cl and O)

This occurs because the number of oxygen atoms are increasing from hypochlorite to perchlorate, yet the overall charge of the polyatomic ion is still -1. To correctly specify how many oxygen atoms are in the ion, prefixes and suffixes are again used.

Polyatomic Ions

In **polyatomic ions**, polyatomic (meaning two or more atoms) are joined together by **covalent bonds**. Although there may be a element with positive charge like H$^+$, it is not joined with another element with an ionic bond. This occurs because if the atoms formed an ionic bond, then it would have already become a compound, thus not needing to gain or loose any electrons. Polyatomic anions are more common than polyatomic cations as shown in the chart below. Polyatomic anions have negative charges while polyatomic cations have positive charges. To indicate different polyatomic ions made up of the same elements, the name of the ion is modified according to the example below:

Table: Common Polyatomic ions

Name: Cation/Anion	Formula
Ammonium ion	NH_4^+
Hydronium ion	H_3O^+
Acetate ion	$C_2H_3O_2^-$
Arsenate ion	AsO_4^{3-}
Carbonate ion	CO_3^{2-}
Hypochlorite ion	ClO^-
Chlorite ion	ClO_2^-
Chlorate ion	ClO_3^-
Perchlorate ion	ClO_4^-
Chromate ion	CrO_4^{2-}
Dichromate ion	$Cr_2O_7^{2-}$
Cyanide ion	CN^-
Hydroxide ion	OH^-
Nitrite ion	NO_2^-
Nitrate ion	NO_3^-
Oxalate ion	$C_2O_4^{2-}$
Permanganate ion	MnO_4^-
Phosphate ion	PO_4^{3-}
Sulfite ion	SO_3^{2-}
Sulfate ion	SO_4^{2-}
Thiocyanate ion	SCN^-
Thiosulfate ion	$S_2O_3^{2-}$

To combine the topic of acids and polyatomic ions, there is nomenclature of aqueous acids. Such acids include sulfuric acid (H_2SO_4) or carbonic acid (H_2CO_3). To name them, follow these quick, simple rules:

1. If the ion ends in **-ate** and is added with an acid, the acid name will have an **-ic** ending. Examples: nitrate ion (NO_3^-) + H^+ (denoting formation of acid) = nitr**ic** acid (HNO_3)
2. If the ion ends in **-ite** and is added with an acid, then the acid name will have an **-ous** ending. Example: nitite ion (NO_2^-) + H^+ (denoting formation of acid) = nitr**ous** acid (HNO_2)

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Problems

1. What is the correct formula for Calcium Carbonate?

a. $Ca^+ + CO_2^-$

b. $CaCO_2^-$

c. $CaCO_3$

d. $2CaCO_3$

2. What is the correct name for FeO?

a. Iron oxide

b. Iron dioxide

c. Iron(III) oxide

d. Iron(II) oxide

3. What is the correct name for $Al(NO_3)_3$?

a. Aluminum nitrate

b. Aluminum(III) nitrate

c. Aluminum nitrite

d. Aluminum nitrogen trioxide

4. What is the correct formula of phosphorus trichloride?

a. P_2Cl_2

b. PCl_3

c. PCl_4

d. P_4Cl_2

5. What is the correct formula of lithium perchlorate?

a. Li_2ClO_4

b. $LiClO_2$

c. $LiClO$

d. None of these

6. Write the correct name for these compounds.

a. BeC_2O_4:

b. NH_4MnO_4:

c. CoS_2O_3:

7. What is $W(HSO_4)_5$?

8. How do you write diphosphorus trioxide?

9. What is H_3P?

10. By adding oxygens to the molecule in number 9, we now have H_3PO_4? What is the name of this molecule?

Answer

1.C; Calcium + Carbonate --> Ca^{2+} + CO_3^{2-} --> $CaCO_3$

2.D; FeO --> Fe + O^{2-} --> Iron must have a charge of +2 to make a neutral compound --> Fe^{2+} + O^{2-} --> Iron(II) Oxide

3.A; $Al(NO_3)_3$ --> Al^{3+} + $(NO_3^-)_3$ --> Aluminum nitrate

4.B; Phosphorus trichloride --> P + 3Cl --> PCl_3

5.D, $LiClO_4$; Lithium perchlorate --> Li^+ + ClO_4^- --> $LiClO_4$

6. a. Beryllium Oxalate; BeC_2O_4 --> Be^{2+} + $C_2O_4^{2-}$ --> Beryllium Oxalate

b. Ammonium Permanganate; NH_4MnO_4 --> NH_4^+ + MnO_4^- --> Ammonium Permanganate

c. Cobalt (II) Thiosulfate; CoS_2O_3 --> Co + $S_2O_3^{2-}$ --> Cobalt must have +2 charge to make a neutral compund --> Co^{2+} + $S_2O_3^{2-}$ --> Cobalt(II) Thiosulfate

7. Tungsten (V) hydrogen sulfate

8. P_2O_3

9. Hydrophosphoric Acid

10. Phosphoric Acid

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CHAPTER OVERVIEW

3: Stoichiometry

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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3.1: Atomic Mass

Learning Objectives

- to know the meaning of isotopes and atomic masses.

Atomic and Molecular Weights

The subscripts in chemical formulas, and the coefficients in chemical equations represent *exact* quantities. H_2O, for example, indicates that a water molecule comprises exactly **two** atoms of hydrogen and **one** atom of oxygen. The following equation:

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l) \tag{3.1.1}$$

not only tells us that propane reacts with oxygen to produce carbon dioxide and water, but that ***1*** molecule of propane reacts with ***5*** molecules of oxygen to produce ***3*** molecules of carbon dioxide and ***4*** molecules of water. Since counting individual atoms or molecules is a little difficult, quantitative aspects of chemistry rely on knowing the *masses* of the compounds involved.

Atoms of different elements have different masses. Early work on the separation of water into its constituent elements (hydrogen and oxygen) indicated that 100 grams of water contained 11.1 grams of hydrogen and 88.9 grams of oxygen:

$$100 \text{ grams Water} \rightarrow 11.1 \text{ grams Hydrogen} + 88.9 \text{ grams Oxygen} \tag{3.1.2}$$

Later, scientists discovered that water was composed of ***two atoms*** of hydrogen ***for each atom*** of oxygen. Therefore, in the above analysis, *in the 11.1 grams of hydrogen there were twice as many atoms as in the 88.9 grams of oxygen.* Therefore, an oxygen atom must weigh about 16 times as much as a hydrogen atom:

$$\frac{\dfrac{88.9\ g\ Oxygen}{1\ atom}}{\dfrac{111\ g\ Hydrogen}{2\ atoms}} = 16 \tag{3.1.3}$$

Hydrogen, the lightest element, was assigned a relative mass of '1', and the other elements were assigned 'atomic masses' relative to this value for hydrogen. Thus, oxygen was assigned an atomic mass of 16. We now know that a **hydrogen** atom has a mass of **1.6735×10^{-24}** grams, and that the **oxygen** atom has a mass of **2.6561×10^{-23}** grams. As we saw earlier, it is convenient to use a reference unit when dealing with such small numbers: the **atomic mass unit**. The atomic mass unit (***amu***) was not standardized against hydrogen, but rather, against the ^{12}C isotope of **carbon** (***amu* = 12**).

Thus, the mass of the **hydrogen atom** (^1H) is 1.0080 *amu*, and the mass of **an oxygen atom** (^{16}O) is 15.995 *amu*. Once the masses of atoms were determined, the ***amu*** could be assigned an actual value:

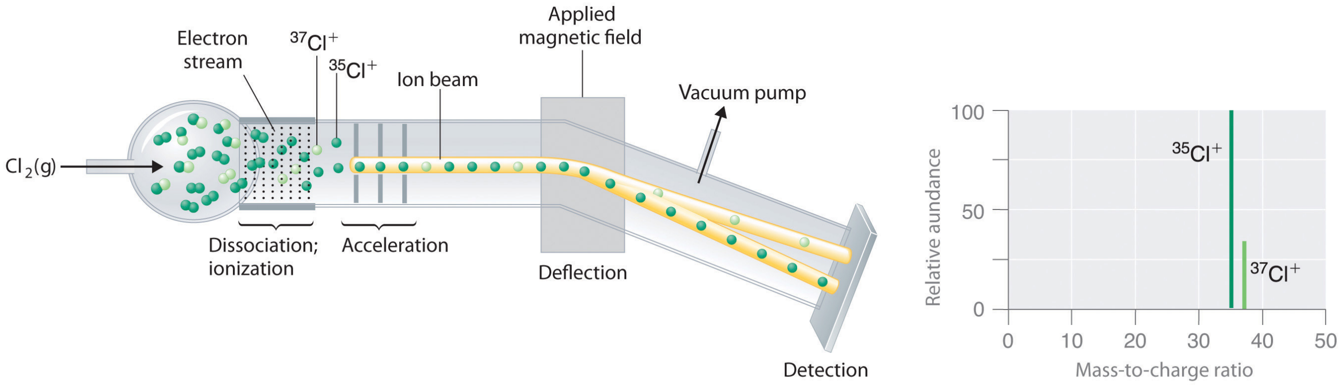
1 ***amu*** = 1.66054×10^{-24} **grams** conversely: 1 **gram** = 6.02214×10^{23} ***amu***

Mass Numbers and Atomic Mass of Elements: Mass Numbers and Atomic Mass of Elements, YouTube(opens in new window) [youtu.be]

Average Atomic Mass

Although the masses of the electron, the proton, and the neutron are known to a high degree of precision (Table 2.3.1), the mass of any given atom is not simply the sum of the masses of its electrons, protons, and neutrons. For example, the ratio of the masses of ^1H (hydrogen) and ^2H (deuterium) is actually 0.500384, rather than 0.49979 as predicted from the numbers of neutrons and protons present. Although the difference in mass is small, it is extremely important because it is the source of the huge amounts of energy released in nuclear reactions.

Because atoms are much too small to measure individually and do not have charges, there is no convenient way to accurately measure absolute atomic masses. Scientists can measure relative atomic masses very accurately, however, using an instrument called a mass spectrometer. The technique is conceptually similar to the one Thomson used to determine the mass-to-charge ratio of the electron. First, electrons are removed from or added to atoms or molecules, thus producing charged particles called ions. When an electric field is applied, the ions are accelerated into a separate chamber where they are deflected from their initial trajectory by a magnetic field, like the electrons in Thomson's experiment. The extent of the deflection depends on the mass-to-charge ratio of the ion. By measuring the relative deflection of ions that have the same charge, scientists can determine their relative masses (Figure $3.1.1$). Thus it is not possible to calculate absolute atomic masses accurately by simply adding together the masses of the electrons, the protons, and the neutrons, and absolute atomic masses cannot be measured, but relative masses can be measured very accurately. It is actually rather common in chemistry to encounter a quantity whose magnitude can be measured only relative to some other quantity, rather than absolutely. We will encounter many other examples later in this text. In such cases, chemists usually define a standard by arbitrarily assigning a numerical value to one of the quantities, which allows them to calculate numerical values for the rest.



(a) Mass spectrometer

(b) Mass spectrum

Figure $3.1.1$: Determining Relative Atomic Masses Using a Mass Spectrometer. Chlorine consists of two isotopes, ^{35}Cl and ^{37}Cl, in approximately a 3:1 ratio. (a) When a sample of elemental chlorine is injected into the mass spectrometer, electrical energy is used to dissociate the Cl_2 molecules into chlorine atoms and convert the chlorine atoms to Cl^+ ions. The ions are then accelerated into a magnetic field. The extent to which the ions are deflected by the magnetic field depends on their relative mass-to-charge ratios. Note that the lighter $^{35}Cl^+$ ions are deflected more than the heavier $^{37}Cl^+$ ions. By measuring the relative deflections of the ions, chemists can determine their mass-to-charge ratios and thus their masses. (b) Each peak in the mass spectrum corresponds to an ion with a particular mass-to-charge ratio. The abundance of the two isotopes can be determined from the heights of the peaks.

A: Diagram of a mass spectrometer, showing analysis of gaseous chlorine. B: Mass spectrum of chlorine.

The arbitrary standard that has been established for describing atomic mass is the atomic mass unit (amu or u), defined as one-twelfth of the mass of one atom of ^{12}C. Because the masses of all other atoms are calculated relative to the ^{12}C standard, ^{12}C is the only atom listed in Table 2.3.2 whose exact atomic mass is equal to the mass number. Experiments have shown that 1 amu = 1.66 × 10^{-24} g.

Mass spectrometric experiments give a value of 0.167842 for the ratio of the mass of ^2H to the mass of ^{12}C, so the **absolute mass** of ^2H is

$$\frac{\text{mass of }^2\text{H}}{\text{mass of }^{12}\text{C}} \times \text{mass of }^{12}\text{C} = 0.167842 \times 12 \text{ amu} = 2.104104 \text{ amu} \tag{3.1.4}$$

The masses of the other elements are determined in a similar way.

The periodic table lists the atomic masses of all the elements. Comparing these values with those given for some of the isotopes in Table 2.3.2 reveals that the atomic masses given in the periodic table never correspond exactly to those of any of the isotopes.

Because most elements exist as mixtures of several stable isotopes, the atomic mass of an element is defined as the weighted average of the masses of the isotopes. For example, naturally occurring carbon is largely a mixture of two isotopes: 98.89% ^{12}C (mass = 12 amu by definition) and 1.11% ^{13}C (mass = 13.003355 amu). The percent abundance of ^{14}C is so low that it can be ignored in this calculation. The average atomic mass of carbon is then calculated as follows:

$$(0.9889 \times 12 \text{ amu}) + (0.0111 \times 13.003355 \text{ amu}) = 12.01 \text{ amu} \tag{3.1.5}$$

Carbon is predominantly ^{12}C, so its average atomic mass should be close to 12 amu, which is in agreement with this calculation.

The value of 12.01 is shown under the symbol for C in the periodic table, although without the abbreviation amu, which is customarily omitted. Thus the tabulated atomic mass of carbon or any other element is the weighted average of the masses of the naturally occurring isotopes.

✓ Example 3.1.1: Bromine

Naturally occurring bromine consists of the two isotopes listed in the following table:

Solutions to Example 2.4.1

Isotope	Exact Mass (amu)	Percent Abundance (%)
^{79}Br	78.9183	50.69
^{81}Br	80.9163	49.31

Calculate the atomic mass of bromine.

Given: exact mass and percent abundance

Asked for: atomic mass

Strategy:

A. Convert the percent abundances to decimal form to obtain the mass fraction of each isotope.
B. Multiply the exact mass of each isotope by its corresponding mass fraction (percent abundance ÷ 100) to obtain its weighted mass.
C. Add together the weighted masses to obtain the atomic mass of the element.
D. Check to make sure that your answer makes sense.

Solution:

A The atomic mass is the weighted average of the masses of the isotopes. In general, we can write

atomic mass of element = [(mass of isotope 1 in amu) (mass fraction of isotope 1)] + [(mass of isotope 2) (mass fraction of isotope 2)] + …

Bromine has only two isotopes. Converting the percent abundances to mass fractions gives

$$^{79}\text{Br}: \frac{50.69}{100} = 0.5069$$

$$^{81}\text{Br}: \frac{49.31}{100} = 0.4931$$

B Multiplying the exact mass of each isotope by the corresponding mass fraction gives the isotope's weighted mass:

$$^{79}\text{Br}: 79.9183\ amu \times 0.5069 = 40.00\ amu$$

$$^{81}\text{Br}: 80.9163\ amu \times 0.4931 = 39.90\ amu$$

C The sum of the weighted masses is the atomic mass of bromine is

40.00 amu + 39.90 amu = 79.90 amu

D This value is about halfway between the masses of the two isotopes, which is expected because the percent abundance of each is approximately 50%.

? Exercise 3.1.1

Magnesium has the three isotopes listed in the following table:

Solutions to Example 2.4.1

Isotope	Exact Mass (amu)	Percent Abundance (%)
^{24}Mg	23.98504	78.70
^{25}Mg	24.98584	10.13
^{26}Mg	25.98259	11.17

Use these data to calculate the atomic mass of magnesium.

Answer

24.31 amu

Finding the Averaged Atomic Weight of an Element: Finding the Averaged Atomic Weight of an Element(opens in new window) [youtu.be]

Summary

The mass of an atom is a weighted average that is largely determined by the number of its protons and neutrons, whereas the number of protons and electrons determines its charge. Each atom of an element contains the same number of protons, known as the atomic number (Z). Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called isotopes. Each isotope of a given element has the same atomic number but a different mass number (A), which is the sum of the numbers of protons and neutrons. The relative masses of atoms are reported using the atomic mass unit (amu), which is defined as one-twelfth of the mass of one atom of carbon-12, with 6 protons, 6 neutrons, and 6 electrons. The atomic mass of an element is the weighted average of the masses of the naturally occurring isotopes. When one or more electrons are added to or removed from an atom or molecule, a charged particle called an ion is produced, whose charge is indicated by a superscript after the symbol.

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3.2: The Mole

The number of moles in a system can be determined using the atomic mass of an element, which can be found on the periodic table. This mass is usually an **average** of the abundant forms of that element found on earth. An element's mass is listed as the average of all its isotopes on earth.

Avogadro's Constant

One mole of oxygen atoms contains $6.02214179 \times 10^{23}$ oxygen atoms. Also, one mole of nitrogen atoms contains $6.02214179 \times 10^{23}$ nitrogen atoms. The number $6.02214179 \times 10^{23}$ is called *Avogadro's number* (N_A) or *Avogadro's constant*, after the 19th century scientist Amedeo Avogadro.

Each carbon-12 atom weighs about $1.99265 \times 10^{-23}\ g$; therefore,

$$(1.99265 \times 10^{-23}\ g) \times (6.02214179 \times 10^{23}\ atoms) = 12\ g\ \text{ of carbon-12}$$

Applications of the Mole

The mass of a mole of substance is called the **molar mass** of that substance. The molar mass is used to convert grams of a substance to moles and is used often in chemistry. The molar mass of an element is found on the periodic table, and it is the element's atomic weight in grams/mole (g/mol). If the mass of a substance is known, the number of moles in the substance can be calculated. Converting the mass, in grams, of a substance to moles requires a conversion factor of (one mole of substance/molar mass of substance).

The mole concept is also applicable to the composition of chemical compounds. For instance, consider methane, CH_4. This molecule and its molecular formula indicate that per mole of methane there is 1 mole of carbon and 4 moles of hydrogen. In this case, the mole is used as a common unit that can be applied to a ratio as shown below:

$$2 \text{ mol H } + 1 \text{ mol O } = 1 \text{ mol } \mathrm{H_2O}$$

In this this chemical reactions, the moles of H and O describe the number of atoms of each element that react to form 1 mol of H_2O.

To think about what a mole means, one should relate it to quantities such as dozen or pair. Just as a pair can mean two shoes, two books, two pencils, two people, or two of anything else, a mole means $6.02214179 \times 10^{23}$ of anything. Using the following relation:

$$1 \text{ mole} = 6.02214179 \times 10^{23} \tag{3.2.1}$$

is analogous to saying:

$$1 \text{ Dozen} = 12 \text{ eggs} \tag{3.2.2}$$

It is quite difficult to visualize a mole of something because Avogadro's constant is extremely large. For instance, consider the size of one single grain of wheat. If all the people who have existed in Earth's history did nothing but count individual wheat grains for their entire lives, the total number of wheat grains counted would still be much less than Avogadro's constant; the number of wheat grains produced throughout history does not even approach Avogadro's Number.

✓ Example 3.2.1: Converting Mass to Moles

How many moles of potassium (K) atoms are in 3.04 grams of pure potassium metal?

Solution

In this example, multiply the mass of K by the conversion factor (inverse molar mass of potassium):

$$\frac{1\ mol\ K}{39.10\ grams\ K}$$

39.10 grams is the molar mass of one mole of K; cancel out grams, leaving the moles of K:

$$3.04\ g\ \cancel{K}\left(\frac{1\ mol\ K}{39.10\ \ g\ \cancel{K}}\right) = 0.0778\ mol\ K$$

Similarly, if the moles of a substance are known, the number grams in the substance can be determined. Converting moles of a substance to grams requires a conversion factor of *molar mass of substance/one mole of substance*. One simply needs to follow the same method but in the opposite direction.

✓ Example 3.2.2: Converting Moles to mass

How many grams are 10.78 moles of Calcium (Ca)?

Solution

Multiply moles of Ca by the conversion factor (molar mass of calcium) **40.08 g Ca/ 1 mol Ca,** which then allows the cancelation of moles, leaving grams of Ca.

$$10.78\ \ mol\ \cancel{Ca}\left(\frac{40.08\ g\ Ca}{1\ \ mol\ \cancel{Ca}}\right) = 432.1\ g\ Ca$$

The total number of atoms in a substance can also be determined by using the relationship between grams, moles, and atoms. If given the mass of a substance and asked to find the number of atoms in the substance, one must first convert the mass of the substance, in grams, to moles, as in Example 3.2.1. Then the number of moles of the substance must be converted to atoms. Converting moles of a substance to atoms requires a conversion factor of **Avogadro's constant (6.02214179×10^{23}) / one mole of substance**. Verifying that the units cancel properly is a good way to make sure the correct method is used.

✓ Example 3.2.3: Atoms to Mass

How many atoms are in a 3.5 g sample of sodium (Na)?

Solution

$$3.5\ \ g\ \cancel{Na}\left(\frac{1\ mol\ Na}{22.98\ \ g\ \cancel{Na}}\right) = 0.152\ mol\ Na$$

$$0.152\ \ mol\ \cancel{Na}\left(\frac{6.02214179\times 10^{23}\ atoms\ Na}{1\ \ mol\ \cancel{Na}}\right) = 9.15\times 10^{22}\ atoms\ of\ Na$$

In this example, multiply the grams of Na by the conversion factor 1 mol Na/ 22.98 g Na, with 22.98g being the molar mass of one mole of Na, which then allows cancelation of grams, leaving moles of Na. Then, multiply the number of moles of Na by the conversion factor 6.02214179×10^{23} atoms Na/ 1 mol Na, with 6.02214179×10^{23} atoms being the number of atoms in one mole of Na (Avogadro's constant), which then allows the cancelation of moles, leaving the number of atoms of Na.

Using Avogadro's constant, it is also easy to calculate the number of atoms or molecules present in a substance (Table 3.2.1). By multiplying the number of moles by Avogadro's constant, the mol units cancel out, leaving the number of atoms. The following table provides a reference for the ways in which these various quantities can be manipulated:

Table 3.2.1: Conversion Factors

Known Information	Multiply By	Result
Mass of substance (g)	1/ Molar mass (mol/g)	Moles of substance
Moles of substance (mol)	Avogadro's constant (atoms/mol)	Atoms (or molecules)
Mass of substance (g)	1/Molar mass (mol/g) × Avogadro's constant (atoms/mol))	Atoms (or molecules)

✓ Example 3.2.4: Mass to Moles

How many moles are in 3.00 grams of potassium (K)?

Solution

$$3.00\ \ g\ \cancel{K}\left(\frac{1\ mol\ K}{39.10\ \ g\ \cancel{K}}\right)=0.0767\ mol\ K$$

In this example, multiply the mass of K by the conversion factor:

$$\frac{1\ mol\ K}{39.10\ grams\ K}$$

39.10 grams is the molar mass of one mole of K. Grams can be canceled, leaving the moles of K.

✓ Example 3.2.5: Moles to Mass

How many grams is in 10.00 moles of calcium (Ca)?

Solution

This is the calculation in Example $3.2.2$ performed in reverse. Multiply moles of Ca by the conversion factor **40.08 g Ca/ 1 mol Ca,** with 40.08 g being the molar mass of one mole of Ca. The moles cancel, leaving grams of Ca:

$$10.00\ \ mol\ \cancel{Ca}\left(\frac{40.08\ g\ Ca}{1\ \ mol\ \cancel{Ca}}\right)=400.8\ grams\ of\ Ca$$

The number of atoms can also be calculated using **Avogadro's Constant (6.02214179×10^{23}) / one mole of substance**.

✓ Example 3.2.6: Mass to Atoms

How many atoms are in a 3.0 g sample of sodium (Na)?

Solution

Convert grams to moles

$$3.0\ \ g\ \cancel{Na}\left(\frac{1\ mol\ Na}{22.98\ \ g\ \cancel{Na}}\right)=0.130\ mol\ Na$$

Convert moles to atoms

$$0.130548\ \ mol\ \cancel{Na}\left(\frac{6.02214179\times 10^{23}\ atoms\ Na}{1\ \ mol\ \cancel{Na}}\right)=7.8\times 10^{22}\ atoms\ of\ \ Na$$

Summary

The mole, abbreviated mol, is an SI unit which measures the number of particles in a specific substance. One mole is equal to 6.02214179×10^{23} atoms, or other elementary units such as molecules.

Problems

1. Using a periodic table, give the molar mass of the following:
    a. H
    b. Se
    c. Ne
    d. Cs
    e. Fe

2. Convert to moles and find the total number of atoms.
   a. 5.06 grams of oxygen
   b. 2.14 grams of K
   c. 0.134 kg of Li
3. Convert the following to grams
   a. 4.5 mols of C
   b. 7.1 mols of Al
   c. 2.2 mols of Mg
4. How many moles are in the product of the reaction
   a. 6 mol H + 3 mol O → ? mol H_2O
   b. 1 mol Cl + 1 mol Cl → ? mol Cl_2
   c. 5 mol Na + 4 mol Cl → ? mol NaCl

Answers

1. Question 2
   a. 1.008 g/mol
   b. 78.96 g/mol
   c. 20.18 g/mol
   d. 132.91g/mol
   e. 55.85 g/mol
2. Question 2

   2. 5.06g O (1mol/16.00g)= 0.316 mol of O

   0.316 mols ($6.022\text{x}10^{23}$ atoms/ 1mol) = $1.904\text{x}10^{23}$ atoms of O

   3. 2.14g K (1mol/39.10g)= 0.055 mol of K

   0.055 mols ($6.022\text{x}10^{23}$ atoms/ 1mol) **=** $3.312\text{x}10^{22}$ atoms of K

   4. 0.134kg Li (1000g/1kg)= 134g Li (1mol/6.941g)= 19.3 mols Li

   19.3 ($6.022\text{x}10^{23}$ atoms/ 1mol) = $1.16\text{x}10^{25}$ atoms of Li

3. Question 3
   a. 4.5 mols of C (12.011g/1mol) = 54.05 g of C
   b. 7.1 mols of Al (26.98g/1mol) = 191.56 g of Al
   c. 2.2 mols of Mg (24.31g/1mol) = 53.48 g of MG
4. Question 4
   1. **8.** 6 mol H + 3 mol O → 3 mol H_2O
   2. **9.** 1 mol Cl + 1 mol Cl → 1 mol Cl_2
   3. **10.** 5 mol Na + 4 mol Cl → 4 mol NaCl + 1 mol Na (excess)

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3.3: Molar Mass

Mass is a basic physical property of matter. The mass of an atom or a molecule is referred to as the **atomic mass.** The atomic mass is used to find the average mass of elements and molecules and to solve stoichiometry problems.

Introduction

In chemistry, there are many different concepts of mass. It is often assumed that **atomic mass** is the mass of an atom indicated in **unified atomic mass units (u)**. However, the book *Quantities, Units and Symbols in Physical Chemistry* published by the IUPAC clearly states:

> "Neither the name of the physical quantity, nor the symbol used to denote it, should imply a particular choice of unit."

The name "atomic mass" is used for historical reasons, and originates from the fact that chemistry was the first science to investigate the same physical objects on macroscopic and microscopic levels. In addition, the situation is rendered more complicated by the isotopic distribution. On the macroscopic level, most mass measurements of pure substances refer to a mixture of isotopes. This means that from a physical stand point, these mixtures are not pure. For example, the macroscopic mass of oxygen (O_2) does not correspond to the microscopic mass of O_2. The former usually implies a certain isotopic distribution, whereas the latter usually refers to the most common isotope ($^{16}O_2$). Note that the former is now often referred to as the "molecular weight" or "atomic weight".

Mass Concepts in Chemistry

name in chemistry	physical meaning	symbol	units
atomic mass	mass on microscopic scale	m, m_a	Da, u, kg, g
molecular mass	mass of a molecule	m	Da, u, kg, g
isotopic mass	mass of a specific isotope		Da, u, kg, g
mass of entity	mass of a chemical formula	m, m_f	Da, u, kg, g
average mass	average mass of a isotopic distribution	m	Da, u, kg, g
molar mass	average mass per mol	M = m/n	kg/mol or g/mol
atomic weight	average mass of an element	$A_r = m / m_u$	unitless
molecular weight	average mass of a molecule	$M_r = m / m_u$	unitless
relative atomic mass	ratio of mass m and and the atomic mass constant m_u	$A_r = m / m_u$	unitless
atomic mass constant	$m_u = m(^{12}C)/12$	m_u = 1 Da = 1 u	Da, u, kg, g
relative molecular mass	ratio of mass m of a molecule and and the atomic mass constant m_u	$M_r = m / m_u$	unitless
relative molar mass	?	?	?
mass number	nucleon number	A	nucleons, or unitless
integer mass	nucleon number * Da	m	Da, u
nominal mass	integer mass of molecule consisting of most abundant isotopes	m	Da, u

name in chemistry	physical meaning	symbol	units
exact mass	mass of molecule calculated from the mass of its isotopes (in contrast of measured ba a mass spectrometer)		Da, u, kg, g
accurate mass	mass (not normal mass)		Da, u, kg, g

These concepts are further explained below.

Average Mass

Isotopes are atoms with the same atomic number, but different mass numbers. A different mass size is due to the difference in the number of neutrons that an atom contains. Although mass numbers are whole numbers, the actual masses of individual atoms are never whole numbers (except for carbon-12, by definition). This explains how lithium can have an atomic mass of 6.941 Da. The atomic masses on the periodic table take these isotopes into account, weighing them based on their abundance in nature; more weight is given to the isotopes that occur most frequently in nature. Average mass of the element E is defined as:

$$m(E) = \sum_{n=1} m(I_n) \times p(I_n) \tag{3.3.1}$$

where $\sum$ represents a n-times summation over all isotopes I_n of element E, and p(I) represents the relative abundance of the isotope I.

✓ Example 1

Find the average atomic mass of boron using the Table 1 below:

Mass and abundance of Boron isotopes

n	isotope I_n		mass m (Da)	isotopic abundance p
1	^{10}B		10.013	0.199
2	^{11}B		11.009	0.801

Solution

The average mass of Boron is:

$$m(B) = (10.013\ Da)(0.199) + (11.009\ Da)(0.801) = 1.99\ Da + 8.82\ Da = 10.81\ Da \tag{3.3.2}$$

Relative Mass

Traditionally it was common practice in chemistry to avoid using any units when indicating atomic masses (e.g. masses on microscopic scale). Even today, it is common to hear a chemist say, "^{12}C has exactly mass 12". However, because mass is not a dimensionless quantity, it is clear that a mass indication needs a unit. Chemists have tried to rationalize the omission of a unit; the result is the concept of relative mass, which strictly speaking is not even a mass but a ratio of two masses. Rather than using a unit, these chemists claim to indicate the ratio of the mass they want to indicate and the atomic mass constant m_u which is defined analogous to the unit they want to avoid. Hence the relative atomic mass of the mass m is defined as:

$$A_r = \frac{m}{m_u} \tag{3.3.3}$$

The quantity is now dimensionless. As this unit is confusing and against the standards of modern metrology, the use of relative mass is discouraged.

Molecular Weight, Atomic Weight, Weight vs. Mass

Until recently, the concept of mass was not clearly distinguished from the concept of weight. In colloquial language this is still the case. Many people indicate their "weight" when they actually mean their mass. Mass is a fundamental property of objects, whereas weight is a force. Weight is the force F exerted on a mass m by a gravitational field. The exact definition of the weight is controversial. The weight of a person is different on ground than on a plane. Strictly speaking, weight even changes with location on earth.

When discussing atoms and molecules, the mass of a molecule is often referred to as the "molecular weight". There is no univerally-accepted definition of this term; however, mosts chemists agree that it means an average mass, and many consider it dimensionless. This would make "molecular weight" a synonym to "average relative mass".

Integer Mass

Because the proton and the neutron have similar mass, and the electron has a very small mass compared to the former, most molecules have a mass that is close to an integer value when measured in daltons. Therefore it is quite common to only indicate the **integer mass** of molecules. Integer mass is only meaningful when using dalton (or u) units.

Accurate Mass

Many mass spectrometers can determine the mass of a molecule with accuracy exceeding that of the integer mass. This measurement is therefore called the **accurate mass** of the molecule. Isotopes (and hence molecules) have atomic masses that are not integer masses due to a mass defect caused by binding energy in the nucleus.

Units

The atomic mass is usually measured in the units *unified atomic mass unit* (u), or dalton (Da). Both units are derived from the carbon-12 isotope, as 12 u is the exact atomic mass of that isotope. So 1 u is 1/12 of the mass of a carbon-12 isotope:

$$1\text{ u} = 1\text{ Da} = m(^{12}\text{C})/12$$

The first scientists to measure atomic mass were John Dalton (between 1803 and 1805) and Jons Jacoband Berzelius (between 1808 and 1826). Early atomic mass theory was proposed by the English chemist William Prout in a series of published papers in 1815 and 1816. Known was Prout's Law, Prout suggested that the known elements had atomic weights that were whole number multiples of the atomic mass of hydrogen. Berzelius demonstrated that this is not always the case by showing that chlorine (Cl) has a mass of 35.45, which is not a whole number multiple of hydrogen's mass.

Some chemists use the atomic mass unit (amu). The amu was defined differently by physicists and by chemists:

- Physics: 1 amu = $m(^{16}\text{O})/16$
- Chemistry: 1 amu = m(O)/16

Chemists used oxygen in the naturally occurring isotopic distribution as the reference. Because the isotopic distribution in nature can change, this definition is a moving target. Therefore, both communities agreed to the compromise of using $m(^{12}\text{C})/12$ as the new unit, naming it the "unified atomic mass unit" (u). Hence, the amu is no longer in use; those who still use it do so with the definition of the u in mind. For this reason, the dalton (Da) is increasingly recommended as the accurate mass unit.

Neither u nor Da are SI units, but both are recognized by the SI.

Molar Mass

The molar mass is the mass of one mole of substance, whether the substance is an element or a compound. A mole of substance is equal to Avogadro's number (6.023×10^{23}) of that substance. The molar mass has units of g/mol or kg/mol. When using the unit g/mol, the numerical value of the molar mass of a molecule is the same as its average mass in daltons:

- Average mass of C: 12.011 Da
- Molar mass of C: 12.011 g/mol

This allows for a smooth transition from the microscopic world, where mass is measured in daltons, to the macroscopic world, where mass is measured in kilograms.

✓ Example 2

What is the molar mass of phenol, C_6H_5OH?

Average mass m = 6 × 12.011 Da + 6 × 1.008 Da + 1 × 15.999 Da = 94.113 Da

Molar mass = 94.113 g/mol = 0.094113 kg/mo

Measuring Masses in the Atomic Scale

Masses of atoms and molecules are measured by mass spectrometry. Mass spectrometry is a technique that measures the mass-to-charge ratio (m/q) of ions. It requires that all molecules and atoms to be measured be ionized. The ions are then separated in a mass analyzer according to their mass-to-charge ratio. The charge of the measured ion can then be determined, because it is a multiple of the elementary charge. The the ion's mass can be deduced. The average masses indicated in the periodic table are then calculated using the isotopic abundances, as explained above.

The masses of all isotopes have been measured with very high accuracy. Therefore, it is much simpler and more accurate to calculate the mass of a molecule of interest as a sum of its isotopes than measuring it with a commercial mass spectrometer.

Note that the same is not true on the nucleon scale. The mass of an isotope cannot be calculated accurately as the sum of its particles (given in the table below); this would ignore the mass defect caused by the binding energy of the nucleons, which is significant.

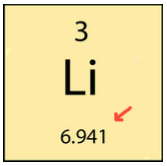
Table 2: Mass of three sub-atomic particles

Particle	SI (kg)	Atomic (Da)	Mass Number A
Proton	1.6726×10^{-27}	1.0073	1
Neutron	1.6749×10^{-27}	1.0087	1
Electron	9.1094×10^{-31}	0.00054858	0

As shown in Table 2, the mass of an electron is relatively small; it contributes less than 1/1000 to the overall mass of the atom.

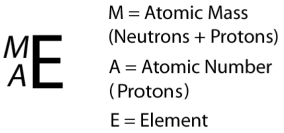
Where to Find Atomic Mass

The atomic mass found on the Periodic Table (below the element's name) is the average atomic mass. For example, for Lithium:



The red arrow indicates the atomic mass of lithium. As shown in Table 2 above and mathematically explained below, the masses of a protons and neutrons are about 1u. This, however, does not explain why lithium has an atomic mass of 6.941 Da where 6 Da is expected. This is true for all elements on the periodic table. The atomic mass for lithium is actually the average atomic mass of its isotopes. This is discussed further in the next section.

One particularly useful way of writing an isotope is as follows:



Applications

Applications Include:

1. Average Molecular Mass
2. Stoichiometry

Note: One particularly important relationship is illustrated by the fact that an atomic mass unit is equal to 1.66 × 10^{-24} g. This is the reciprocal of Avogadro's constant, and it is no coincidence:

$$\frac{\text{Atomic Mass (g)}}{1\text{g}} \times \frac{1\text{mol}}{6.022\times10^{23}} = \frac{\text{Mass (g)}}{1\text{atom}} \tag{3.3.4}$$

Because a mol can also be expressed as gram × atoms,

$$1\ u = \frac{M_u\ (molar\ mass\ unit)}{N_A\ (Avogadro's\ Number)} = 1\ \frac{g}{mol\ N_A} \tag{3.3.5}$$

`1u = `M_u`(molar mass unit)/`N_A`(Avogadro's Number)=1g/mol/`N_A

N_A known as Avogadro's number (Avogadro's constant) is equal to 6.023×10^{23} atoms.

Atomic mass is particularly important when dealing with stoichiometry.

Practice Problems

a. What is the molecular mass of radium bicarbonate, $Ra(HCO_3)_2$?
b. List the following, from least to greatest, in terms of their number of neutrons, and then atomic mass: ^{14}N, ^{42}Cl, ^{25}Na, ^{10}Be
c. A new element, Zenium, has 3 isotopes, ^{59}Ze, ^{61}Ze, and ^{67}Ze, with abundances of 62%, 27%, and 11% respectively. What is the atomic mass of Zenium?
d. An isotope with a mass number of 55 has 5 more neutrons than protons. What element is it?
e. How much mass does 3.71 moles of Fluorine have?
f. How many grams are there in 4.3×10^{22} molecules of $POCl_3$?
g. How many moles are there in 23 grams of sodium carbonate?

Solutions

a) Molecular mass of $Ra(HCO_3)_2$

= 226 + 2(1.01 u + 12.01 u + (16.00 u)(3)) = 348 u or g/mol

b) Number of neutrons: ^{10}Be, ^{14}N, ^{25}Na, ^{42}Cl

Atomic Mass: ^{10}Be, ^{14}N, ^{25}Na, ^{42}Cl

Note: It is the same increasing order for both number of neutrons and atomic mass because more neutrons means more mass.

c) Atomic mass of Zenium:

(59 u)(0.62) + (61 u)(0.27) + (67 u)(0.11)

= 37 u + 16 u + 7.4 u

= 60.4 u or g/mol

d) Mn

e) (3.71 moles F_2)(19 × 2 g/mol F_2)

= (3.71 mol F_2)(38 g/mol F_2)

= 140 g F_2

f) (4.3×10^{22} molecules $POCI_3$)(1 mol/6.022×10^{23} molecules POCI3)(30.97 + 16.00 + 35.45 x 3 g/mol $POCI_3$)

= (4.3×10^{22} molecules $POCI_3$)(mol/6.022×10^{23} molecules POCI3)(153.32 g/mol $POCI_3$)

= 11 g $POCI_3$

g) (23 g Na_2CO_3)(1 mol/22.99 × 2 + 12.01 + 16.00 × 3 g Na_2CO_3)

= (23 g Na_2CO_3)(1 mol/105.99 g Na_2CO_3)

= (0.22 mol Na_2CO_3)

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3.5 Percent Composition of Compounds

CHEMTUTOR

Every chemist has dreamed that atoms were large enough to see and manipulate one at a time. The same chemist realizes after considering it, that if individual molecules were available for manipulation, it would take far too long to get anything done. The view from the atom is very different from the view of trillions and trillions of atoms. The mass action of the atoms that we see on our ‘macro’ view of the world is the result of the action of an incredibly large number of atoms averaged in their actions. The most usual way we count the atoms is by weighing them. The mass of material as weighed on a balance and the atomic weight of the material being weighed is the way we have of knowing how many atoms or molecules we are working with. Instead of counting eggs, we can count cartons of eggs, each carton of which has a given number, a dozen. Instead of counting B-B’s, we can count liters of B-B’s and find out how many B-B’s are in a liter. Instead of counting oats, we buy train cars of oats and know the number of oats in a full train car.

WHY DO WE NEED MOLS?

There are less than one hundred naturally occurring elements. Each element has a characteristic atomic weight. Most Periodic Charts include the atomic weight of an element in the box with the element. The atomic weight is usually not an integer because it is close to being the number of protons plus the average number of neutrons of an element. Let’s use the atomic weight as a number of grams. This will give us the same number of any atom we choose. If we weigh out 1.008 grams of hydrogen and 35.45 grams of chlorine and 24.3 grams of magnesium, we will have the same number of atoms of each one of these elements. The neat trick with this system is that we can weigh the atoms on a grand scale of number of atoms and get a count of them. This number of atoms that is the atomic weight expressed in grams is Avogadro’s number, 6.022 E 23. The name for Avogadro’s number of ANYTHING is a mole or mol. A mol of aluminum is 27.0 grams of aluminum atoms. Aluminum is an element, so the particles of aluminum are atoms. There are Avogadro’s number of aluminum atoms in 27.0 grams of it. But 1.008 grams of hydrogen is NOT a mol of hydrogen! Why not? Remember that hydrogen is one of the diatomic gases. There is really no such thing as loose hydrogen atoms. The total mass of a single hydrogen diatomic molecule (H_2) is 2. 016 AMU. A mol of hydrogen gas has a mass of 2.016 grams. In that 2.016 gram mass is Avogadro’s number of H_2 molecules because that is the way hydrogen comes. A mol of water is 18.016 grams because each water molecule has two hydrogen atoms and one oxygen atom. A mol of water has in it Avogadro’s number of water molecules. Another way to view the same thing is that a formula weight is the total mass of a formula in AMU expressed with units of grams per mol.

So Avogadro’s number is just a number, like dozen or gross or million or billion, but it is a **very** large number. You could consider a mol of sand grains or a mol of stars. We are more likely to speak of a mol of some chemical, for which we can find the mass of a mol of the material by adding the atomic weights of all the atoms in a formula of the chemical. The unit of atomic weight or formula weight is grams/mol.

The chemical formula of a material should tell you; (a) which elements are in the material, (b) how many atoms of each element are in the formula, (c) the total formula weight, and (d) how the elements are attached to each other. The symbols of the elements tell you which elements are in the material. The numbers to the right of each symbol tells how many atoms of that element are in the formula. The type of atoms and their arrangement in the formula will tell how the elements are attached to each other. A metal and a nonmetal or negative polyatomic ion shows an ionic compound. A pair of non-metals are bonded by covalent bonds. Some crystals have water of hydration loosely attached in the crystal. This is indicated by the dot such as in blue vitriol, $Cu(SO_4)\cdot 5H_2O$, showing five molecules of water of hydration to one formula of cupric sulfate.

The unit of the formula weight or molecular weight or atomic weight is "grams per mol," so it provides a relationship between mass in grams and mols of material.

$$nF_w = m$$

'n' is the number of mols, 'Fw is the formula weight, and 'm' is the mass.

PERCENTS BY WEIGHT

All men weigh 200 pounds. All women weigh 125 pounds. What is the percent by weight of woman in married couples? A married couple is one man and one woman. The total weight is 325 pounds. The formula for percent is:

In this case the woman is the target.

125 # 325 #	x	100%	=	38.461%	=	36.5%

Notice that the units of pound cancel to make the percent a pure number of comparison.

The weights of atoms are the atomic weights. What is the percentage of chloride in potassium chloride? The atomic weight of potassium is 39.10 g/mol. The atomic weight of chlorine is 35.45 g/mol. So the formula weight of potassium chloride is 74.55 g/mol. The chloride is the target and the potassium chloride is the total. 35.45 g/mol / x 100% = 47.55198 % or 47.6 % to three significant figures.

35.45~~g/mol~~ 74.55~~g/mol~~	x	100%	=	47.5520%	=	47.6%

You can do that with any part of a compound. What is the percentage of sulfate in beryllium sulfate tetrahydrate?

Notice that the examples here are done to two decimal points of the atomic weights. The problems in the practice bunch at the end of this chapter are done to one decimal point of the atomic weight.

BASIC STOICHIOMETRY

Pronounce stoichiometry as “stoy-kee-ah-met-tree,” if you want to sound like you know what you are talking about, or “stoyk:,” if you want to sound like a real geek. Stoichiometry is just a five dollar idea dressed up in a fifty dollar name. You can compare the amounts of any materials in the same chemical equation using the formula weights and the coefficients of the materials in the equation. Let’s consider the equation for the Haber reaction, the combination of nitrogen gas and hydrogen gas to make ammonia.

N2 + 3 H2 2 NH3

The formula for nitrogen is N_2 and the formula for hydrogen is $H_{2.}$ They are both diatomic gases. The formula for ammonia is NH_3

The balanced equation requires one nitrogen molecule and three hydrogen molecules to make two ammonia molecules, meaning that one nitrogen molecule reacts with three hydrogen molecules to make two ammonia molecules or one MOL of nitrogen and three MOLS of hydrogen make two MOLS of ammonia. Now we are getting somewhere. The real way we measure amounts is by weight (actually, mass), so (to two significant digits) 28 grams (14 g/mol times two atoms of nitrogen per molecule) of nitrogen and 6 grams of hydrogen (1 g/mol times two atoms of hydrogen per molecule times three mols) make 34 grams of ammonia. Notice that no mass is lost or gained, since the formula weight for ammonia is 17 (one nitrogen at 14 and three hydrogens at one g/mol) and there are two mols of ammonia made. Once you have the mass proportions, any mass-mass stoichiometry can be done by good old proportionation. What is the likelihood you will get just a simple mass-mass stoich problem on your test? You should live so long. Well, you should get ONE.

Rather than thinking in terms of proportions, think in mols and mol ratios, a much more general and therefore more useful type of thinking. A mol ratio is just the ratio of one material in a chemical equation to another material in the same equation. The mol ratio uses the coefficients of the materials as they appear in the balanced chemical equation. What is the mol ratio of hydrogen to ammonia in the Haber equation? 3 mols of hydrogen to 2 mols of ammonia. Easy. In the standard stoichiometry calculations you should know, ALL ROADS LEAD TO MOLS. You can change any amount of any measurement of any material in the same equation with any other material in any measurement in the same equation. That is powerful. The setup is similar to Dimensional Analysis.

1. Start with what you know (GIVEN), expressing it as a fraction.
2. Use definitions or other information to change what you know to mols of that material.

3. Use the mol ratio to exchange mols of the material given to the mols of material you want to find.
4. Change the mols of material you are finding to whatever other measurement you need.

How many grams of ammonia can you make with 25 grams of hydrogen? (Practice your mol math rather than doing this by proportion. Check it by proportion in problems that permit it.)

You are given the mass of 25 grams of hydrogen. Start there.

Visual for solving stoichiometry problems in a Dimensional Analysis style.

25 g H2/1 Change to mols of hydrogen by the formula weight of hydrogen 1 mol of H2 = 2.0 g. (The 2.0 g goes in the denominator to cancel with the gram units in the material given.) Change mols of hydrogen to mols of ammonia by the mol ratio. 3 mols of hydrogen = 2 mols of ammonia. (The mols of hydrogen go in the denominator to cancel with the mols of hydrogen. You are now in units of mols of ammonia.) Convert the mols of ammonia to grams of ammonia by the formula weight of ammonia, 1 mol of ammonia = 17 g. (Now the mols go in the denominator to cancel with the mols of ammonia.) Cancel the units as you go.

The math on the calculator should be the last thing you do. 2 5 ÷ 2 . 0 x 2 ÷ 3 x 1 7 = and the number you get (141.66667) will be a number of grams of ammonia as the units in your calculations show. Round it to the number of significant digits your instructor requires (often three sig. figs.) and put into scientific notation if required. Most professors suggest that scientific notation be used if the answer is over one thousand or less than a thousandth. The answer is 142 grams of ammonia.

The calculator technique in the preceding paragraph illustrates a straightforward way to do the math. If you include all the numbers in order as they appear, you will have less chance of making an error. Many times students have been observed gathering all the numbers in the numerator, gathering all the numbers in the denominator, presenting a new fraction of the collected numbers, and then doing the division to find an answer. While this method is not wrong, the extra handling of the numbers has seen to produce many more errors.

See the Stoichiometry Roadmap for a way to consider this idea graphically. This example starts at "mass given" and goes throught the mol ratio to "mass find."

mass1--Fw1--mol1--mol ratio2/1--mol2--Fw2--mass2

Notice by the chart above we may get the number of mols of material given if we change the mass by the formula weight, but in our continuous running math problem, we don't have to stop and calculate a number of mols. Students who insist on doing so tend to get more calculator errors.

The more traditional formula for converting mols to mass would be, where Fw is the formula weight, m is the mass, and n is the number of mols: n x Fw = m. You should be able to "see" these formula relationships on the roadmap.

DENSITY TIMES MASS OF A PURE MATERIAL

Density multiplied by the volume of a pure material is equal to the mass of that material. If we know the density of a material and the volume of the pure material, with D = density and V = volume, DV = m so:

D1V1--mass1--Fw1--mol1--mol ratio2/1--mol2--Fw2--mass2--1/D2=V2

If you were given the density and volume of pure material you could calculate the volume of another material in that equation if you know it's density. Notice that the density must be inverted to cancel the units properly if you want the volume to find. If you need to find the density, the volume must be inverted.

See the Stoichiometry Roadmap for a graphic view of this idea. Start with "Given density times volume of a pure material.

ATOMS OR MOLECULES TO MOLS

One of the hardest ideas for some students is that the individual particles of a material are a single one of a formula of that material. Copper element comes only in the form of atoms. Water only comes in the form of a molecule with one oxygen and two hydrogen atoms. A mol, then is Avogadro's number of individual particles of whatever type of pure material the substance is made. There is no such thing as a mol of mud because mud is a mixture. There is no one mud molecule.

The word "pure" also can be misunderstood. We do not mean that a material is one hundred percent the same material for us to use it, but that we are only considering the amount of that material.

The formula behind this relationship is: where n is the number of mols, A is Avogadro's number, and # is the number of individual particles of material,

A x n =

Refer to the Stoichiometry Roadmap for a graphic view of this idea.

CONCENTRATION TIMES VOLUME OF A SOLUTION

A *solution* is a mixture of a fluid (often water, but not always) and another material mixed in with it. The material mixed in with it is called the *solute*. There is more on solutions in the chapter devoted to that. The volume of a solution, V, is measured the same way the volume of a pure liquid is measured. The concentration can be expressed in a number of ways, the most common in chemistry is the M, molar. One molar is one mol of solute in a liter of fluid. It is important to notice that the fluid is usually nothing more than a diluting agent. For most of the reactions, the fluid does not participate in any reaction.

Concentration times volume is number of mols of the solute material.

C x V = n

The "given" side of concentration times volume is easy. As with density times volume of a pure material, but the "find" side may need more work. You need one or the other of the concentration and volume before you can calculate the other. At the end of the Dimensional Analysis if you want concentration, you will be using the volume inverted. If you want the volume, you will be using the concentration inverted. This is not so difficult because the units will guide you.

Refer to the Stoichiometry Roadmap for a graphic view of this idea.

GASES

Standard temperature is zero degrees Celsius. Standard pressure is one atmosphere. A mol of ANY gas at standard temperature and pressure (STP) occupies 22.4 liters. That number is good to three significant digits. The equation would be 1 mol gas = 22.4 L @STP. The conversion factor, the Molar Volume of Gas, is 1 mol gas/22.4 L @STP or 22.4 L @STP/1 mol gas

Where n is the number of mols, V is the volume of a gas, and MVG is the molar volume of gas,

V = n x MVG

Gases not at STP will require the Ideal Gas Law Formula,

P V = n R T

where P is the pressure of the gas in atmospheres, V is the volume of the gas in liters, n is the number of mols of gas, T is the Kelvin temperature of the gas, and R is the "universal gas constant" with the measurement of 0.0821 liter-atmospheres per mol-degree. We will have to do some algebra on the PV = nRT gas equation to do the gas portion of the stoichiometry problems.

In GIVEN we only need to solve for n. n = PV/RT. If we need to find the volume, pressure, or temperature of a gas, we need to solve for the unknown and include the "mols find" as the n. More about gases later. See the Chemtutor section on Gases for math problems using the gas laws.

The earmarks of a stoichiometry problem are: There is a reaction. (A new material is made.) You know the amount of one material and you are asked to calculate the amount of another matierial in the same equation.

HOW TO USE THE "ROADMAP" FOR SOLVING CHEMISTRY PROBLEMS

1. Write all the compounds and elements in the problem correctly.
2. Write the balanced chemical equation for the problem.
3. Write the MATERIAL you have enough information about to use as GIVEN. (This has been one of the major stumbling blocks in using the roadmap.) If you know the number of moles, the mass, or the number of molecules of a material, you have all you need to start the problem. You need CONCENTRATION AND VOLUME of a solution to have the amount of solute that reacts. You need VOLUME AND DENSITY of a solid or liquid to have an amount of that. You need VOLUME, PRESSURE AND TEMPERATURE of a gas to have a complete set of information. (Notice it is useful to understand the properties of the states of matter as you do this.)

4. Write what you need to FIND and all the other pertinent information about that material. For instance, if you need to find the volume of a gas, you must also list the pressure and temperature of that gas in FIND. In this manner: FIND V, volume of gas at 79 °C and 1.8 atm.
5. Sketch out an outline of the math according to the roadmap. You know there are some points in the roadmap that you miss on the outline because they are calculated in the process, for instance if you are given a mass of one material and asked to find the density of another material with its volume, you would start at the MASS GIVEN and use the FORMULA WEIGHT to get to the MOLES GIVEN, but MOLES GIVEN does not appear in the outline because it is already calculated. You next need the MOLE RATIO to get the MOLES FIND. Again, MOLES FIND does not appear in the outline.
6. Fill in the outline with the numbers, units and materials (for instance, 15 kg Mg) and do the calculations. Be careful of numbers that need to be inverted. You can tell the coefficients that need to be inverted by the units.

STOICHIOMETRY ROADMAP

One of the really nice things about the Stoichiometry Roadmap is that once you understand it thoroughly, it can be carried around with you between your ears. Just remember that ALL ROADS LEAD TO MOLS.

MOLE AND PERCENT WORKSHEET

1. How many pennies are in a mole of pennies? How many thousand-dollar bills (k-notes!) is that mole of pennies equal to?

2. $NO2$ is the molecular formula for nitrous dioxide (also known as nitrogen dioxide). List the information available to you from this formula?.

3. $C2H2$ is the molecular formula for ethylyne (A.K.A. acetylene). (a) How many atoms are in one molecule? (b) Which atoms make up acetylene? (c) How many moles of atoms are in one molecule of acetylene? (d) How many molecules are in 5.3 moles of acetylene? (e) How many atoms are in a mole of acetylene?

4. Calculate the molar mass of a mole of the following materials: (a) Al (b) Ra (c) Co (d) CO (e) $CO2$ (f) HCl (g) $Na2CO3$ (h) $Ca(NO3)2$(i) $(NH4)3(PO4)$ (j) $H2O$ (k) Epsom salts - $Mg(SO4)\cdot 7H2O$ (m) blue vitriol - $Cu(SO4)\cdot 5H2O$?

5. Calculate the number of moles in: (a) 2.3 # of carbon (b) 0.014 g of Tin (c) a 5 Oz silver bracelet (d) a pound of table salt (e) a 350 kg cast iron engine block (f) a gal. of water (8.3 #) (g) a ton of sand $(SiO2)$ (h) 6.2 grams of blue vitriol (i) a pound of Epsom salts ?

6. Calculate the number of atoms in: (a) 100 g of Argon (b) 1.21 kg aluminum foil (c) a 28 # lead brick (d) the E7 kg of water in an olympic swimming pool (e) 7 kg of hydrogen gas (f) a tonne of calcium nitrate ?

7. What is the percentage composition of oxygen in each of the following materials: (a) CO (b) $CO2$ (c) $(NO3)^-$ (d) isopropyl alcohol $C3H8O$ (e) calcium nitrate (f) blue vitriol - $Cu(SO4)\cdot 5H2O$?

8. What is the percentage composition of phosphate in each of the following materials: (a) phosphoric acid (b) sodium carbonate (c) ammonium phosphate (d) calcium phosphate ?

9. What is the percentage composition of sulfate in each of the following materials: (a) sulfuric acid (b) sodium sulfate (c) Epsom salts (d) aluminum sulfate ?

ANSWERS TO MOL AND PERCENT PROBLEMS

1a. 6.023 E23 pennies		**1b. 6.023 E18 k-Notes**		**2a. Covalent**
2b. Elements in it (N and O)		**2c. Number of atoms of each element**		
3a. 4	**3b. C & H**	**3c. 6.64 E-24**	**3d. 3.1922 E24**	**3e. 2.4092 E24**
4a. 27.0	**4b. 226.0**	**4c. 58.9**	**4d. 28.0**	**4e. 44.0**
4f. 36.5	**4g. 106.0**	**4h. 164.1**	**4i. 149.0**	**4j. 18.0**

4k. 246.4	**4m. 249.6**	**5a. 86.9**	**5b. 1.18 E-4**	**5c. 1.31**
5d. 7.75	**5e. 6.27 E3**	**5f. 210**	**5g. 1.51 E4**	**5h. 0.0248**
5i. 1.84	**6a. 1.51 E24**	**6b. 2.69 E25**	**6c. 3.69 E25**	**6d. 1.00 E33**
6e. 4.22E27	**6f. 3.30 E28**	**7a. 57.1%**	**7b. 72.7%**	**7c. 77.4%**
7d. 26.7%	**7e. 58.5%**	**7f. 57.7%**	**8a. 96.9%**	**8b. 0%**
8c. 63.8%	**8d. 61.2%**	**9a. 98.0%**	**9b. 67.6%**	**9c. 39.0%**
9d. 84.2%				

STP GAS AND MASS STOICHIOMETRY PROBLEMS (PRELIMINARY TO GAS LAW)

All of the problems below are stoichiometry problems with at least one equation participant as a gas at STP. (a) Write and balance the chemical equation. (2) Do the math in DA style using 1 mole gas at STP = 22.4 liters as a factor. In the following problems ALL GASES ARE AT STP. Click here for a general idea of how to do the problems in this set.

1. How many moles of nitrogen gas is needed to react with 44.8 liters of hydrogen gas to produce ammonia gas?
2. How many liters of ammonia are produced when 89.6 liters of hydrogen are used in the above reaction?
3. Ten grams of calcium carbonate was produced when carbon dioxide was added to lime water (calcium hydroxide in solution). What volume of carbon dioxide at STP was needed?
4. When 11.2 liters of hydrogen gas is made by adding zinc to sulfuric acid, what mass of zinc is needed?
5. What volume of ammonia at STP is needed to add to water to produce 11 moles of ammonia water?
6. How many grams of carbonic acid is produced when 55 liters of carbon dioxide is pressed into water?
7. magnesium hydroxide + ammonium sulfate magnesium sulfate + water + ammonia
    1. How much (grams) magnesium hydroxide do you need to use in the above reaction to produce 500 liters of ammonia?
8. How much strontium bromide is needed to add to chlorine gas to produce 75 liters of bromine?
9. What mass of ammonium chlorate is needed to decompose to give off 200 liters of oxygen?
10. Your car burns mostly octane, C8H18, as a fuel. How many liters of oxygen is needed to burn a kilogram of octane?
11. copper + sulfuric acid copper II sulfate + water + sulfur dioxide
    1. How many moles of copper are needed to produce 1000 L of SO2?
12. What volume of oxygen is needed to burn a pound of magnesium?
13. How many grams of sodium do you have to put into water to make 30 liters of hydrogen at STP?
14. ammonia gas and hydrogen chloride gas combine to make ammonium chloride.
    1. What volume of ammonia at STP is needed to react with 47.7 liters of hydrogen chloride at STP?
15. How many liters of oxygen are needed to burn 10 liters of acetylene?

ANSWERS TO STP GAS AND MASS STOICHIOMETRY PROBLEMS

1. 0.667 mol	2. 59.7 L	3. 2.24 L	4. 32.7 g
5. 246 L	6. 152 g	7. 651 g	8. 828 g
9. 604 g	10. 2.46 kL	11. 44.6 mol	12. 210 L

13. 61.6 g	14. 47.7 L	15. 25 L	

PROBLEMS ON CONCENTRATION AND DENSITY

WRITE AND BALANCE THE CHEMICAL EQUATION FOR THOSE PROBLEMS THAT NEED IT. SHOW ALL YOUR WORK. USE W5P OR DA METHOD ACCORDING TO THE ROADMAP.

1. The lead brick on my desk measures 3 by 5 by 11 cm. Lead has a density of 11.34 g/cc. How many lead atoms are in that block?
2. The lab technician at the Planter's Peanut packing factory takes a bag of peanuts, puts water into it to dissolve the salt, and dilutes the solution to one liter. She then takes ten ml of that solution and titrates it against 0.132 M silver nitrate. One bag sample takes 31.5 ml of silver nitrate to endpoint. What mass of salt was in the bag?
3. What is the concentration of sugar $(C_{12}H_{22}O_{11})$ if twenty grams are dissolved in enough water to make 2 liters?
4. Methyl alcohol (CH_3OH) has a density of 0.793 kg/l. What volume of it is needed to add to water to make five liters of 0.25 M solution?
5. Magnesium has a density of 1.741 g/cc. What volume of Mg will burn in 20 liters of oxygen at 2.1 atm and 0°C?
6. Uranium metal can be purified from uranium hexafluoride by adding calcium metal. Calcium metal has a density of 1.54 g/cc. Uranium has a density of 18.7 g/cc. What mass of uranium do you get for a Kg of Ca? What volume of uranium do you get for a cubic meter of calcium?
7. What volume of 0.27 M sodium hydroxide is needed to react with 29.5 ml of 0.55 M phosphoric acid?
8. What volume of carbon dioxide is produced at 1 atm and 87 °C when 1.6 liters of methyl alcohol burns? What volume of liquid water is produced in this reaction?
9. Seven kilograms of mercury II oxide decomposes into mercury and oxygen. Mercury has a density of 13.6 g/cc/ What volume of mercury is produced?
10. Water and calcium oxide produce calcium hydroxide. How many grams of calcium hydroxide are made if you add 275 liters of water to enough calcium oxide?
11. Gasoline (C_7H_{16}) has a density of 0.685 kg/liter. How many liters of oxygen at 37 °C and 950 mmHg are needed to burn 15 liters of gasoline?
12. Sodium hydroxide and hydrochloric acid combine to make table salt and water. 14 mL of 0.1 M sodium hydroxide is added to an excess of acid. How many moles of table salt are made? How many grams of salt is that?
13. 50 mL of 0.25 M copper II sulfate evaporates to leave $CuSO_4 \cdot 5H_2O$. (That is the pentahydrate crystal of copper II sulfate.) What is the mass of this beautiful blue crystal from the solution?
14. Chlorine gas is bubbled into 100 mL of 0.25 M potassium bromide solution. This produces potassium chloride and bromine gas. The bromine (which dissolves in water) is taken from the solution and measured at 27 °C and 825 mmHg. What is the volume of bromine?
15. 95.0 mL of 0.55 M sulfuric acid is put on an excess of zinc. This produces zinc sulfate and hydrogen. How many grams of zinc sulfate are made?
16. and some dissolved sodium nitrate. (a) How many moles of silver chloride are made? (b) How many grams of silver chloride is that? (c) How many moles of sodium nitrate are made? (d) What is the concentration of sodium nitrate in the final solution?
17. How many grams of potassium permanganate, $KMnO_4$, is needed to make 1.72 liters of 0.29 M solution?
18. By my calculations, a drop of ethyl alcohol, C_2H_5OH , in an olympic-sized swimming pool produces a 1.20 E-10 M solution of alcohol in water. A drop is a twentieth of a mL. How many molecules of ethyl alcohol are in a drop of the water in the pool?
19. 93.0 mL of 0.150 M magnesium hydroxide is added to 57.0 mL of 0.4 M nitric acid. (Magnesium nitrate and water are formed. What is the concentration of the magnesium nitrate after the reaction?

ANSWERS TO PROBLEMS ON CONCENTRATION AND DENSITY

1. 5.44 E24 atoms	2. 24.3 g	3. 0.0292 M	4. 0.0504 L
5. 52.3 ml(cc) Mg	6a. 1.98 kg of U	6b. 1.63 E6 mL	7. 180 mL
8a. 1.17 kL CO_2	8b. 1.43 L	9. 0.477 L	10. 1.13 E 6 g

11. 23.0 kL	12a. 1.4 E-3 mols	12b. 0.0819 g	13. 3.12 g
14. 284 mL	15. 8.44 g	16a. 5.24E-3 mol	16b. 0.752 g
16c. 5.24E-3 mols	16d. 122 mmolar	17. 78.8 mg	18. 3.61E9 molecules
19. 0.152 M			

PROBLEMS USING COMPLETE ROADMAP

1. How many liters of ammonia at 0 °C and 25 atm. are produced when 10 g of hydrogen is combined with nitrogen?
2. How many milliliters of hydrogen at 0 deg C and 1400 mmHg are made if magnesium reacts with 15 mL of 6 M sulfuric acid?
3. How many atoms are in 25 liters of fluorine gas at 2.85 atm and 450 °C?
4. Liquid butane (C4H10) has a density of 0.60 g/cc. It burns to make carbon dioxide at 120 °C. What volume of carbon dioxide is produced at one atm when 350 liters of liquid butane burns?
5. Isopropyl alcohol, C3H7OH , makes a good fuel for cars. What volume of oxygen at 785 mmHg and 23 °C is needed to burn 8.54 E25 molecules of isopropyl alcohol?
6. How many moles of NaCl are in a liter of a 0.15 M NaCl solution? (0.15 M NaCl is physiological saline when sterilized.)
7. How many grams of NaCl must you put into a 50 liter container to make a physiological saline solution?
8. Chlorine gas is bubbled into 100 mL of 0.25 M potassium bromide solution. This produces potassium chloride and bromine gas. The bromine dissolves completely in the water. What is the concentration of bromine?
9. 95 mL of 0.55 M sulfuric acid is put on an excess of zinc. This produces zinc sulfate and hydrogen. How many grams of zinc sulfate are made?
10. Methyl alcohol (CH3OH) has a density of 0.793 Kg/L. What volume of it is needed to add to water to make twenty-five liters of 0.15 M solution?
11. Magnesium has a density of 1.741 g/cc. What volume of Mg will burn to produce a kilogram of magnesium oxide?
12. What volume of water vapor is produced at 716 mmHg and 87°C when 2.6 liters of methyl alcohol burns?

ANSWERS TO PROBLEMS USING COMPLETE ROADMAP

1. 2.99 L	2. 1.10 E3 mL	3. 1.45 E24 atoms	4. 4.67 E5 L
5. 1.50 E4 L	6. 0.15 moles	7. 439 g	8. 0.125 M
9. 8.44 g	10. 151 mL	11. 0.346 L	12. 1.29 E5 L

Contributors

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3.6 Determining the Formula of a Compound

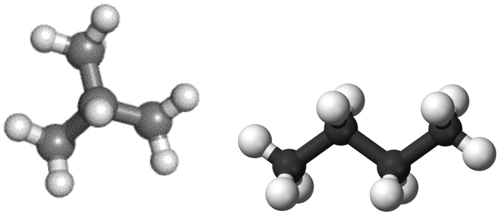
Chemistry is the experimental and theoretical study of materials on their properties at both the macroscopic and microscopic levels. Understanding the relationship between properties and structures/bonding is also a hot pursuit. Chemistry is traditionally divided into organic and inorganic chemistry. The former is the study of compounds containing at least one carbon-hydrogen bonds. By default, the chemical study of all other substances is called inorganic chemistry, a less well defined subject.

However, the boundary between organic and inorganic compounds is not always well defined. For example, oxalic acid, $H_2C_2O_4$, is a compound formed in plants, and it is generally considered an organic acid, but it does not contain any C-H bond. Inorganic chemistry is also closely related to other disciplines such as materials sciences, physical chemistry, thermodynamics, earth sciences, mineralogy, crystallography, spectroscopy etc.

A chemical formula is a format used to express the structure of atoms. The formula tells which elements and how many of each element are present in a compound. Formulas are written using the elemental symbol of each atom and a subscript to denote the number of elements. This notation can be accredited to Swedish chemist Jons Jakob Berzeliu. The most common elements present in organic compounds are carbon, hydrogen, oxygen, and nitrogen. With carbon and hydrogen present, other elements, such as phosphorous, sulfur, silicon, and the halogens, may exist in organic compounds. Compounds that do not pertain to this rule are called inorganic compounds.

Molecular Geometry and Structural Formula

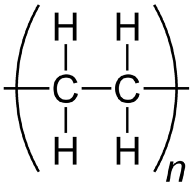
Understanding how atoms in a molecules are arranged and how they are bonded together is very important in giving the molecule its identity. Isomers are compounds in which two molecules can have the same number of atoms, and thus the same molecular formula, but can have completely different physical and chemical properties because of differences in structural formula.



Methylpropane and butane have the same molecular formula of C_4H_{10}, but are structurally different (methylpropane on the left, butane on the right).

Polymers

A polymer is formed when small molecules of identical structure, monomers, combine into a large cluster. The monomers are joined together by covalent bonds. When monomers repeat and bind, they form a polymer. While they can be comprised of natural or synthetic molecules, polymers often include plastics and rubber. When a molecule has more than one of these polymers, square parenthesis are used to show that all the elements within the polymer are multiplied by the subscript outside of the parenthesis. The subscript (shown as n in the example below) denotes the number of monomers present in the macromolecule (or polymer).



Ethylene becomes the polymer polyethylene.

Molecular Formula

The molecular formula is based on the actual makeup of the compound. Although the molecular formula can sometimes be the same as the empirical formula, molecular compounds tend to be more helpful. However, they do not describe how the atoms are put together. Molecular compounds are also misleading when dealing with isomers, which have the same number and types of atoms (see above in molecular geometry and structural formula).

Ex. Molecular Formula for Ethanol: C_2H_6O.

Empirical Formula

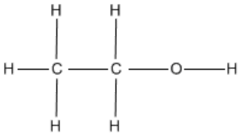
An empirical formula shows the most basic form of a compound. Empirical formulas show the number of atoms of each element in a compound in the most simplified state using whole numbers. Empirical formulas tend to tell us very little about a compound because one cannot determine the structure, shape, or properties of the compound without knowing the molecular formula. Usefulness of the empirical formula is decreased because many chemical compounds can have the same empirical formula.

Ex. Find the empirical formula for $C_8H_{16}O_2$.

Answer: C_4H_8O (divide all subscripts by 2 to get the smallest, whole number ratio).

Structural Formula

A structural formula displays the atoms of the molecule in the order they are bonded. It also depicts how the atoms are bonded to one another, for example single, double, and triple covalent bond. Covalent bonds are shown using lines. The number of dashes indicate whether the bond is a single, double, or triple covalent bond. Structural formulas are helpful because they explain the properties and structure of the compound which empirical and molecular formulas cannot always represent.

Ex. Structural Formula for Ethanol: 

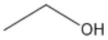
Condensed Structural Formula

Condensed structural formulas show the order of atoms like a structural formula but are written in a single line to save space and make it more convenient and faster to write out. Condensed structural formulas are also helpful when showing that a group of atoms is connected to a single atom in a compound. When this happens, parenthesis are used around the group of atoms to show they are together.

Ex. Condensed Structural Formula for Ethanol: CH_3CH_2OH (Molecular Formula for Ethanol C_2H_6O).

Line-Angle Formula

Because organic compounds can be complex at times, line-angle formulas are used to write carbon and hydrogen atoms more efficiently by replacing the letters with lines. A carbon atom is present wherever a line intersects another line. Hydrogen atoms are then assumed to complete each of carbon's four bonds. All other atoms that are connected to carbon atoms are written out. Line angle formulas help show structure and order of the atoms in a compound making the advantages and disadvantages similar to structural formulas.

Ex. Line-Angle Formula for Ethanol: 

Formulas of Inorganic Compounds

Inorganic compounds are typically not of biological origin. Inorganic compounds are made up of atoms connected using ionic bonds. These inorganic compounds can be binary compounds, binary acids, or polyatomic ions.

Binary compounds

Binary compounds are formed between two elements, either a metal paired with a nonmetal or two nonmetals paired together. When a metal is paired with a nonmetal, they form ionic compounds in which one is a negatively charged ion and the other is positvely charged. The net charge of the compound must then become neutral. Transition metals have different charges; therefore, it is important to specify what type of ion it is during the naming of the compound. When two nonmetals are paired together, the compound is a molecular compound. When writing out the formula, the element with a positive oxidation state is placed first.

Ex. Ionic Compound: $BaBr_2$(Barium Bromide)

Ex. Molecular Compound: N_2O_4 (Dinitrogen Tetroxide)

Binary acids

Binary acids are binary compounds in which hydrogen bonds with a nonmetal forming an acid. However, there are exceptions such as NH_3, which is a base. This is because it shows no tendency to produce a H^+. Because hydrogen is positively charged, it is placed first when writing out these binary acids.

Ex. HBr (Hydrobromic Acid)

Polyatomic ions

Polyatomic ions is formed when two or more atoms are connected with covalent bonds. Cations are ions that have are postively charged, while anions are negatively charged ions. The most common polyatomic ions that exists are those of anions. The two main polyatomic cations are Ammonium and Mercury (I). Many polyatomic ions are typically paired with metals using ionic bonds to form chemical compounds.

Ex. MnO_4^- (Polyatomic ion); $NaMnO_4$ (Chemical Compound)

Oxoacids

Many acids have three different elements to form ternary compounds. When one of those three elements is oxygen, the acid is known as a oxoacid. In other words, oxacids are compounds that contain hydrogen, oxgygen, and one other element.

Ex. HNO_3 (Nitric Acid)

Complex Compounds

Certain compounds can appear in multiple forms yet mean the same thing. A common example is hydrates: water molecules bond to another compound or element. When this happens, a dot is shown between H_2O and the other part of the compound. Because the H_2O molecules are embedded within the compound, the compound is not necessarily "wet". When hydrates are heated, the water in the compound evaporates and the compound becomes anhydrous. These compounds can be used to attract water such as $CoCl_2$. When $CoCl_2$ is dry, $CoCl_2$ is a blue color wherease the hexahydrate (written below) is pink in color.

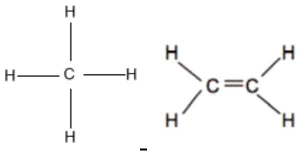
Ex. $CoCl_2 {}^{\bullet}6\ H_2O$

Formulas of Organic Compounds

Organic compounds contain a combination carbon and hydrogen or carbon and hydrogen with nitrogen and a few other elements, such as phosphorous, sulfur, silicon, and the halogens. Most organic compounds are seen in biological origin, as they are found in nature.

Hydrocarbons

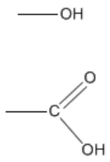
Hydrocarbons are compounds that consist of only carbon and hydrogen atoms. Hydrocarbons that are bonded together with only single bonds are alkanes. The simplest example is methane (shown below). When hydrocarbons have one or more double bonds, they are called alkenes. The simplest alkene is Ethene (C_2H_4) which contains a double bond between the two carbon atoms.



Ex. Methane on left, Ethene on right

Functional Groups

Functional groups are atoms connected to carbon chains or rings of organic molecules. Compounds that are within a functional group tend to have similar properties and characteristics. Two common functional groups are hydroxyl groups and carboxyl groups. Hydroxyl groups end in -OH and are alcohols. Carboxyl groups end in -COOH, making compounds containing -COOH carboxylic acids. Functional groups also help with nomenclature by using prefixes to help name the compounds that have similar chemical properties.



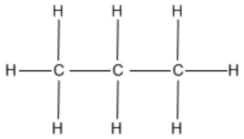
Ex. Hydroxyl Group on top; Carboxyl Group on bottom

References

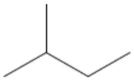
1. Miessler, Gary L. Inorganic Chemistry. 2nd. Upper Saddle River: Prentince Hall, 1999.
2. Munowitz, Michael. Principles of Chemistry. Norton & Company: New York, 2000.
3. Pettrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007.

Problems

1. Which of the following formulas are organic?
    a. $HClO$
    b. C_5H_{10}
    c. CO_2
2. What is the name of the following formula?



3. Classify the following formulas into their appropriate functional group
    a. Acetic acid
    b. Butanol
    c. Oxalic acid
4. What are the empirical formulas for the following compounds?
    a. $C_{12}H_{10}O_6$
    b. $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
    c. H_3O
5. What is the name of the following figure and what is the molecular formula of the following figure?



Answer Key:

1. b and c. 2. Propane. 3. a. carboxyl group, b. hydroxyl group, c. carboxyl group. 4. a. $C_6H_5O_3$, b. C_7H_{16}, c. H_3O. 5. Methylbutane, C_5H_{12}

Contributors and Attributions

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3.7 Chemical Equations

Learning Objectives

- To describe a chemical reaction.
- To calculate the quantities of compounds produced or consumed in a chemical reaction

What happens to matter when it undergoes chemical changes? The Law of conservation of mass says that "***Atoms are neither created, nor destroyed, during any chemical reaction***." Thus, the same collection of atoms is present after a reaction as before the reaction. The changes that occur during a reaction just involve the *rearrangement* of atoms. In this section we will discuss ***stoichiometry*** (the "measurement of elements").

Chemical Equations

As shown in Figure 1, applying a small amount of heat to a pile of orange ammonium dichromate powder results in a vigorous reaction known as the ammonium dichromate volcano. Heat, light, and gas are produced as a large pile of fluffy green chromium(III) oxide forms. This reaction is described with a chemical equation, an expression that gives the identities and quantities of the substances in a chemical reaction.

Figure 1: An Ammonium Dichromate Volcano: Change during a Chemical Reaction. The starting material is solid ammonium dichromate. A chemical reaction transforms it to solid chromium(III) oxide, depicted showing a portion of its chained structure, nitrogen gas, and water vapor (in addition, energy in the form of heat and light is released). During the reaction, the distribution of atoms changes, but the number of atoms of each element does not change. Because the numbers of each type of atom are the same in the reactants and the products, the chemical equation is balanced. (CC BY-SA 3.0; Mikk Mihkel Vaabel via Wikipedia). See video here: www.youtube.com/watch?v=CW4hN0dYnkM

Chemical reactions are represented on paper by ***chemical equations***. For example, hydrogen gas (H_2) can react (burn) with oxygen gas (O_2) to form water (H_2O). The *chemical equation* for this *reaction* is written as:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

Chemical formulas and other symbols are used to indicate the starting materials, or reactants, which by convention are written on the left side of the equation, and the final compounds, or products, which are written on the right. An arrow points from the reactant to the products. The chemical reaction for the ammonium dichromate volcano in Figure 1 is

$$\underbrace{(NH_4)_2Cr_2O_7}_{reactant} \rightarrow \underbrace{Cr_2O_3 + N_2 + 4\,H_2O}_{products} \tag{1}$$

The arrow is read as “yields” or “reacts to form.” Equation 1 indicates that ammonium dichromate (the reactant) yields chromium(III) oxide, nitrogen, and water (the products). The equation for this reaction is even more informative when written as follows:

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + N_2(g) + 4\,H_2O(g) \tag{2}$$

Equation 2 is identical to Equation 1 except for the addition of abbreviations in parentheses to indicate the physical state of each species. The abbreviations are (s) for solid, (l) for liquid, (g) for gas, and (aq) for an aqueous solution, a solution of the substance in water.

Consistent with the law of conservation of mass, the numbers of each type of atom are the same on both sides of Equations 1 and 2. Each side of the reaction has two chromium atoms, seven oxygen atoms, two nitrogen atoms, and eight hydrogen atoms.

In a balanced chemical equation, both the numbers of each type of atom and the total charge are the same on both sides. Equations 1 and 2 are balanced chemical equations. What is different on each side of the equation is how the atoms are arranged to make molecules or ions. A chemical reaction represents a change in the distribution of atoms, but not in the number of atoms. In this reaction, and in most chemical reactions, bonds are broken in the reactants (here, Cr–O and N–H bonds), and new bonds are formed to create the products (here, O–H and N≡N bonds). If the numbers of each type of atom are different on the two sides of a chemical equation, then the equation is unbalanced, and it cannot correctly describe what happens during the reaction. To proceed, the equation must first be balanced.

A chemical reaction changes only the distribution of atoms, not the number of atoms.

Introduction to Chemical Reaction Equations: Introduction to Chemical Reaction Equations, YouTube(opens in new window) [youtu.be]

Balancing Simple Chemical Equations

When a chemist encounters a new reaction, it does not usually come with a label that shows the balanced chemical equation. Instead, the chemist must identify the reactants and products and then write them in the form of a chemical equation that may or may not be balanced as first written. Consider, for example, the combustion of n-heptane (C_7H_{16}), an important component of gasoline:

$$\mathrm{C_7H_{16}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)} \tag{3}$$

The complete combustion of any hydrocarbon with sufficient oxygen always yields carbon dioxide and water.

Figure 2: An Example of a Combustion Reaction. The wax in a candle is a high-molecular-mass hydrocarbon, which produces gaseous carbon dioxide and water vapor in a combustion reaction (Equation 3).

Equation 3 is not balanced: the numbers of each type of atom on the reactant side of the equation (7 carbon atoms, 16 hydrogen atoms, and 2 oxygen atoms) is not the same as the numbers of each type of atom on the product side (1 carbon atom, 2 hydrogen atoms, and 3 oxygen atoms). Consequently, the coefficients of the reactants and products must be adjusted to give the same numbers of atoms of each type on both sides of the equation. Because the identities of the reactants and products are fixed, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure 3.

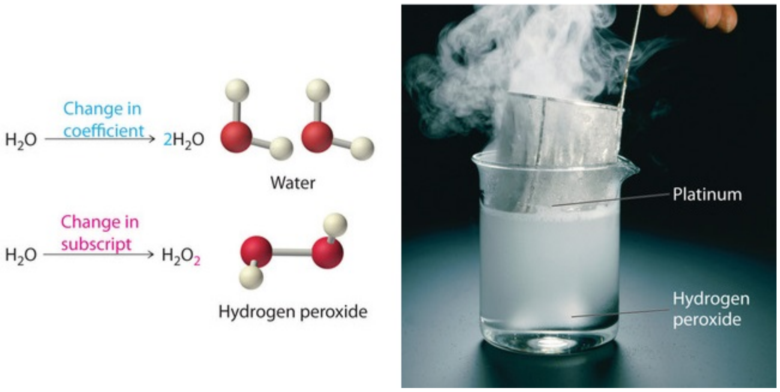

Figure 3: Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances. H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.

Left: Example of changing coefficients or subscripts. Right: Platinum dissolving in hydrogen peroxide.

Balancing Combustion Reactions: Balancing Combustions Reactions, YouTube(opens in new window) [youtu.be]

The simplest and most generally useful method for balancing chemical equations is “inspection,” better known as trial and error. The following is an efficient approach to balancing a chemical equation using this method.

Steps in Balancing a Chemical Equation

1. Identify the most complex substance.
2. Beginning with that substance, choose an element that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element on both sides.
3. Balance polyatomic ions (if present) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.
5. Check your work by counting the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

Example $1A$: Combustion of Heptane

To demonstrate this approach, let’s use the combustion of n-heptane (Equation 3) as an example.

1. **Identify the most complex substance**. The most complex substance is the one with the largest number of different atoms, which is C_7H_{16}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.

2. **Adjust the coefficients**. Try to adjust the coefficients of the molecules on the other side of the equation to obtain the same numbers of atoms on both sides. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which contains 1 carbon atom, on the right side:

$$C_7H_{16} + O_2 \rightarrow 7\,CO_2 + H_2O \tag{4}$$

3. **Balance polyatomic ions as a unit**. There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms**. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H2O molecules, each of which contains 2 hydrogen atoms, on the right side:

$$C_7H_{16} + O_2 \rightarrow 7\,CO_2 + 8\,H_2O \tag{5}$$

The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O_2, on the reactant side:

$$C_7H_{16}(l) + 11\,O_2(g) \rightarrow 7\,CO_2(g) + 8\,H_2O(g) \tag{6}$$

5. **Check your work**. The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. Always check to be sure that a chemical equation is balanced.The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start.

✓ Example 1B: Combustion of Isooctane

Consider, for example, a similar reaction, the combustion of isooctane (C_8H_{18}). Because the combustion of any hydrocarbon with oxygen produces carbon dioxide and water, the unbalanced chemical equation is as follows:

$$C_8H_{18}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g) \tag{7}$$

1. **Identify the most complex substance**. Begin the balancing process by assuming that the final balanced chemical equation contains a single molecule of isooctane.
2. **Adjust the coefficients**. The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that there must be 8 CO_2 molecules in the products:

$$C_8H_{18} + O_2 \rightarrow 8\,CO_2 + H_2O \tag{8}$$

3. **Balance polyatomic ions as a unit**. This step does not apply to this equation.
4. **Balance the remaining atoms**. Eighteen hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products:

$$C_8H_{18} + O_2 \rightarrow 8\,CO_2 + 9\,H_2O \tag{9}$$

The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 molecule, we must use a fractional coefficient (25/2) to balance the oxygen atoms:

$$C_8H_{18} + \tfrac{25}{2}O_2 \rightarrow 8\,CO_2 + 9\,H_2O \tag{10}$$

Equation 10 is now balanced, but we usually write equations with whole-number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by 2:

$$2\,C_8H_{18}(l) + 25\,O_2(g) \rightarrow 16\,CO_2(g) + 18\,H_2O(g) \tag{11}$$

5. **Check your work**. The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side.

Balancing Complex Chemical Equations: Balancing Complex Chemical Equations, YouTube(opens in new window) [youtu.be]

Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

✓ Example $1C$: Hydroxyapatite

The reaction of the mineral hydroxyapatite ($Ca_5(PO_4)_3(OH)$) with phosphoric acid and water gives $Ca(H_2PO_4)_2 \bullet H_2O$ (calcium dihydrogen phosphate monohydrate). Write and balance the equation for this reaction.

Hydroxyapatite (($Ca5(PO4)3(OH)$**)** crystal

Given: reactants and product

Asked for: balanced chemical equation

Strategy:

A. Identify the product and the reactants and then write the unbalanced chemical equation.
B. Follow the steps for balancing a chemical equation.

Solution:

A We must first identify the product and reactants and write an equation for the reaction. The formulas for hydroxyapatite and calcium dihydrogen phosphate monohydrate are given in the problem (recall that phosphoric acid is H_3PO_4). The initial (unbalanced) equation is as follows:

$$Ca_5(PO_4)_3(OH)(s) + H_3PO_4(aq) + H_2O_{(l)} \rightarrow Ca(H_2PO_4)_2 \cdot H_2O_{(s)}$$

1. **B Identify the most complex substance**. We start by assuming that only one molecule or formula unit of the most complex substance, $Ca_5(PO_4)_3(OH)$, appears in the balanced chemical equation.

2. **Adjust the coefficients**. Because calcium is present in only one reactant and one product, we begin with it. One formula unit of $Ca_5(PO_4)_3(OH)$ contains 5 calcium atoms, so we need 5 $Ca(H_2PO_4)_2 \bullet H_2O$ on the right side:

$$Ca_5(PO_4)_3(OH) + H_3PO_4 + H_2O \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O$$

3. **Balance polyatomic ions as a unit**. It is usually easier to balance an equation if we recognize that certain combinations of atoms occur on both sides. In this equation, the polyatomic phosphate ion (PO_4^{3-}), shows up in three places. In H_3PO_4, the phosphate ion is combined with three H^+ ions to make phosphoric acid (H_3PO_4), whereas in $Ca(H_2PO_4)_2 \cdot H_2O$ it is combined with two H^+ ions to give the dihydrogen phosphate ion. Thus it is easier to balance PO_4 as a unit rather than counting individual phosphorus and oxygen atoms. There are 10 PO_4 units on the right side but only 4 on the left. The simplest way to balance the PO_4 units is to place a coefficient of 7 in front of H_3PO_4:

$$\mathrm{Ca_5(PO_4)_3(OH) + 7\,H_3PO_4 + H_2O \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O}$$

Although OH^- is also a polyatomic ion, it does not appear on both sides of the equation. So oxygen and hydrogen must be balanced separately.

4. **Balance the remaining atoms**. We now have 30 hydrogen atoms on the right side but only 24 on the left. We can balance the hydrogen atoms using the least complex substance, H_2O, by placing a coefficient of 4 in front of H_2O on the left side, giving a total of 4 H_2O molecules:

$$\mathrm{Ca_5(PO_4)_3(OH)(s) + 7\,H_3PO_4(aq) + 4\,H_2O(l) \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O(s)}$$

The equation is now balanced. Even though we have not explicitly balanced the oxygen atoms, there are 41 oxygen atoms on each side.

5. **Check your work**. Both sides of the equation contain 5 calcium atoms, 10 phosphorus atoms, 30 hydrogen atoms, and 41 oxygen atoms.

? Exercise 1: Fermentation

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose are converted to ethanol (CH_3CH_2OH and carbon dioxide CO_2. Write a balanced chemical reaction for the fermentation of glucose.

***Commercial use of fermentation**. (a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.*

Answer

$$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

Balancing Reactions Which Contain Polyatomics: Balancing Reactions Which Contain Polyatomics, YouTube(opens in new window) [youtu.be]

Interpreting Chemical Equations

In addition to providing qualitative information about the identities and physical states of the reactants and products, a balanced chemical equation provides quantitative information. Specifically, it gives the relative amounts of reactants and products consumed or produced in a reaction. The number of atoms, molecules, or formula units of a reactant or a product in a balanced chemical equation is the coefficient of that species (e.g., the 4 preceding H_2O in Equation 1). When no coefficient is written in front of a species, the coefficient is assumed to be 1. As illustrated in Figure 4, the coefficients allow Equation 1 to be interpreted in any of the following ways:

- Two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion yield 1 formula unit of Cr_2O_3, 1 N_2 molecule, and 4 H_2O molecules.
- One mole of $(NH_4)_2Cr_2O_7$ yields 1 mol of Cr_2O_3, 1 mol of N_2, and 4 mol of H_2O.
- A mass of 252 g of $(NH_4)_2Cr_2O_7$ yields 152 g of Cr_2O_3, 28 g of N_2, and 72 g of H_2O.
- A total of 6.022×10^{23} formula units of $(NH_4)_2Cr_2O_7$ yields 6.022×10^{23} formula units of Cr_2O_3, 6.022×10^{23} molecules of N_2, and 24.09×10^{23} molecules of H_2O.

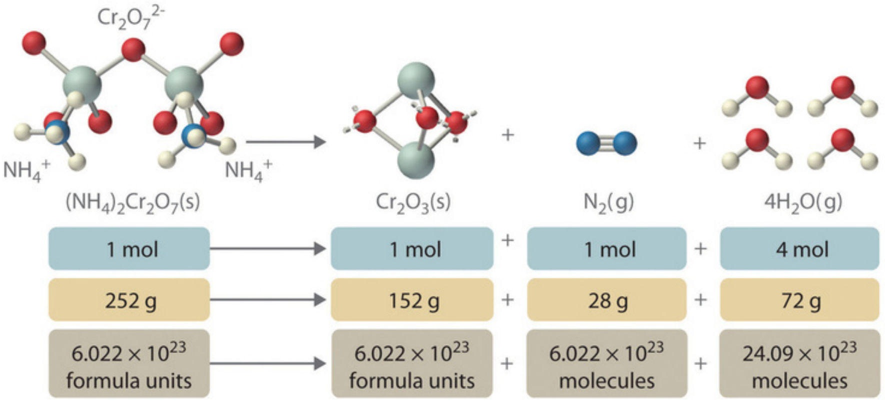

Figure 4: The Relationships among Moles, Masses, and Formula Units of Compounds in the Balanced Chemical Reaction for the Ammonium Dichromate Volcano

Chemical equation: (N H 4) 2 C r 2 O 7 dissociates into C r 2 O 3, N 2, and H 2 O. Conversions are given between moles, mass, and molecules.

These are all chemically equivalent ways of stating the information given in the balanced chemical equation, using the concepts of the mole, molar or formula mass, and Avogadro's number. The ratio of the number of moles of one substance to the number of moles of another is called the mole ratio. For example, the mole ratio of H_2O to N_2 in Equation 1 is 4:1. The total mass of reactants equals the total mass of products, as predicted by Dalton's law of conservation of mass:

$$252\ g \text{ of } (\mathrm{NH_4})_2\mathrm{Cr_2O_7}$$

yield

$$152 + 28 + 72 = 252 \; g \text{ of products.}$$

The chemical equation does not, however, show the rate of the reaction (rapidly, slowly, or not at all) or whether energy in the form of heat or light is given off. These issues are considered in more detail in later chapters.

An important chemical reaction was analyzed by Antoine Lavoisier, an 18th-century French chemist, who was interested in the chemistry of living organisms as well as simple chemical systems. In a classic series of experiments, he measured the carbon dioxide and heat produced by a guinea pig during respiration, in which organic compounds are used as fuel to produce energy, carbon dioxide, and water. Lavoisier found that the ratio of heat produced to carbon dioxide exhaled was similar to the ratio observed for the reaction of charcoal with oxygen in the air to produce carbon dioxide—a process chemists call combustion. Based on these experiments, he proposed that “Respiration is a combustion, slow it is true, but otherwise perfectly similar to that of charcoal.” Lavoisier was correct, although the organic compounds consumed in respiration are substantially different from those found in charcoal. One of the most important fuels in the human body is glucose ($C_6H_{12}O_6$), which is virtually the only fuel used in the brain. Thus combustion and respiration are examples of chemical reactions.

✓ Example 2: Combustion of Glucose

The balanced chemical equation for the combustion of glucose in the laboratory (or in the brain) is as follows:

$$\mathrm{C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)}$$

Construct a table showing how to interpret the information in this equation in terms of

a. a single molecule of glucose.
b. moles of reactants and products.
c. grams of reactants and products represented by 1 mol of glucose.
d. numbers of molecules of reactants and products represented by 1 mol of glucose.

The combustion of a sugar cube consisting of sucrose with a similar reaction to the combustion of glucose. from Wikipedia.

Given: balanced chemical equation

Asked for: molecule, mole, and mass relationships

Strategy:

A. Use the coefficients from the balanced chemical equation to determine both the molecular and mole ratios.
B. Use the molar masses of the reactants and products to convert from moles to grams.
C. Use Avogadro’s number to convert from moles to the number of molecules.

Solution:

This equation is balanced as written: each side has 6 carbon atoms, 18 oxygen atoms, and 12 hydrogen atoms. We can therefore use the coefficients directly to obtain the desired information.

a. One molecule of glucose reacts with 6 molecules of O_2 to yield 6 molecules of CO_2 and 6 molecules of H_2O.
b. One mole of glucose reacts with 6 mol of O_2 to yield 6 mol of CO_2 and 6 mol of H_2O.
c. To interpret the equation in terms of masses of reactants and products, we need their molar masses and the mole ratios from part b. The molar masses in grams per mole are as follows: glucose, 180.16; O_2, 31.9988; CO_2, 44.010; and H_2O, 18.015.

$$\text{mass of reactants} = \text{mass of products}$$

$$g\,glucose + g\,O_2 = g\,CO_2 + g\,H_2O$$

$$1\,mol\,glucose\left(\frac{180.16\,g}{1\,mol\,glucose}\right) + 6\,mol\,O_2\left(\frac{31.9988\,g}{1\,mol\,O_2}\right)$$

$$= 6\,mol\,CO_2\left(\frac{44.010\,g}{1\,mol\,CO_2}\right) + 6\,mol\,H_2O\left(\frac{18.015\,g}{1\,mol\,H_2O}\right)$$

$$372.15\,g = 372.15\,g$$

C One mole of glucose contains Avogadro's number (6.022 × 10^{23}) of glucose molecules. Thus 6.022 × 10^{23} glucose molecules react with (6 × 6.022 × 10^{23}) = 3.613 × 10^{24} oxygen molecules to yield (6 × 6.022 × 10^{23}) = 3.613 × 10^{24} molecules each of CO_2 and H_2O.

In tabular form:

Solution to Example 3.1.2

	$C_6H_{12}O_{6\,(s)}$	+	$6O_{2\,(g)}$	→	$6CO_{2\,(g)}$		$6H_2O_{(l)}$
a.	1 molecule		6 molecules		6 molecules		6 molecules
b.	1 mol		6 mol		6 mol		6 mol
c.	180.16 g		191.9928 g		264.06 g		108.09 g
d.	6.022 × 10^{23} molecules		3.613 × 10^{24} molecules		3.613 × 10^{24} molecules		3.613 × 10^{24} molecule

? Exercise 2: Ammonium Nitrate Explosion

Ammonium nitrate is a common fertilizer, but under the wrong conditions it can be hazardous. In 1947, a ship loaded with ammonium nitrate caught fire during unloading and exploded, destroying the town of Texas City, Texas.

Ammonium nitrate can be hazardous. This aerial photograph of Texas City, Texas, shows the devastation caused by the explosion of a shipload of ammonium nitrate on April 16, 1947. For a video click here.

The explosion resulted from the following reaction:

$$2NH_4NO_{3\,(s)} \rightarrow 2N_{2\,(g)} + 4H_2O_{(g)} + O_{2\,(g)}$$

Construct a table showing how to interpret the information in the equation in terms of

a. individual molecules and ions.
b. moles of reactants and products.
c. grams of reactants and products given 2 mol of ammonium nitrate.
d. numbers of molecules or formula units of reactants and products given 2 mol of ammonium nitrate.

Answer:

Answer to Exercise 3.1.2

	$2NH_4NO_{3\ (s)}$	→	$2N_{2\ (g)}$	+	$4H_2O_{(g)}$	+	$O_{2\ (g)}$
a.	$2NH_4^+$ ions and $2NO_3^-$ ions		2 molecules		4 molecules		1 molecule
b.	2 mol		2 mol		4 mol		1 mol
c.	160.0864 g		56.0268 g		72.0608 g		31.9988 g
d.	1.204×10^{24} formula units		1.204×10^{24} molecules		2.409×10^{24} molecules		6.022×10^{23} molecules

Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors (Mol Ratios): Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors, YouTube(opens in new window) [youtu.be]

Summary

A chemical reaction is described by a chemical equation that gives the identities and quantities of the reactants and the products. In a chemical reaction, one or more substances are transformed to new substances. A chemical reaction is described by a **chemical equation**, an expression that gives the identities and quantities of the substances involved in a reaction. A chemical equation shows the starting compound(s)—the **reactants**—on the left and the final compound(s)—the **products**—on the right, separated by an arrow. In a balanced chemical equation, the numbers of atoms of each element and the total charge are the same on both sides of the equation. The number of atoms, molecules, or formula units of a reactant or product in a balanced chemical equation is the **coefficient** of that species. The **mole ratio** of two substances in a chemical reaction is the ratio of their coefficients in the balanced chemical equation.

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3.8 Balancing Chemical Equations

Learning Objectives

- To balance equations that describe reactions in solution.
- To calculate the quantities of compounds produced or consumed in a chemical reaction.
- To solve quantitative problems involving the stoichiometry of reactions in solution.

A balanced chemical equation gives the identity of the reactants and the products as well as the accurate number of molecules or moles of each that are consumed or produced. **Stoichiometry** is a collective term for the quantitative relationships between the masses, the numbers of moles, and the numbers of particles (atoms, molecules, and ions) of the reactants and the products in a balanced chemical equation. **A stoichiometric quantity** is the amount of product or reactant specified by the coefficients in a balanced chemical equation. This section describes how to use the stoichiometry of a reaction to answer questions like the following: How much oxygen is needed to ensure complete combustion of a given amount of isooctane? (This information is crucial to the design of nonpolluting and efficient automobile engines.) How many grams of pure gold can be obtained from a ton of low-grade gold ore? (The answer determines whether the ore deposit is worth mining.) If an industrial plant must produce a certain number of tons of sulfuric acid per week, how much elemental sulfur must arrive by rail each week?

All these questions can be answered using the concepts of the mole, molar and formula masses, and solution concentrations, along with the coefficients in the appropriate balanced chemical equation.

Stoichiometry Problems

When carrying out a reaction in either an industrial setting or a laboratory, it is easier to work with masses of substances than with the numbers of molecules or moles. The general method for converting from the mass of any reactant or product to the mass of any other reactant or product using a balanced chemical equation is outlined in and described in the following text.

Steps in Converting between Masses of Reactant and Product

1. Convert the mass of one substance (substance A) to the corresponding number of moles using its molar mass.
2. From the balanced chemical equation, obtain the number of moles of another substance (B) from the number of moles of substance A using the appropriate mole ratio (the ratio of their coefficients).
3. Convert the number of moles of substance B to mass using its molar mass. It is important to remember that some species are present in excess by virtue of the reaction conditions. For example, if a substance reacts with the oxygen in air, then oxygen is in obvious (but unstated) excess.

Converting amounts of substances to moles—and vice versa—is the key to all stoichiometry problems, whether the amounts are given in units of mass (grams or kilograms), weight (pounds or tons), or volume (liters or gallons).

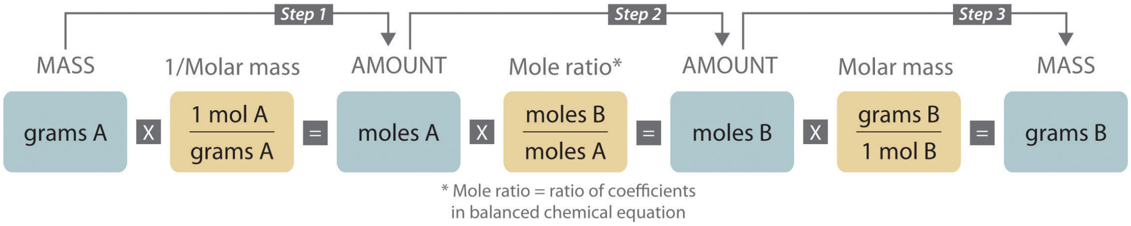


Figure 1: A Flowchart for Stoichiometric Calculations Involving Pure Substances. The molar masses of the reactants and the products are used as conversion factors so that you can calculate the mass of product from the mass of reactant and vice versa.

Flowchart of steps in stoichiometric calculations. Step 1: grams of A is converted to moles by multiplying by the inverse of the molar mass. Step 2: moles of A is converted to moles of B by multiplying by the molar ratio. Step 3: moles of B is converted to grams of B by the molar mass.

To illustrate this procedure, consider the combustion of glucose. Glucose reacts with oxygen to produce carbon dioxide and water:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \tag{1}$$

Just before a chemistry exam, suppose a friend reminds you that glucose is the major fuel used by the human brain. You therefore decide to eat a candy bar to make sure that your brain does not run out of energy during the exam (even though there is no direct evidence that consumption of candy bars improves performance on chemistry exams). If a typical 2 oz candy bar contains the equivalent of 45.3 g of glucose and the glucose is completely converted to carbon dioxide during the exam, how many grams of carbon dioxide will you produce and exhale into the exam room?

The initial step in solving a problem of this type is to write the balanced chemical equation for the reaction. Inspection shows that it is balanced as written, so the strategy outlined above can be adapted as follows:

1. Use the molar mass of glucose (to one decimal place, 180.2 g/mol) to determine the number of moles of glucose in the candy bar:

$$moles\,glucose = 45.3\,g\,glucose \times \frac{1\,mol\,glucose}{180.2\,g\,glucose} = 0.251\,mol\,glucose$$

2. According to the balanced chemical equation, 6 mol of CO_2 is produced per mole of glucose; the mole ratio of CO_2 to glucose is therefore 6:1. The number of moles of CO_2 produced is thus

$$\begin{aligned} moles\,CO_2 &= mol\,glucose \times \frac{6\,mol\,CO_2}{1\,mol\,glucose} \\ &= 0.251\,mol\,glucose \times \frac{6\,mol\,CO_2}{1\,mol\,glucose} \\ &= 1.51\,mol\,CO_2 \end{aligned}$$

3. Use the molar mass of CO_2 (44.010 g/mol) to calculate the mass of CO_2 corresponding to 1.51 mol of CO_2:

$$mass\,of\,CO_2 = 1.51\,mol\,CO_2 \times \frac{44.010\,g\,CO_2}{1\,mol\,CO_2} = 66.5\,g\,CO_2$$

These operations can be summarized as follows:

$$45.3\,g\,glucose \times \frac{1\,mol\,glucose}{180.2\,g\,glucose} \times \frac{6\,mol\,CO_2}{1\,mol\,glucose} \times \frac{44.010\,g\,CO_2}{1\,mol\,CO_2} = 66.4\,g\,CO_2$$

Discrepancies between the two values are attributed to rounding errors resulting from using stepwise calculations in steps 1–3. (Remember that you should generally carry extra significant digits through a multistep calculation to the end to avoid this!) This amount of gaseous carbon dioxide occupies an enormous volume—more than 33 L. Similar methods can be used to calculate the amount of oxygen consumed or the amount of water produced.

The balanced chemical equation was used to calculate the mass of product that is formed from a certain amount of reactant. It can also be used to determine the masses of reactants that are necessary to form a certain amount of product or, as shown in Example 1, the mass of one reactant that is required to consume a given mass of another reactant.

✓ Example 1: The US Space Shuttle

The combustion of hydrogen with oxygen to produce gaseous water is extremely vigorous, producing one of the hottest flames known. Because so much energy is released for a given mass of hydrogen or oxygen, this reaction was used to fuel the NASA (National Aeronautics and Space Administration) space shuttles, which have recently been retired from service. NASA engineers calculated the exact amount of each reactant needed for the flight to make sure that the shuttles did not carry excess fuel into orbit. Calculate how many tons of hydrogen a space shuttle needed to carry for each 1.00 tn of oxygen (1 tn = 2000 lb).

The US space shuttle Discovery during liftoff*. The large cylinder in the middle contains the oxygen and hydrogen that fueled the shuttle's main engine.*

Given: reactants, products, and mass of one reactant

Asked for: mass of other reactant

Strategy:

A. Write the balanced chemical equation for the reaction.
B. Convert mass of oxygen to moles. From the mole ratio in the balanced chemical equation, determine the number of moles of hydrogen required. Then convert the moles of hydrogen to the equivalent mass in tons.

Solution:

We use the same general strategy for solving stoichiometric calculations as in the preceding example. Because the amount of oxygen is given in tons rather than grams, however, we also need to convert tons to units of mass in grams. Another conversion is needed at the end to report the final answer in tons.

A We first use the information given to write a balanced chemical equation. Because we know the identity of both the reactants and the product, we can write the reaction as follows:

$$H_2(g) + O_2(g) \rightarrow H_2O(g)$$

This equation is not balanced because there are two oxygen atoms on the left side and only one on the right. Assigning a coefficient of 2 to both H_2O and H_2 gives the balanced chemical equation:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Thus 2 mol of H_2 react with 1 mol of O_2 to produce 2 mol of H_2O.

1. **B** To convert tons of oxygen to units of mass in grams, we multiply by the appropriate conversion factors:

$$mass\, of\, O_2 = 1.00\, tn \times \frac{2000\, lb}{tn} \times \frac{453.6\, g}{lb} = 9.07 \times 10^5\, g\, O_2$$

Using the molar mass of O_2 (32.00 g/mol, to four significant figures), we can calculate the number of moles of O_2 contained in this mass of O_2:

$$mol\, O_2 = 9.07 \times 10^5\, g\, O_2 \times \frac{1\, mol\, O_2}{32.00\, g\, O_2} = 2.83 \times 10^4\, mol\, O_2$$

2. Now use the coefficients in the balanced chemical equation to obtain the number of moles of H_2 needed to react with this number of moles of O_2:

$$mol\, H_2 = mol\, O_2 \times \frac{2\, mol\, H_2}{1\, mol\, O_2}$$

$$= 2.83 \times 10^4\, mol\, O_2 \times \frac{2\, mol\, H_2}{1\, mol\, O_2} = 5.66 \times 10^4\, mol\, H_2$$

3. The molar mass of H_2 (2.016 g/mol) allows us to calculate the corresponding mass of H_2:

$$mass\, of\, H_2 = 5.66 \times 10^4\, mol\, H_2 \times \frac{2.016\, g\, H_2}{mol\, H_2} = 1.14 \times 10^5\, g\, H_2$$

Finally, convert the mass of H2 to the desired units (tons) by using the appropriate conversion factors:

$$tons\, H_2 = 1.14 \times 10^5\, g\, H_2 \times \frac{1\, lb}{453.6\, g} \times \frac{1\, tn}{2000\, lb} = 0.126\, tn\, H_2$$

The space shuttle had to be designed to carry 0.126 tn of H_2 for each 1.00 tn of O_2. Even though 2 mol of H_2 are needed to react with each mole of O_2, the molar mass of H_2 is so much smaller than that of O_2 that only a relatively small mass of H_2 is needed compared to the mass of O_2.

? Exercise 1: Roasting Cinnabar

Cinnabar, (or Cinnabarite) HgS is the common ore of mercury. Because of its mercury content, cinnabar can be toxic to human beings; however, because of its red color, it has also been used since ancient times as a pigment.

Cinnabar ore. from Wikipedia

Alchemists produced elemental mercury by roasting cinnabar ore in air:

$$HgS(s) + O_2(g) \rightarrow Hg(l) + SO_2(g)$$

The volatility and toxicity of mercury make this a hazardous procedure, which likely shortened the life span of many alchemists. Given 100 g of cinnabar, how much elemental mercury can be produced from this reaction?

Answer

86.2 g

Calculating Moles from Volume

Quantitative calculations involving reactions in solution are carried out with *masses*, however, *volumes* of solutions of known concentration are used to determine the number of moles of reactants. Whether dealing with volumes of solutions of reactants or masses of reactants, the coefficients in the balanced chemical equation give the number of moles of each reactant needed and the number of moles of each product that can be produced. An expanded version of the flowchart for stoichiometric calculations is shown in Figure 2. The balanced chemical equation for the reaction and *either* the masses of solid reactants and products *or* the volumes of solutions of reactants and products can be used to determine the amounts of other species, as illustrated in the following examples.

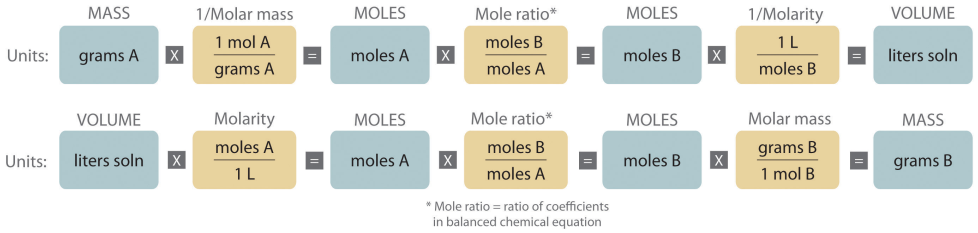


Figure 2: An Expanded Flowchart for Stoichiometric Calculations. Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in a balanced chemical equation.

Top: flowchart of steps to convert mass of one substance to moles to moles of another substance to volume using molarity. Bottom: flowchart of steps to convert volume of a substance to mass of another substance.

> The balanced chemical equation for a reaction and either the masses of solid reactants and products or the volumes of solutions of reactants and products can be used in stoichiometric calculations.

✓ Example 2 : Extraction of Gold

Gold is extracted from its ores by treatment with an aqueous cyanide solution, which causes a reaction that forms the soluble $[Au(CN)_2]^−$ ion. Gold is then recovered by reduction with metallic zinc according to the following equation:

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

What mass of gold can be recovered from 400.0 L of a 3.30×10^{-4} M solution of $[Au(CN)_2]^−$?

Given: chemical equation and molarity and volume of reactant

Asked for: mass of product

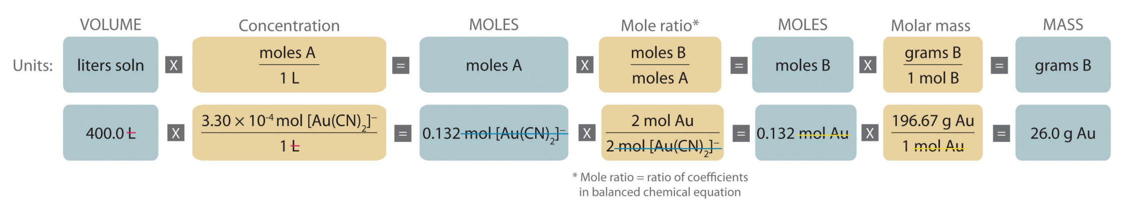
Strategy:

A. Check the chemical equation to make sure it is balanced as written; balance if necessary. Then calculate the number of moles of $[Au(CN)_2]^−$ present by multiplying the volume of the solution by its concentration.

B. From the balanced chemical equation, use a mole ratio to calculate the number of moles of gold that can be obtained from the reaction. To calculate the mass of gold recovered, multiply the number of moles of gold by its molar mass.

Solution:

A The equation is balanced as written; proceed to the stoichiometric calculation. Figure 2 is adapted for this particular problem as follows:



Flowchart. Top: volume is converted to moles of A via the concentration. Moles of A is then converted to moles of B via the mole ratio. The molar mass of B is then used to convert moles of B to grams. Bottom: same flowchart as above, filled in with information given in the exercise.

As indicated in the strategy, start by calculating the number of moles of $[Au(CN)_2]^−$ present in the solution from the volume and concentration of the $[Au(CN)_2]^−$ solution:

$$moles\ [Au(CN)_2]^- = V_L M_{mol/L} \tag{2}$$

$$= 400.0\ \cancel{L} \left(\frac{3.30 \times 10^{4-}\ mol\ [Au(CN)_2]^-}{1\ \cancel{L}} \right) = 0.132\ mol\ [Au(CN)_2]^- \tag{3}$$

B Because the coefficients of gold and the $[Au(CN)_2]^−$ ion are the same in the balanced chemical equation, assuming that Zn(s) is present in excess, the number of moles of gold produced is the same as the number of moles of $[Au(CN)_2]^−$ (i.e., 0.132 mol of Au). The problem asks for the mass of gold that can be obtained, so the number of moles of gold must be converted to the corresponding mass using the molar mass of gold:

$$mass\ of\ Au = (moles\ Au)(molar\ mass\ Au) \tag{4}$$

$$= 0.132\ \ mol\ \cancel{Au} \left(\frac{196.97\ g\ Au}{1\ \ mol\ \cancel{Au}} \right) = 26.0\ g\ Au \tag{5}$$

At a 2011 market price of over \$1400 per troy ounce (31.10 g), this amount of gold is worth \$1170.

$$26.0\ \ g\ \cancel{Au} \times \frac{1\ \ troy\ \cancel{oz}}{31.10\ \ \cancel{g}} \times \frac{\$1400}{1\ \ troy\ oz\ \cancel{Au}} = \$1170$$

? Exercise 2 : Lanthanum Oxalate

What mass of solid lanthanum(III) oxalate nonahydrate [$La_2(C_2O_4)_3 \cdot 9H_2O$] can be obtained from 650 mL of a 0.0170 M aqueous solution of $LaCl_3$ by adding a stoichiometric amount of sodium oxalate?

Answer

3.89 g

Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors (Mol Ratios): Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors, YouTube(opens in new window) [youtu.be]

Summary

Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in the balanced chemical equation. Quantitative calculations that involve the stoichiometry of reactions in solution use volumes of solutions of known concentration instead of masses of reactants or products. The coefficients in the balanced chemical equation tell how many moles of reactants are needed and how many moles of product can be produced.

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3.9 Stoichiometric Calculations: Amounts of Reactants and Products

Stoichiometry is a section of chemistry that involves using relationships between reactants and/or products in a chemical reaction to determine desired quantitative data. In Greek, *stoikhein* means element and *metron* means measure, so stoichiometry literally translated means the measure of elements. In order to use stoichiometry to run calculations about chemical reactions, it is important to first understand the relationships that exist between products and reactants and why they exist, which require understanding how to balance reactions.

Balancing

In chemistry, chemical reactions are frequently written as an equation, using chemical symbols. The reactants are displayed on the left side of the equation and the products are shown on the right, with the separation of either a single or double arrow that signifies the direction of the reaction. The significance of single and double arrow is important when discussing solubility constants, but we will not go into detail about it in this module. To balance an equation, it is necessary that there are the same number of atoms on the left side of the equation as the right. One can do this by raising the coefficients.

Reactants to Products

A chemical equation is like a recipe for a reaction so it displays all the ingredients or terms of a chemical reaction. It includes the elements, molecules, or ions in the reactants and in the products as well as their states, and the proportion for how much of each particle reacts or is formed relative to one another, through the stoichiometric coefficient. The following equation demonstrates the typical format of a chemical equation:

$$2\,\mathrm{Na(s)} + 2\,\mathrm{HCl(aq)} \rightarrow 2\,\mathrm{NaCl(aq)} + \mathrm{H_2(g)}$$

In the above equation, the elements present in the reaction are represented by their chemical symbols. Based on the Law of Conservation of Mass, which states that matter is neither created nor destroyed in a chemical reaction, every chemical reaction has the same elements in its reactants and products, though the elements they are paired up with often change in a reaction. In this reaction, sodium (Na), hydrogen (H), and chloride (Cl) are the elements present in both reactants, so based on the law of conservation of mass, they are also present on the product side of the equations. Displaying each element is important when using the chemical equation to convert between elements.

Stoichiometric Coefficients

In a balanced reaction, both sides of the equation have the same number of elements. The stoichiometric coefficient is the number written in front of atoms, ion and molecules in a chemical reaction to balance the number of each element on both the reactant and product sides of the equation. Though the stoichiometric coefficients can be fractions, whole numbers are frequently used and often preferred. This stoichiometric coefficients are useful since they establish the mole ratio between reactants and products. In the balanced equation:

$$2\,\mathrm{Na(s)} + 2\,\mathrm{HCl(aq)} \rightarrow 2\,\mathrm{NaCl(aq)} + \mathrm{H_2(g)}$$

we can determine that 2 moles of HCl will react with 2 moles of $Na_{(s)}$ to form 2 moles of $NaCl_{(aq)}$ and 1 mole of $H_{2(g)}$. If we know how many moles of Na reacted, we can use the ratio of 2 moles of $NaCl$ to 2 moles of Na to determine how many moles of $NaCl$ were produced or we can use the ratio of 1 mole of H_2 to 2 moles of Na to convert to $NaCl$. This is known as the coefficient factor. The balanced equation makes it possible to convert information about the change in one reactant or product to quantitative data about another reactant or product. Understanding this is essential to solving stoichiometric problems.

✓ Example 1

Lead (IV) hydroxide and sulfuric acid react as shown below. Balance the reaction.

$$\mathrm{Pb(OH)_4} + \mathrm{H_2SO_4} \rightarrow \mathrm{Pb(SO_4)_2} + \mathrm{H_2O}$$

Solution

Start by counting the number of atoms of each element.

UNBALANCED

Element	Reactant (# of atoms)	Product (# of atoms)
Pb	1	1
O	8	9
H	6	2
S	1	2

The reaction is not balanced; the reaction has 16 reactant atoms and only 14 product atoms and does not obey the conservation of mass principle. Stoichiometric coefficients must be added to make the equation balanced. In this example, there are only one sulfur atom present on the reactant side, so a coefficient of 2 should be added in front of H_2SO_4 to have an equal number of sulfur on both sides of the equation. Since there are 12 oxygen on the reactant side and only 9 on the product side, a 4 coefficient should be added in front of H_2O where there is a deficiency of oxygen. Count the number of elements now present on either side of the equation. Since the numbers are the same, the equation is now balanced.

$$\mathrm{Pb(OH)_4 + 2\,H_2SO_4 \rightarrow Pb(SO_4)_2 + 4\,H_2O}$$

BALANCED

Element	Reactant (# of atoms)	Product (# of atoms)
Pb	1	1
O	12	12
H	8	8
S	2	2

Balancing reactions involves finding least common multiples between numbers of elements present on both sides of the equation. In general, when applying coefficients, add coefficients to the molecules or unpaired elements last.

A balanced equation ultimately has to satisfy two conditions.

1. The numbers of each element on the left and right side of the equation must be equal.
2. The charge on both sides of the equation must be equal. It is especially important to pay attention to charge when balancing redox reactions.

Stoichiometry and Balanced Equations

In stoichiometry, balanced equations make it possible to compare different elements through the **stoichiometric factor** discussed earlier. This is the mole ratio between two factors in a chemical reaction found through the ratio of stoichiometric coefficients. Here is a real world example to show how stoichiometric factors are useful.

✓ Example 2

There are 12 party invitations and 20 stamps. Each party invitation needs 2 stamps to be sent. How many party invitations can be sent?

Solution

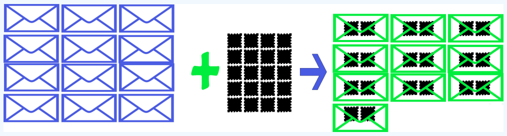
The equation for this can be written as

$$\mathrm{I + 2\,S \rightarrow IS_2}$$

where

- I represents invitations,
- S represents stamps, and
- IS_2 represents the sent party invitations consisting of one invitation and two stamps.

Based on this, we have the ratio of 2 stamps for 1 sent invite, based on the balanced equation.



Invitations Stamps Party Invitations Sent

In this example are all the reactants (stamps and invitations) used up? No, and this is normally the case with chemical reactions. There is often excess of one of the reactants. The limiting reagent, the one that runs out first, prevents the reaction from continuing and determines the maximum amount of product that can be formed.

✓ Example 3

What is the limiting reagent in this example?

Solution

Stamps, because there was only enough to send out invitations, whereas there were enough invitations for 12 complete party invitations. Aside from just looking at the problem, the problem can be solved using stoichiometric factors.

$$12\ \text{I x } (1\text{IS}_2/1\text{I}) = 12\ \text{IS}_2 \text{ possible}$$

$$20\ \text{S x } (1\text{IS}_2/2\text{S}) = 10\ \text{IS}_2 \text{ possible}$$

When there is no limiting reagent because the ratio of all the reactants caused them to run out at the same time, it is known as *stoichiometric proportions*.

Types of Reactions

There are 6 basic types of reactions.

- **Combustion**: Combustion is the formation of CO_2 and H_2O from the reaction of a chemical and O_2
- **Combination (synthesis)**: Combination is the addition of 2 or more simple reactants to form a complex product.
- **Decomposition:** Decomposition is when complex reactants are broken down into simpler products.
- **Single Displacement**: Single displacement is when an element from on reactant switches with an element of the other to form two new reactants.
- **Double Displacement:** Double displacement is when two elements from on reactants switched with two elements of the other to form two new reactants.
- **Acid-Base:** Acid- base reactions are when two reactants form salts and water.

Molar Mass

Before applying stoichiometric factors to chemical equations, you need to understand molar mass. Molar mass is a useful chemical ratio between mass and moles. The atomic mass of each individual element as listed in the periodic table established this relationship for atoms or ions. For compounds or molecules, you have to take the sum of the atomic mass times the number of each atom in order to determine the molar mass

✓ Example 4

What is the molar mass of H_2O?

Solution

$$\text{Molar mass} = 2 \times (1.00794\ g/mol) + 1 \times (15.9994\ g/mol) = 18.01528\ g/mol$$

Using molar mass and coefficient factors, it is possible to convert mass of reactants to mass of products or vice versa.

✓ Example 5: Combustion of Propane

Propane (C_3H_8) burns in this reaction:

$$C_3H_8 + 5\,O_2 \rightarrow 4\,H_2O + 3\,CO_2$$

If 200 g of propane is burned, how many g of H_2O is produced?

Solution

Steps to getting this answer: Since you cannot calculate from grams of reactant to grams of products you must convert from grams of C_3H_8 to moles of C_3H_8 then from moles of C_3H_8 to moles of H_2O. Then convert from moles of H_2O to grams of H_2O.

- Step 1: 200 g C_3H_8 is equal to 4.54 mol C_3H_8.
- Step 2: Since there is a ratio of 4:1 H_2O to C_3H_8, for every 4.54 mol C_3H_8 there are 18.18 mol H_2O.
- Step 3: Convert 18.18 mol H_2O to g H_2O. 18.18 mol H_2O is equal to 327.27 g H_2O.

Variation in Stoichiometric Equations

Almost every quantitative relationship can be converted into a ratio that can be useful in data analysis.

Density

Density (ρ) is calculated as mass/volume. This ratio can be useful in determining the volume of a solution, given the mass or useful in finding the mass given the volume. In the latter case, the inverse relationship would be used.

$$\text{Volume x (Mass/Volume) = Mass}$$

$$\text{Mass x (Volume/Mass) = Volume}$$

Percent Mass

Percents establish a relationship as well. A percent mass states how many grams of a mixture are of a certain element or molecule. The percent X% states that of every 100 grams of a mixture, X grams are of the stated element or compound. This is useful in determining mass of a desired substance in a molecule.

✓ Example 6

A substance is 5% carbon by mass. If the total mass of the substance is 10 grams, what is the mass of carbon in the sample? How many moles of carbon are there?

Solution

$$\text{10 g sample x (5 g carbon/100 g sample) = 0.5 g carbon}$$

$$\text{0.5g carbon x (1 mol carbon/12.011g carbon) = 0.0416 mol carbon}$$

Molarity

Molarity (moles/L) establishes a relationship between moles and liters. Given volume and molarity, it is possible to calculate mole or use moles and molarity to calculate volume. This is useful in chemical equations and dilutions.

✓ Example 7

How much 5 M stock solution is needed to prepare 100 mL of 2 M solution?

Solution

100 mL of dilute solution (1 L/1000 mL)(2 mol/1L solution)(1 L stock solution/5 mol solution)(1000 ml stock solution/1L stock solution) = 40 mL stock solution.

These ratios of molarity, density, and mass percent are useful in complex examples ahead.

Determining Empirical Formulas

An empirical formula can be determined through chemical stoichiometry by determining which elements are present in the molecule and in what ratio. The ratio of elements is determined by comparing the number of moles of each element present.

✓ Example 8: Combustion of Organic Molecules

1.000 gram of an organic molecule burns completely in the presence of excess oxygen. It yields 0.0333 mol of CO_2 and 0.599 g of H_2O. What is the empirical formula of the organic molecule?

Solution

This is a combustion reaction. The problem requires that you know that organic molecules consist of some combination of carbon, hydrogen, and oxygen elements. With that in mind, write the chemical equation out, replacing unknown numbers with variables. Do not worry about coefficients here.

$$\mathrm{CxHyOz(g)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} + \mathrm{H_2O(g)}$$

Since all the moles of C and H in CO_2 and H_2O, respectively have to have came from the 1 gram sample of unknown, start by calculating how many moles of each element were present in the unknown sample.

$$0.0333\text{mol } CO_2 \text{ (1mol C/ 1mol } CO_2) = 0.0333\text{mol C in unknown}$$

$$0.599\text{g } H_2O \text{ (1mol } H_2O\text{/ 18.01528g } H_2O)\text{(2mol H/ 1mol } H_2O) = 0.0665 \text{ mol H in unknown}$$

Calculate the final moles of oxygen by taking the sum of the moles of oxygen in CO_2 and H_2O. This will give you the number of moles from both the unknown organic molecule and the O_2 so you must subtract the moles of oxygen transferred from the O_2.

Moles of oxygen in CO_2:

$$0.0333\text{mol } CO_2 \text{ (2mol O/1mol } CO_2) = 0.0666 \text{ mol O}$$

Moles of oxygen in H_2O:

$$0.599\text{g } H_2O \text{ (1mol } H_2O\text{/18.01528 g } H_2O)\text{(1mol O/1mol } H_2O) = 0.0332 \text{ mol O}$$

Using the Law of Conservation, we know that the mass before a reaction must equal the mass after a reaction. With this we can use the difference of the final mass of products and initial mass of the unknown organic molecule to determine the mass of the O_2 reactant.

$$0.333\text{mol } CO_2\text{(44.0098g } CO_2\text{/ 1mol } CO_2) = 1.466\text{g } CO_2$$

$$1.466\text{g } CO_2 + 0.599\text{g } H_2O \text{ - 1.000g unknown organic} = 1.065\text{g } O_2$$

Moles of oxygen in O_2

$$1.065\text{g } O_2\text{(1mol } O_2\text{/ 31.9988g } O_2)\text{(2mol O/1mol } O_2) = 0.0666\text{mol O}$$

Moles of oxygen in unknown

$$(0.0666\text{mol O} + 0.0332 \text{ mol O}) - 0.0666\text{mol O} = 0.0332 \text{ mol O}$$

Construct a mole ratio for C, H, and O in the unknown and divide by the smallest number.

$$(1/0.0332)(0.0333\text{mol C} : 0.0665\text{mol H} : 0.0332 \text{ mol O}) \Rightarrow \text{1mol C: 2 mol H: 1 mol O}$$

From this ratio, the empirical formula is calculated to be CH_2O.

Determining Molecular Formulas

To determine a molecular formula, first determine the empirical formula for the compound as shown in the section above and then determine the molecular mass experimentally. Next, divide the molecular mass by the molar mass of the empirical formula (calculated by finding the sum the total atomic masses of all the elements in the empirical formula). Multiply the subscripts of the molecular formula by this answer to get the molecular formula.

✓ Example 9

In the example above, it was determined that the unknown molecule had an empirical formula of CH_2O.

1. Find the molar mass of the empircal formula CH_2O.

$$12.011\text{g C} + (1.008\text{ g H}) * (2\text{ H}) + 15.999\text{g O} = 30.026\text{ g/mol } CH_2O$$

2. Determine the molecular mass experimentally. For our compound, it is 120.056 g/mol.

3. Divide the experimentally determined molecular mass by the mass of the empirical formula.

$$(120.056\text{ g/mol}) / (30.026\text{ g/mol}) = 3.9984$$

4. Since 3.9984 is very close to four, it is possible to safely round up and assume that there was a slight error in the experimentally determined molecular mass. If the answer is not close to a whole number, there was either an error in the calculation of the empirical formula or a large error in the determination of the molecular mass.

5. Multiply the ratio from step 4 by the subscripts of the empirical formula to get the molecular formula.

$$CH_2O * 4 = ?$$

$$\text{C: } 1 * 4 = 4$$

$$\text{H: } 2 * 4 = 8$$

$$\text{O } 1 * 4 = 4$$

$$CH_2O * 4 = C_4H_8O_4$$

6. Check your result by calculating the molar mass of the molecular formula and comparing it to the experimentally determined mass.

$$\text{molar mass of } C_4H_8O_4 = 120.104\text{ g/mol}$$

$$\text{experimentally determined mass} = 120.056\text{ g/mol}$$

$$\%\text{ error} = |\text{ theoretical - experimental }| / \text{ theoretical} * 100\%$$

$$\%\text{ error} = |\ 120.104\text{ g/mol} - 120.056\text{ g/mol }| / 120.104\text{ g/mol} * 100\%$$

$$\%\text{ error} = 0.040\ \%$$

✓ Example 10: Complex Stoichiometry Problem

An amateur welder melts down two metals to make an alloy that is 45% copper by mass and 55% iron(II) by mass. The alloy's density is 3.15 g/L. One liter of alloy completely fills a mold of volume 1000 cm^3. He accidentally breaks off a 1.203 cm^3 piece of the homogenous mixture and sweeps it outside where it reacts with acid rain over years. Assuming the acid reacts with all the iron(II) and not with the copper, how many grams of $H_2(g)$ are released into the atmosphere because of the amateur's carelessness? (Note that the situation is fiction.)

Solution

Step 1: Write a balanced equation after determining the products and reactants. In this situation, since we assume copper does not react, the reactants are only $H^+(aq)$ and Fe(s). The given product is H2(g) and based on knowledge of redox reactions, the other product must be $Fe^{2+}(aq)$.

$$\mathrm{Fe(s)} + 2\,\mathrm{H^+(aq)} \rightarrow \mathrm{H_2(g)} + \mathrm{Fe^{2\,+}(aq)}$$

Step 2: Write down all the given information

Alloy density = (3.15g alloy/ 1L alloy)

x grams of alloy = 45% copper = (45g Cu(s)/100g alloy)

x grams of alloy = 55% iron(II) = (55g Fe(s)/100g alloy)

1 liter alloy = 1000cm^3 alloy

alloy sample = $1.203 cm^3$ alloy

Step 3: Answer the question of what is being asked. The question asks how much H2(g) was produced. You are expected to solve for the amount of product formed.

Step 4: Start with the compound you know the most about and use given ratios to convert it to the desired compound.

Convert the given amount of alloy reactant to solve for the moles of Fe(s) reacted.

$1.203 cm^3$ alloy(1liter alloy/$1000 cm^3$ alloy)(3.15g alloy/1liter alloy)(55g Fe(s)/100g alloy)(1mol Fe(s)/55.8g Fe(s))=3.74 x 10^{-5} mol Fe(s)

Make sure all the units cancel out to give you moles of $\mathrm{Fe(s)}$. *The above conversion involves using multiple stoichiometric relationships from density, percent mass, and molar mass.*

The balanced equation must now be used to convert moles of Fe(s) to moles of H_2(g). Remember that the balanced equation's coefficients state the stoichiometric factor or mole ratio of reactants and products.

3.74 x 10^{-5} mol Fe (s) (1mol H_2(g)/1mol Fe(s)) = 3.74 x 10^{-5} mol H_2(g)

Step 5: Check units

The question asks for how many grams of H_2(g) were released so the moles of H_2(g) must still be converted to grams using the molar mass of H_2(g). Since there are two H in each H_2, its molar mass is twice that of a single H atom.

molar mass = 2(1.00794g/mol) = 2.01588g/mol

3.74 x 10^{-5} mol H_2(g) (2.01588g H_2(g)/1mol H_2 (g)) = **7.53 x 10^{-5} g H_2(g) released**

Problems

Stoichiometry and balanced equations make it possible to use one piece of information to calculate another. There are countless ways stoichiometry can be used in chemistry and everyday life. Try and see if you can use what you learned to solve the following problems.

1) Why are the following equations not considered balanced?

a. $H_2O_{(l)} \rightarrow H_{2(g)} + O_{2(g)}$
b. $Zn_{(s)} + Au^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Ag_{(s)}$

2) Hydrochloric acid reacts with a solid chunk of aluminum to produce hydrogen gas and aluminum ions. Write the balanced chemical equation for this reaction.

3) Given a 10.1M stock solution, how many mL must be added to water to produce 200 mL of 5M solution?

4) If 0.502g of methane gas react with 0.27g of oxygen to produce carbon dioxide and water, what is the limiting reagent and how many moles of water are produced? The unbalanced equation is provided below.

$$\mathrm{CH_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)}$$

5) A 0.777g sample of an organic compound is burned completely. It produces 1.42g CO_2 and 0.388g H_2O. Knowing that all the carbon and hydrogen atoms in CO_2 and H_2O came from the 0.777g sample, what is the empirical formula of the organic compound?

Weblinks for further reference

- 1. Refer to http://chemistry.about.com/cs/stoich.../aa042903a.htm as an outside resource on how to balance chemical reactions.
- 2. Refer to http://www.learnchem.net/tutorials/stoich.shtml as an outside resource on stoichiometry.

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3.10: Calculations Involving a Limiting Reactant

Learning Objectives

- To understand the concept of limiting reactants and quantify incomplete reactions

In all the examples discussed thus far, the reactants were assumed to be present in stoichiometric quantities. Consequently, none of the reactants was left over at the end of the reaction. This is often desirable, as in the case of a space shuttle, where excess oxygen or hydrogen was not only extra freight to be hauled into orbit but also an explosion hazard. More often, however, reactants are present in mole ratios that are not the same as the ratio of the coefficients in the balanced chemical equation. As a result, one or more of them will not be used up completely but will be left over when the reaction is completed. In this situation, the amount of product that can be obtained is limited by the amount of only one of the reactants. The reactant that restricts the amount of product obtained is called the limiting reactant. The reactant that remains after a reaction has gone to completion is in excess.

Consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is thus

$$1 \text{ box mix} + 2 \text{ eggs} \rightarrow 1 \text{ batch brownies} \tag{3.10.1}$$

If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes in is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant. Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

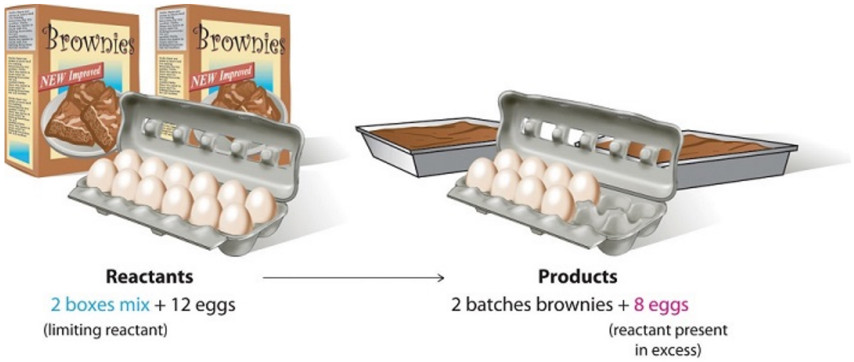


Figure 3.10.1: The Concept of a Limiting Reactant in the Preparation of Brownies

Reactants: 2 boxes of brownie mix + 12 eggs produces 2 batches of brownies + 8 eggs. Brownie mix is the limiting reactant. Eggs are the reactant present in excess.

Introduction to Limiting Reactant Problems: Introduction to Limiting Reactant Problems, YouTube(opens in new window) [youtu.be]

Now consider a chemical example of a limiting reactant: the production of pure titanium. This metal is fairly light (45% lighter than steel and only 60% heavier than aluminum) and has great mechanical strength (as strong as steel and twice as strong as aluminum). Because it is also highly resistant to corrosion and can withstand extreme temperatures, titanium has many applications in the aerospace industry. Titanium is also used in medical implants and portable computer housings because it is light and resistant to corrosion. Although titanium is the ninth most common element in Earth’s crust, it is relatively difficult to extract from its ores. In the first step of the extraction process, titanium-containing oxide minerals react with solid carbon and chlorine gas to form titanium tetrachloride ($\mathrm{TiCl_4}$) and carbon dioxide.

$$\mathrm{TiO_2(s) + Cl_2(g) \rightarrow TiCl_4(g) + CO_2(g)}$$

Titanium tetrachloride is then converted to metallic titanium by reaction with molten magnesium metal at high temperature:

$$\mathrm{TiCl_4(g) + 2\ Mg(l) \rightarrow Ti(s) + 2\ MgCl_2(l)} \tag{3.10.2}$$

Because titanium ores, carbon, and chlorine are all rather inexpensive, the high price of titanium (about $100 per kilogram) is largely due to the high cost of magnesium metal. Under these circumstances, magnesium metal is the limiting reactant in the production of metallic titanium.

Figure 3.10.2: Medical use of titanium. Here is an example of its successful use in joint replacement implants. An A-P X-ray of a pelvis showing a total hip joint replacement. The right hip joint (on the left in the photograph) has been replaced. A metal prostheses is cemented in the top of the right femur and the head of the femur has been replaced by the rounded head of the prosthesis. Figure courtesy of NIH (NIADDK) 9AO4 (Connie Raab)

With 1.00 kg of titanium tetrachloride and 200 g of magnesium metal, how much titanium metal can be produced according to Equation 3.10.2?

Solving this type of problem requires that you carry out the following steps

1. Determine the number of moles of each reactant.
2. Compare the mole ratio of the reactants with the ratio in the balanced chemical equation to determine which reactant is limiting.
3. Calculate the number of moles of product that can be obtained from the limiting reactant.
4. Convert the number of moles of product to mass of product.

Step 1: To determine the number of moles of reactants present, calculate or look up their molar masses: 189.679 g/mol for titanium tetrachloride and 24.305 g/mol for magnesium. The number of moles of each is calculated as follows:

$$\begin{aligned}\text{moles } \mathrm{TiCl_4} &= \frac{\text{mass } \mathrm{TiCl_4}}{\text{molar mass } \mathrm{TiCl_4}} \\ &= 1000 \cancel{g} \ \mathrm{TiCl_4} \times \frac{1\, mol\ TiCl_4}{189.679 \ \cancel{g} \ \mathrm{TiCl_4}} \\ &= 5.272\, mol \ \mathrm{TiCl_4}\end{aligned} \tag{3.10.3}$$

$$\begin{aligned}\text{moles } \mathrm{Mg} &= \frac{\text{mass } \mathrm{Mg}}{\text{molar mass } \mathrm{Mg}} \\ &= 200 \ \cancel{g} \ \mathrm{Mg} \times \frac{1 \ mol\, \mathrm{Mg}}{24.305 \ \cancel{g} \ \mathrm{Mg}} \\ &= 8.23 \,\mathrm{mol\ Mg}\end{aligned} \tag{3.10.4}$$

Step 2: There are more moles of magnesium than of titanium tetrachloride, but the ratio is only the following:

$$\frac{mol\, \mathrm{Mg}}{mol\, \mathrm{TiCl_4}} = \frac{8.23\, mol}{5.272\, mol} = 1.56$$

Because the ratio of the coefficients in the balanced chemical equation is,

$$\frac{2\, mol\, \mathrm{Mg}}{1\, mol\, \mathrm{TiCl_4}} = 2$$

there is not have enough magnesium to react with all the titanium tetrachloride. If this point is not clear from the mole ratio, calculate the number of moles of one reactant that is required for complete reaction of the other reactant. For example, there are 8.23 mol of Mg, so (8.23 ÷ 2) = 4.12 mol of $\mathrm{TiCl_4}$ are required for complete reaction. Because there are 5.272 mol of $\mathrm{TiCl_4}$, titanium tetrachloride is present in excess. Conversely, 5.272 mol of $\mathrm{TiCl_4}$ requires 2 × 5.272 = 10.54 mol of Mg, but there are only 8.23 mol. Therefore, magnesium is the limiting reactant.

Step 3: Because magnesium is the limiting reactant, the number of moles of magnesium determines the number of moles of titanium that can be formed:

$$mol \ \mathrm{Ti} = 8.23\, mol \ \mathrm{Mg} = \frac{1\, mol \ \mathrm{Ti}}{2\, mol \ \mathrm{Mg}} = 4.12\, mol \ \mathrm{Ti}$$

Thus only 4.12 mol of Ti can be formed.

Step 4. To calculate the mass of titanium metal that can obtain, multiply the number of moles of titanium by the molar mass of titanium (47.867 g/mol):

$$\begin{aligned}\text{moles } \mathrm{Ti} &= \text{mass } \mathrm{Ti} \times \text{molar mass } \mathrm{Ti} \\ &= 4.12\, mol \ \mathrm{Ti} \times \frac{47.867\, g\, \mathrm{Ti}}{1\, mol \ \mathrm{Ti}} \\ &= 197\, g\, \mathrm{Ti}\end{aligned}$$

Here is a simple and reliable way to identify the limiting reactant in any problem of this sort:

1. Calculate the number of moles of each reactant present: 5.272 mol of $\mathrm{TiCl_4}$ and 8.23 mol of Mg.
2. Divide the actual number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation:

$$TiCl_4: \frac{5.272\, mol\, (actual)}{1\, mol\, (stoich)} = 5.272$$

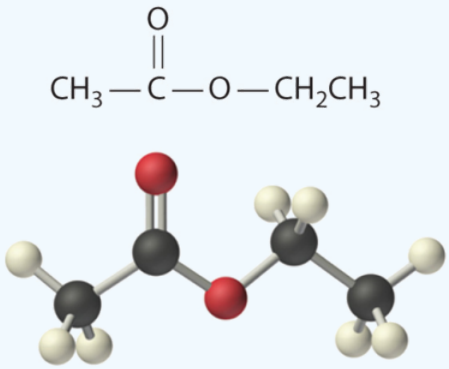
$$Mg: \frac{8.23\, mol\, (actual)}{2\, mol\, (stoich)} = 4.12$$

3. The reactant with the smallest mole ratio is limiting. Magnesium, with a calculated stoichiometric mole ratio of 4.12, is the limiting reactant.

Density is the mass per unit volume of a substance. If we are given the density of a substance, we can use it in stoichiometric calculations involving liquid reactants and/or products, as Example $3.10.1$ demonstrates.

✓ Example 3.10.1: Fingernail Polish Remover

Ethyl acetate ($CH_3CO_2C_2H_5$) is the solvent in many fingernail polish removers and is used to decaffeinate coffee beans and tea leaves. It is prepared by reacting ethanol (C_2H_5OH) with acetic acid (CH_3CO_2H); the other product is water. A small amount of sulfuric acid is used to accelerate the reaction, but the sulfuric acid is not consumed and does not appear in the balanced chemical equation. Given 10.0 mL each of acetic acid and ethanol, how many grams of ethyl acetate can be prepared from this reaction? The densities of acetic acid and ethanol are 1.0492 g/mL and 0.7893 g/mL, respectively.



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

Ethyl acetate

Given: reactants, products, and volumes and densities of reactants

Asked for: mass of product

Strategy:

A. Balance the chemical equation for the reaction.
B. Use the given densities to convert from volume to mass. Then use each molar mass to convert from mass to moles.
C. Using mole ratios, determine which substance is the limiting reactant. After identifying the limiting reactant, use mole ratios based on the number of moles of limiting reactant to determine the number of moles of product.
D. Convert from moles of product to mass of product.

Solution:

A Always begin by writing the balanced chemical equation for the reaction:

$$C_2H_5OH(l) + CH_3CO_2H(aq) \rightarrow CH_3CO_2C_2H_5(aq) + H_2O(l)$$

B We need to calculate the number of moles of ethanol and acetic acid that are present in 10.0 mL of each. Recall that the density of a substance is the mass divided by the volume:

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

Rearranging this expression gives mass = (density)(volume). We can replace mass by the product of the density and the volume to calculate the number of moles of each substance in 10.0 mL (remember, 1 mL = 1 cm^3):

$$\begin{aligned}
\text{moles } C_2H_5OH &= \frac{\text{mass } C_2H_5OH}{\text{molar mass } C_2H_5OH} \\
&= \frac{(\text{volume } C_2H_5OH)\times(\text{density } C_2H_5OH)}{\text{molar mass } C_2H_5OH} \\
&= 10.0\ \cancel{ml}\ C_2H_5OH \times \frac{0.7893\ \cancel{g}\ C_2H_5OH}{1\ \cancel{ml}\ C_2H_5OH} \times \frac{1\, mol\ C_2H_5OH}{46.07\ \cancel{g}\ C_2H_5OH} \\
&= 0.171\, mol\ C_2H_5OH
\end{aligned}$$

$$\begin{aligned}
\text{moles } CH_3CO_2H &= \frac{\text{mass } CH_3CO_2H}{\text{molar mass } CH_3CO_2H} \\
&= \frac{(\text{volume } CH_3CO_2H)\times(\text{density } CH_3CO_2H)}{\text{molar mass } CH_3CO_2H} \\
&= 10.0\ \cancel{ml}\ CH_3CO_2H \times \frac{1.0492\ \cancel{g}\ CH_3CO_2H}{1\ \cancel{ml}\ CH_3CO_2H} \times \frac{1\, mol\ CH_3CO_2H}{60.05\ \cancel{g}\ CH_3CO_2H} \\
&= 0.175\, mol\ CH_3CO_2H
\end{aligned}$$

C The number of moles of acetic acid exceeds the number of moles of ethanol. Because the reactants both have coefficients of 1 in the balanced chemical equation, the mole ratio is 1:1. We have 0.171 mol of ethanol and 0.175 mol of acetic acid, so ethanol is the limiting reactant and acetic acid is in excess. The coefficient in the balanced chemical equation for the product (ethyl acetate) is also 1, so the mole ratio of ethanol and ethyl acetate is also 1:1. This means that given 0.171 mol of ethanol, the amount of ethyl acetate produced must also be 0.171 mol:

$$\begin{aligned}
moles \text{ ethyl acetate } &= mol \text{ ethanol} \times \frac{1\, mol \text{ ethyl acetate}}{1\, mol \text{ ethanol}} \\
&= 0.171\, mol\ C_2H_5OH \times \frac{1\, mol\ CH_3CO_2C_2H_5}{1\, mol\ C_2H_5OH} \\
&= 0.171\, mol\ CH_3CO_2C_2H_5
\end{aligned}$$

D The final step is to determine the mass of ethyl acetate that can be formed, which we do by multiplying the number of moles by the molar mass:

$$\begin{aligned}
\text{mass of ethyl acetate } &= mol \text{ ethyl acetate} \times \text{molar mass ethyl acetate} \\
&= 0.171\, mol\, CH_3CO_2C_2H_5 \times \frac{88.11\, g\, CH_3CO_2C_2H_5}{1\, mol\, CH_3CO_2C_2H_5} \\
&= 15.1\, g\, CH_3CO_2C_2H_5
\end{aligned}$$

Thus 15.1 g of ethyl acetate can be prepared in this reaction. If necessary, you could use the density of ethyl acetate (0.9003 g/cm3) to determine the volume of ethyl acetate that could be produced:

$$\begin{aligned}
\text{volume of ethyl acetate } &= 15.1\, g\, CH_3CO_2C_2H_5 \times \frac{1\, ml\ CH_3CO_2C_2H_5}{0.9003\, g\ CH_3CO_2C_2H_5} \\
&= 16.8\, ml\, CH_3CO_2C_2H_5
\end{aligned}$$

? Exercise 3.10.1

Under appropriate conditions, the reaction of elemental phosphorus and elemental sulfur produces the compound P_4S_{10}. How much P_4S_{10} can be prepared starting with 10.0 g of $\mathrm{P_4}$ and 30.0 g of S_8?

Answer

35.9 g

Determining the Limiting Reactant and Theoretical Yield for a Reaction: Determining the Limiting Reactant and Theoretical Yield for a Reaction, YouTube(opens in new window) [youtu.be]

Limiting Reactants in Solutions

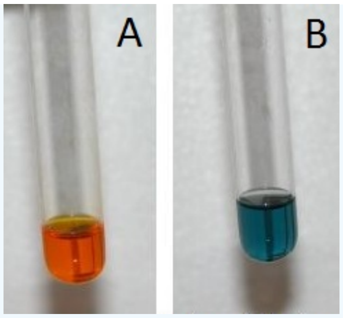
The concept of limiting reactants applies to reactions carried out in solution as well as to reactions involving pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example 3.10.2

✓ Example 3.10.2: Breathalyzer reaction

Because the consumption of alcoholic beverages adversely affects the performance of tasks that require skill and judgment, in most countries it is illegal to drive while under the influence of alcohol. In almost all US states, a blood alcohol level of 0.08% by volume is considered legally drunk. Higher levels cause acute intoxication (0.20%), unconsciousness (about 0.30%), and even death (about 0.50%). The Breathalyzer is a portable device that measures the ethanol concentration in a person's breath, which is directly proportional to the blood alcohol level. The reaction used in the Breathalyzer is the oxidation of ethanol by the dichromate ion:

$$3\,\mathrm{CH_3CH_2OH(aq)} + \underset{yellow-orange}{2\,\mathrm{Cr_2O_7^{2-}}(aq)} + 16\,\mathrm{H^+(aq)} \xrightarrow[\mathrm{H_2SO_4(aq)}]{\mathrm{Ag^+}} 3\,\mathrm{CH_3CO_2H(aq)} + \underset{green}{4\,\mathrm{Cr^{3+}}}(aq) + 11\,\mathrm{H_2O(l)}$$

When a measured volume (52.5 mL) of a suspect's breath is bubbled through a solution of excess potassium dichromate in dilute sulfuric acid, the ethanol is rapidly absorbed and oxidized to acetic acid by the dichromate ions. In the process, the chromium atoms in some of the $\mathrm{Cr_2O_7^{2-}}$ ions are reduced from Cr^{6+} to Cr^{3+}. In the presence of Ag^+ ions that act as a catalyst, the reaction is complete in less than a minute. Because the $\mathrm{Cr_2O_7^{2-}}$ ion (the reactant) is yellow-orange and the Cr^{3+} ion (the product) forms a green solution, the amount of ethanol in the person's breath (the limiting reactant) can be determined quite accurately by comparing the color of the final solution with the colors of standard solutions prepared with known amounts of ethanol.



A Breathalyzer reaction with a test tube before (a) and after (b) ethanol is added. When a measured volume of a suspect's breath is bubbled through the solution, the ethanol is oxidized to acetic acid, and the solution changes color from yellow-orange to green. The intensity of the green color indicates the amount of ethanol in the sample.

A typical Breathalyzer ampul contains 3.0 mL of a 0.25 mg/mL solution of $K_2Cr_2O_7$ in 50% H_2SO_4 as well as a fixed concentration of $AgNO_3$ (typically 0.25 mg/mL is used for this purpose). How many grams of ethanol must be present in 52.5 mL of a person's breath to convert all the Cr^{6+} to Cr^{3+}?

Given: volume and concentration of one reactant

Asked for: mass of other reactant needed for complete reaction

Strategy:

A. Calculate the number of moles of $Cr_2O_7^{2-}$ ion in 1 mL of the Breathalyzer solution by dividing the mass of $K_2Cr_2O_7$ by its molar mass.
B. Find the total number of moles of $Cr_2O_7^{2-}$ ion in the Breathalyzer ampul by multiplying the number of moles contained in 1 mL by the total volume of the Breathalyzer solution (3.0 mL).
C. Use the mole ratios from the balanced chemical equation to calculate the number of moles of C_2H_5OH needed to react completely with the number of moles of $Cr_2O_7^{2-}$ ions present. Then find the mass of C_2H_5OH needed by multiplying the number of moles of C_2H_5OH by its molar mass.

Solution:

A In any stoichiometry problem, the first step is always to calculate the number of moles of each reactant present. In this case, we are given the mass of $K_2Cr_2O_7$ in 1 mL of solution, which can be used to calculate the number of moles of $K_2Cr_2O_7$ contained in 1 mL:

$$\frac{moles\ K_2Cr_2O_7}{1\ mL} = \frac{(0.25\ \cancel{mg}\ K_2Cr_2O_7)}{mL}\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{294.18\ \cancel{g}\ K_2Cr_2O_7}\right) = 8.5 \times 10^{-7}\ moles$$

B Because 1 mol of $K_2Cr_2O_7$ produces 1 mol of $Cr_2O_7^{2-}$ when it dissolves, each milliliter of solution contains 8.5×10^{-7} mol of $Cr_2O_7{}^{2-}$. The total number of moles of $Cr_2O_7{}^{2-}$ in a 3.0 mL Breathalyzer ampul is thus

$$moles\ Cr_2O_7^{2-} = \left(\frac{8.5 \times 10^{-7}\ mol}{1\ \cancel{mL}}\right)(3.0\ \cancel{mL}) = 2.6 \times 10^{-6}\ mol\ Cr_2O_7^{2-}$$

C The balanced chemical equation tells us that 3 mol of C_2H_5OH is needed to consume 2 mol of $Cr_2O_7^{2-}$ ion, so the total number of moles of C_2H_5OH required for complete reaction is

$$moles\ of\ C_2H_5OH = (2.6 \times 10^{-6}\ \cancel{mol\ Cr_2O_7^{2-}})\left(\frac{3\ mol\ C_2H_5OH}{2\ \cancel{mol\ Cr_2O_7^{2-}}}\right) = 3.9 \times 10^{-6}\ mol\ C_2H_5OH$$

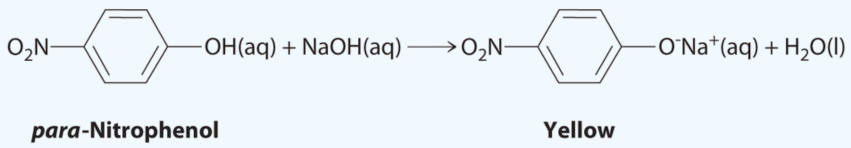
As indicated in the strategy, this number can be converted to the mass of C_2H_5OH using its molar mass:

$$mass\ C_2H_5OH = (3.9 \times 10^{-6}\ \cancel{mol\ C_2H_5OH})\left(\frac{46.07\ g}{\cancel{mol\ C_2H_5OH}}\right) = 1.8 \times 10^{-4}\ g\ C_2H_5OH$$

Thus 1.8×10^{-4} g or 0.18 mg of C_2H_5OH must be present. Experimentally, it is found that this value corresponds to a blood alcohol level of 0.7%, which is usually fatal.

Exercise 3.10.2

The compound *para*-nitrophenol (molar mass = 139 g/mol) reacts with sodium hydroxide in aqueous solution to generate a yellow anion via the reaction



Chemical equation showing conversion of para-nitrophenol to its yellow-colored form with aqueous sodium hydroxide.

Because the amount of *para*-nitrophenol is easily estimated from the intensity of the yellow color that results when excess NaOH is added, reactions that produce *para*-nitrophenol are commonly used to measure the activity of enzymes, the catalysts in biological systems. What volume of 0.105 M NaOH must be added to 50.0 mL of a solution containing 7.20×10^{-4} g of *para*-nitrophenol to ensure that formation of the yellow anion is complete?

Answer

4.93×10^{-5} L or 49.3 μL

In Examples 3.10.1 and 3.10.2, the identities of the limiting reactants are apparent: $[Au(CN)_2]^-$, $LaCl_3$, ethanol, and *para*-nitrophenol. When the limiting reactant is not apparent, it can be determined by comparing the molar amounts of the reactants with their coefficients in the balanced chemical equation. The only difference is that the volumes and concentrations of solutions of reactants, rather than the masses of reactants, are used to calculate the number of moles of reactants, as illustrated in Example 3.10.3.

Example 3.10.3

When aqueous solutions of silver nitrate and potassium dichromate are mixed, an exchange reaction occurs, and silver dichromate is obtained as a red solid. The overall chemical equation for the reaction is as follows:

$$2\,\mathrm{AgNO_3(aq)} + \mathrm{K_2Cr_2O_7(aq)} \rightarrow \mathrm{Ag_2Cr_2O_7(s)} + 2\,\mathrm{KNO_3(aq)}$$

What mass of $Ag_2Cr_2O_7$ is formed when 500 mL of 0.17 M $K_2Cr_2O_7$ are mixed with 250 mL of 0.57 M $AgNO_3$?

Given: balanced chemical equation and volume and concentration of each reactant

Asked for: mass of product

Strategy:

A. Calculate the number of moles of each reactant by multiplying the volume of each solution by its molarity.
B. Determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation.
C. Use mole ratios to calculate the number of moles of product that can be formed from the limiting reactant. Multiply the number of moles of the product by its molar mass to obtain the corresponding mass of product.

Solution:

A The balanced chemical equation tells us that 2 mol of $AgNO_3$(aq) reacts with 1 mol of $K_2Cr_2O_7$(aq) to form 1 mol of $Ag_2Cr_2O_7$(s) (Figure 8.3.2). The first step is to calculate the number of moles of each reactant in the specified volumes:

$$moles\ K_2Cr_2O_7 = 500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.17\ mol\ K_2Cr_2O_7}{1\ \cancel{L}}\right) = 0.085\ mol\ K_2Cr_2O_7$$

$$moles\ AgNO_3 = 250\ m\cancel{L} \left(\frac{1\ \cancel{L}}{1000\ m\cancel{L}}\right)\left(\frac{0.57\ mol\ AgNO_3}{1\ \cancel{L}}\right) = 0.14\ mol\ AgNO_3$$

B Now determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

$$\mathrm{K_2Cr_2O_7}: \frac{0.085\ mol}{1\ mol} = 0.085$$

$$\mathrm{AgNO_3}: \frac{0.14\ mol}{2\ mol} = 0.070$$

Because 0.070 < 0.085, we know that $\mathrm{AgNO_3}$ is the *limiting reactant*.

C Each mole of $\mathrm{Ag_2Cr_2O_7}$ formed requires 2 mol of the limiting reactant ($\mathrm{AgNO_3}$), so we can obtain only 0.14/2 = 0.070 mol of $\mathrm{Ag_2Cr_2O_7}$. Finally, convert the number of moles of $\mathrm{Ag_2Cr_2O_7}$ to the corresponding mass:

$$mass\ of\ Ag_2Cr_2O_7 = 0.070\ \cancel{mol}\left(\frac{431.72\ g}{1\ \cancel{mol}}\right) = 30\ g\ Ag_2Cr_2O_7$$

The Ag^+ and $Cr_2O_7^{2-}$ ions form a red precipitate of solid $\mathrm{Ag_2Cr_2O_7}$, while the $\mathrm{K^+}$ and $\mathrm{NO_3^-}$ ions remain in solution. (Water molecules are omitted from molecular views of the solutions for clarity.)

? Exercise 3.10.3

Aqueous solutions of sodium bicarbonate and sulfuric acid react to produce carbon dioxide according to the following equation:

$$\mathrm{2\,NaHCO_3(aq) + H_2SO_4(aq) \rightarrow 2\,CO_2(g) + Na_2SO_4(aq) + 2\,H_2O(l)}$$

If 13.0 mL of 3.0 M H_2SO_4 are added to 732 mL of 0.112 M $NaHCO_3$, what mass of CO_2 is produced?

Answer

3.4 g

Limiting Reactant Problems Using Molarities: Limiting Reactant Problems Using Molarities, YouTube(opens in new window) [youtu.be]eOXTliL-gNw (opens in new window)

Theoretical Yields

When reactants are not present in stoichiometric quantities, the limiting reactant determines the maximum amount of product that can be formed from the reactants. The amount of product calculated in this way is the theoretical yield, the amount obtained if the reaction occurred perfectly and the purification method were 100% efficient.

In reality, less product is always obtained than is theoretically possible because of mechanical losses (such as spilling), separation procedures that are not 100% efficient, competing reactions that form undesired products, and reactions that simply do not run to completion, resulting in a mixture of products and reactants; this last possibility is a common occurrence. Therefore, the actual yield, the measured mass of products obtained from a reaction, is almost always less than the theoretical yield (often much less). The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, multiplied by 100 to give a percentage:

$$\text{percent yield} = \frac{\text{actual yield }(g)}{\text{theoretical yield }(g)} \times 100\% \tag{3.10.5}$$

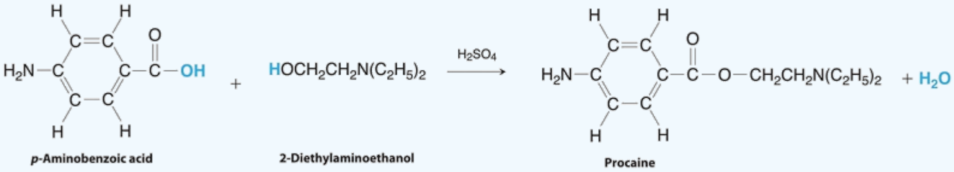
The method used to calculate the percent yield of a reaction is illustrated in Example $3.10.4$

✓ Example 3.10.4: Novocain

Procaine is a key component of Novocain, an injectable local anesthetic used in dental work and minor surgery. Procaine can be prepared in the presence of H2SO4 (indicated above the arrow) by the reaction

$$\underset{\text{p-amino benzoic acid}}{C_7H_7NO_2} + \underset{\text{2-diethylaminoethanol}}{C_6H_{15}NO} \xrightarrow{H_2SO_4} \underset{\text{procaine}}{C_{13}H_{20}N_2O_2} + H_2O$$

If this reaction were carried out with 10.0 g of p-aminobenzoic acid and 10.0 g of 2-diethylaminoethanol, and 15.7 g of procaine were isolated, what is the percent yield?



The preparation of procaine. A reaction of p-aminobenzoic acid with 2-diethylaminoethanol yields procaine and water.

Given: masses of reactants and product

Asked for: percent yield

Strategy:

A. Write the balanced chemical equation.
B. Convert from mass of reactants and product to moles using molar masses and then use mole ratios to determine which is the limiting reactant. Based on the number of moles of the limiting reactant, use mole ratios to determine the theoretical yield.
C. Calculate the percent yield by dividing the actual yield by the theoretical yield and multiplying by 100.

Solution:

A From the formulas given for the reactants and the products, we see that the chemical equation is balanced as written. According to the equation, 1 mol of each reactant combines to give 1 mol of product plus 1 mol of water.

B To determine which reactant is limiting, we need to know their molar masses, which are calculated from their structural formulas: p-aminobenzoic acid ($C_7H_7NO_2$), 137.14 g/mol; 2-diethylaminoethanol ($C_6H_{15}NO$), 117.19 g/mol. Thus the reaction used the following numbers of moles of reactants:

$$mol\text{ p-aminobenzoic acid} = 10.0\,g \times \frac{1\,mol}{137.14\,g} = 0.0729\,mol\text{ p-aminbenzoic acid}$$

$$mol\text{ 2-diethylaminoethanol} = 10.0\,g \times \frac{1\,mol}{117.19\,g} = 0.0853\,mol\text{ 2-diethylaminoethanol}$$

The reaction requires a 1:1 mole ratio of the two reactants, so p-aminobenzoic acid is the limiting reactant. Based on the coefficients in the balanced chemical equation, 1 mol of p-aminobenzoic acid yields 1 mol of procaine. We can therefore obtain only a maximum of 0.0729 mol of procaine. To calculate the corresponding mass of procaine, we use its structural formula (C13H20N2O2) to calculate its molar mass, which is 236.31 g/mol.

$$\text{theoretical yield of procaine} = 0.0729\,mol \times \frac{236.31\,g}{1\,mol} = 17.2\,g$$

C The actual yield was only 15.7 g of procaine, so the percent yield (via Equation 3.10.5) is

$$\text{percent yield} = \frac{15.7\,g}{17.2\,g} \times 100 = 91.3\%$$

(If the product were pure and dry, this yield would indicate very good lab technique!)

? Exercise 3.10.4: Extraction of Lead

Lead was one of the earliest metals to be isolated in pure form. It occurs as concentrated deposits of a distinctive ore called galena (PbS), which is easily converted to lead oxide (PbO) in 100% yield by roasting in air via the following reaction:

$$2\,\mathrm{PbS(s)} + 3\,\mathrm{O_2} \rightarrow 2\,\mathrm{PbO(s)} + 2\,\mathrm{SO_2(g)}$$

The resulting PbO is then converted to the pure metal by reaction with charcoal. Because lead has such a low melting point (327°C), it runs out of the ore-charcoal mixture as a liquid that is easily collected. The reaction for the conversion of lead oxide to pure lead is as follows:

$$\mathrm{PbO(s)} + \mathrm{C(s)} \rightarrow \mathrm{Pb(l)} + \mathrm{CO(g)}$$

If 93.3 kg of PbO is heated with excess charcoal and 77.3 kg of pure lead is obtained, what is the percent yield?

Electrolytically refined pure (99.989 %) superficially oxidized lead nodules and a high purity (99.989 %) 1 cm^3 lead cube for comparison. Figure used with permission from Wikipedia.

Answer

89.2%

Percent yield can range from 0% to 100%. In the laboratory, a student will occasionally obtain a yield that appears to be greater than 100%. This usually happens when the product is impure or is wet with a solvent such as water. If this is not the case, then the student must have made an error in weighing either the reactants or the products. The law of conservation of mass applies even to undergraduate chemistry laboratory experiments. A 100% yield means that everything worked perfectly, and the chemist obtained all the product that could have been produced. Anyone who has tried to do something as simple as fill a salt shaker or add oil to a car’s engine without spilling knows the unlikelihood of a 100% yield. At the other extreme, a yield of 0% means that no product was obtained. A percent yield of 80%–90% is usually considered good to excellent; a yield of 50% is only fair. In part because of the problems and costs of waste disposal, industrial production facilities face considerable pressures to optimize the yields of products and make them as close to 100% as possible.

Summary

The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained. The stoichiometry of a reaction describes the relative amounts of reactants and products in a balanced chemical equation. A stoichiometric quantity of a reactant is the amount necessary to react completely with the other reactant(s). If a quantity of a reactant remains unconsumed after complete reaction has occurred, it is in excess. The reactant that is consumed first and limits the amount of product(s) that can be obtained is the limiting reactant. To identify the limiting reactant, calculate the number of moles of each reactant present and compare this ratio to the mole ratio of the reactants in the balanced chemical equation. The maximum amount of product(s) that can be obtained in a reaction from a given amount of reactant(s) is the theoretical yield of the reaction. The actual yield is the amount of product(s) actually obtained in the reaction; it cannot exceed the theoretical yield. The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, expressed as a percentage.

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3.11: Complex Problem Solving Approaches

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CHAPTER OVERVIEW

4: Chemical Reactions

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Chemical reactions are processes that leads to the transformation of one set of chemical substances (reactants) to another set (products). Chemical reactions encompass changes that only involve the positions of electrons in the forming and breaking of chemical bonds between atoms.

Topic hierarchy

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4.1: Water, the Universal Solvent

With 70% of our earth being ocean water and 65% of our bodies being water, it is hard to not be aware of how important it is in our lives. There are 3 different forms of water, or H_2O: **solid** (ice), **liquid** (water), and **gas** (steam). Because water seems so ubiquitous, many people are unaware of the unusual and unique properties of water, including:

- Boiling Point and Freezing Point
- Surface Tension, Heat of Vaporization, and Vapor Pressure
- Viscosity and Cohesion
- Solid State
- Liquid State
- Gas State

Boiling Point and Freezing Point

If you look at the periodic table and locate tellurium (atomic number: 52), you find that the boiling points of hydrides decrease as molecule size decreases. So the hydride for tellurium: **H_2Te (hydrogen telluride)** has a boiling point of **-4°C**. Moving up, the next hydride would be **H_2Se (hydrogen selenide)** with a boiling point of **-42°C**. One more up and you find that **H_2S (hydrogen sulfide)** has a boiling point at **-62°C**. The next hydride would be **H_2O (WATER!)**. And we all know that the boiling point of water is **100°C**. So despite its *small* molecular weight, water has an incredibly *big* boiling point. This is because water requires more energy to break its hydrogen bonds before it can then begin to boil. The same concept is applied to freezing point as well, as seen in the table below. The boiling and freezing points of water enable the molecules to be very slow to boil or freeze, this is important to the ecosystems living in water. If water was very easy to freeze or boil, drastic changes in the environment and so in oceans or lakes would cause all the organisms living in water to die. This is also why sweat is able to cool our bodies.

COMPOUND	BOILING POINT	FREEZING POINT
Hydrogen Telluride	-4°C	-49°C
Hydrogen Selenide	-42°C	-64°C
Hydrogen Sulfide	-62°C	-84°C
Water	100°C	0 °C

Surface Tension, Heat of Vaporization, and Vapor Pressure

Besides mercury, water has the highest **surface tension** for all liquids. Water's high surface tension is due to the hydrogen bonding in water molecules. Water also has an exceptionally high **heat of vaporization**. Vaporization occurs when a liquid changes to a gas, which makes it an endothermic reaction. Water's heat of vaporization is 41 kJ/mol. **Vapor pressure** is inversely related to intermolecular forces, so those with stronger intermolecular forces have a lower vapor pressure. Water has very strong intermolecular forces, hence the low vapor pressure, but it's even lower compared to larger molecules with low vapor pressures.

- Viscosity is the property of fluid having high resistance to flow. We normally think of liquids like honey or motor oil being viscous, but when compared to other substances with like structures, water is viscous. Liquids with stronger intermolecular interactions are usually more viscous than liquids with weak intermolecular interactions.
- Cohesion is intermolecular forces between like molecules; this is why water molecules are able to hold themselves together in a drop. Water molecules are very cohesive because of the molecule's polarity. This is why you can fill a glass of water just barely above the rim without it spilling.

Solid State (Ice)

All substances, including water, become less dense when they are heated and more dense when they are cooled. So if water is cooled, it becomes more dense and forms ice. Water is one of the few substances whose solid state can float on its liquid state! Why? Water continues to become more dense until it reaches 4°C. After it reaches 4°C, it becomes *LESS* dense. When freezing, molecules within water begin to move around more slowly, making it easier for them to form hydrogen bonds and eventually arrange themselves into an open crystalline, hexagonal structure. Because of this open structure as the water molecules are being held further apart, the volume of water *increases* about 9%. So molecules are more tightly packed in water's liquid state than its solid state. This is why a can of soda can explode in the freezer.

Liquid State (Liquid Water)

It is very rare to find a compound that lacks carbon to be a liquid at standard temperatures and pressures. So it is unusual for water to be a liquid at room temperature! Water is liquid at room temperature so it's able to move around quicker than it is as solid, enabling the molecules to form fewer hydrogen bonds resulting in the molecules being packed more closely together. Each water molecule links to four others creating a tetrahedral arrangement, however they are able to move freely and slide past each other, while ice forms a solid, larger hexagonal structure.

Gas State (Steam)

As water boils, its hydrogen bonds are broken. Steam particles move very far apart and fast, so barely any hydrogen bonds have the time to form. So, less and less hydrogen bonds are present as the particles reach the critical point above steam. The lack of hydrogen bonds explains why steam causes much worse burns that water. Steam contains all the energy used to break the hydrogen bonds in water, so when steam hits your face you first absorb the energy the steam has taken up from breaking the hydrogen bonds it its liquid state. Then, in an exothermic reaction, steam is converted into liquid water and heat is released. This heat adds to the heat of boiling water as the steam condenses on your skin.

Water as the "Universal Solvent"

Because of water's polarity, it is able to dissolve or dissociate many particles. Oxygen has a slightly negative charge, while the two hydrogens have a slightly positive charge. The slightly negative particles of a compound will be attracted to water's hydrogen atoms, while the slightly positive particles will be attracted to water's oxygen molecule; this causes the compound to dissociate. Besides the explanations above, we can look to some attributes of a water molecule to provide some more reasons of water's uniqueness:

- Forgetting fluorine, oxygen is the most electronegative non-noble gas element, so while forming a bond, the electrons are pulled towards the oxygen atom rather than the hydrogen. This creates 2 polar bonds, which make the water molecule more polar than the bonds in the other hydrides in the group.
- A 104.5° bond angle creates a very strong dipole.
- Water has hydrogen bonding which probably is a vital aspect in waters strong intermolecular interaction

Why is this important for the real world?

The properties of water make it suitable for organisms to survive in during differing weather conditions. Ice freezes as it expands, which explains why ice is able to float on liquid water. During the winter when lakes begin to freeze, the surface of the water freezes and then moves down toward deeper water; this explains why people can ice skate on or fall through a frozen lake. If ice was not able to float, the lake would freeze from the bottom up killing all ecosystems living in the lake. However ice floats, so the fish are able to survive under the surface of the ice during the winter. The surface of ice above a lake also shields lakes from the cold temperature outside and insulates the water beneath it, allowing the lake under the frozen ice to stay liquid and maintain a temperature adequate for the ecosystems living in the lake to survive.

Resources

1. Cracolice, Mark S. and Edward Peters I. *Basics of Introductory Chemistry*. Thompson, Brooks/Cole Publishing Company. 2006
2. Petrucci, et al. General Chemistry: Principles & Modern Applications: AIE (Hardcover). Upper Saddle River: Pearson/Prentice Hall, 2007.

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SECTION OVERVIEW

4.2: Strong and Weak Electrolytes

Solutions are *homogeneous mixtures* containing one or more **solutes** in a **solvent**. The solvent that makes up most of the solution, whereas a solute is the substance that is dissolved inside the solvent.

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4.3: The Composition of Solutions

Solutions are *homogeneous mixtures* containing one or more **solutes** in a **solvent**. The solvent that makes up most of the solution, whereas a solute is the substance that is dissolved inside the solvent.

Relative Concentration Units

Concentrations are often expressed in terms of relative unites (e.g. percentages) with three different types of percentage concentrations commonly used:

1. **Mass Percent**: The mass percent is used to express the concentration of a solution when the mass of a solute and the mass of a solution is given:

$$\text{Mass Percent} = \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 100\% \tag{4.3.1}$$

2. **Volume Percent**: The volume percent is used to express the concentration of a solution when the volume of a solute and the volume of a solution is given:

$$\text{Volume Percent} = \frac{\text{Volume of Solute}}{\text{Volume of Solution}} \times 100\% \tag{4.3.2}$$

3. **Mass/Volume Percent:** Another version of a percentage concentration is mass/volume percent, which measures the mass or weight of solute in grams (e.g., in grams) vs. the volume of solution (e.g., in mL). An example would be a 0.9%(w/v) $NaCl$ solution in medical saline solutions that contains 0.9 g of $NaCl$ for every 100 mL of solution (see figure below). The mass/volume percent is used to express the concentration of a solution when the mass of the solute and volume of the solution is given. Since the numerator and denominator have different units, this concentration unit is not a true relative unit (e.g. percentage), however it is often used as an easy concentration unit since volumes of solvent and solutions are easier to measure than weights. Moreover, since the density of dilute aqueous solutions are close to 1 g/mL, if the volume of a solution in measured in mL (as per definition), then this well approximates the mass of the solution in grams (making a true reletive unit (m/m)).

$$\text{Mass/Volume Percent} = \frac{\text{Mass of Solute (g)}}{\text{Volume of Solution (mL)}} \times 100\% \tag{4.3.3}$$

Figure used with permission from Wikipedia.

✓ Example 4.3.1: Alcohol "Proof" as a Unit of Concentration

For example, In the United States, alcohol content in spirits is defined as twice the percentage of alcohol by volume (v/v) called proof. What is the concentration of alcohol in *Bacardi 151* spirits that is sold at 151 proof (hence the name)?

Figure: A mostly-empty bottle of Bacardi 151. from Wikipedia.

Solution

It will have an alcohol content of 75.5% (w/w) as per definition of "proof".

When calculating these percentages, that the units of the solute and solution should be equivalent units (and weight/volume percent (w/v %) is defined in terms of grams and mililiters).

You CANNOT plug in…	You CANNOT plug in…
(2 g Solute) / (1 kg Solution)	(2 g Solute) / (1000 g Solution)
	or (0.002 kg Solute) / (1 kg Solution)
(5 mL Solute) / (1 L Solution)	(5 mL Solute) / (1000 mL Solution)
	or (0.005 L Solute) / (1 L Solution)
(8 g Solute) / (1 L Solution)	(8 g Solute) / (1000 mL Solution)
	or (0.008 kg Solute) / (1 L Solution)

Dilute Concentrations Units

Sometimes when solutions are too dilute, their percentage concentrations are too low. So, instead of using really low percentage concentrations such as 0.00001% or 0.000000001%, we choose another way to express the concentrations. This next way of expressing concentrations is similar to cooking recipes. For example, a recipe may tell you to use 1 part sugar, 10 parts water. As you know, this allows you to use amounts such as 1 cup sugar + 10 cups water in your equation. However, instead of using the recipe's "1 part per ten" amount, chemists often use *parts per million*, *parts per billion* or *parts per trillion* to describe dilute concentrations.

- **Parts per Million**: A concentration of a solution that contained 1 g solute and 1000000 mL solution (same as 1 mg solute and 1 L solution) would create a very small percentage concentration. Because a solution like this would be so dilute, the density of the solution is well approximated by the density of the solvent; for water that is 1 g/mL (but would be different for different solvents). So, after doing the math and converting the milliliters of solution into grams of solution (assuming water is the solvent):

  $$\frac{1 \text{ g solute}}{1000000 \text{ mL solution}} \times \frac{1 \text{ mL}}{1 \text{ g}} = \frac{1 \text{ g solute}}{1000000 \text{ g solution}} \tag{4.3.4}$$

  We get (1 g solute)/(1000000 g solution). Because both the solute and the solution are both now expressed in terms of grams, it could now be said that the solute concentration is 1 part per million (ppm).

  $$1 \text{ ppm} = \frac{1 \text{ mg Solute}}{1 \text{ L Solution}} \tag{4.3.5}$$

  The ppm unit can also be used in terms of volume/volume (v/v) instead (see example below).

- **Parts per Billion**: Parts per billion (ppb) is almost like ppm, except 1 ppb is 1000-fold more dilute than 1 ppm.

$$1 \text{ ppb} = \frac{1\ \mu\text{g Solute}}{1 \text{ L Solution}} \tag{4.3.6}$$

- **Parts per Trillion**: Just like ppb, the idea behind parts per trillion (ppt) is similar to that of ppm. However, 1 ppt is 1000-fold more dilute than 1 ppb and 1000000-fold more dilute than 1 ppm.

$$1 \text{ ppt} = \frac{1 \text{ ng Solute}}{1 \text{ L Solution}} \tag{4.3.7}$$

✓ Example 4.3.2: ppm in the Atmosphere

Here is a table with the volume percent of different gases found in air. Volume percent means that for 100 L of air, there are 78.084 L Nitrogen, 20.946 L Oxygen, 0.934 L Argon and so on; Volume percent mass is different from the composition by mass or composition by amount of moles.

Elements Name	Volume Percent (v/v)	ppm (v/v)
Nitrogen	78.084	780,840
Oxygen	20.946	209,460
Water Vapor	4.0%	40,000
Argon	0.934	9,340
Carbon Dioxide	0.0379	379* (but growing rapidly)
Neon	0.008	8.0
Helium	0.000524	5.24
Methane	0.00017	1.7
Krypton	0.000114	1.14
Ozone	0.000001	0.1
Dinitrogen Monoxide	0.00003	0.305

Concentration Units based on moles

- **Mole Fraction**: The mole fraction of a substance is the fraction of all of its molecules (or atoms) out of the total number of molecules (or atoms). It can also come in handy sometimes when dealing with the $PV = nRT$ equation.

$$\chi_A = \frac{\text{number of moles of substance A}}{\text{total number of moles in solution}} \tag{4.3.8}$$

Also, keep in mind that the sum of each of the solution's substances' mole fractions equals 1.

$$\chi_A + \chi_B + \chi_C + \ldots = 1 \tag{4.3.9}$$

- **Mole Percent**: The mole percent (of substance A) is χ_A in percent form.

$$\text{Mole percent (of substance A)} = \chi_A \times 100\% \tag{4.3.10}$$

- **Molarity**: The molarity (M) of a solution is used to represent the amount of moles of solute per liter of the solution.

$$M = \frac{\text{Moles of Solute}}{\text{Liters of Solution}} \tag{4.3.11}$$

- **Molality**: The molality (m) of a solution is used to represent the amount of moles of solute per kilogram of the solvent.

$$m = \frac{\text{Moles of Solute}}{\text{Kilograms of Solvent}} \tag{4.3.12}$$

Figure: Different molarities of liquids in the laboratory. 50 ml of distilled water (0 M), Sodium Hydroxide solution of 0.1 M, and Hydrochloric acid solution of 0.1 M. from group4swimmingpool.

The molarity and molality equations differ only from their denominators. However, this is a huge difference. As you may remember, volume varies with different temperatures. At higher temperatures, volumes of liquids increase, while at lower temperatures, volumes of liquids decrease. Therefore, molarities of solutions also vary at different temperatures. This creates an advantage for using molality over molarity. Using molalities rather than molarities for lab experiments would best keep the results within a closer range. Because volume is not a part of its equation, it makes molality independent of temperature.

✓ Example 4.3.1

In a solution, there is 111.0 mL (110.605 g) solvent and 5.24 mL (6.0508 g) solute present in a solution. Find the mass percent, volume percent and mass/volume percent of the solute.

Solution

Mass Percent

=(Mass of Solute) / (Mass of Solution) x 100%|

=(6.0508g) / (110.605g + 6.0508g) x 100%

=(0.0518688312) x 100%

=5.186883121%

Mass Percent= 5.186%

Volume Percent

=(Volume of Solute) / (Volume of Solution) x 100%

=(5.24mL) / (111.0mL + 5.24mL) x 100%

=(0.0450791466) x 100%

=4.507914659%

Volume Percent= 4.51%

Mass/Volume Percent

=(Mass of Solute) / (Volume of Solution) x 100%

=(6.0508g) / (111.0mL + 5.24mL) x 100%

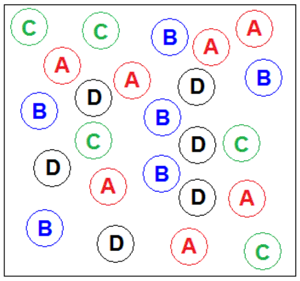
=(0.0520) x 100%

=5.205%

Mass/Volume Percent= 5.2054%

✓ Example 4.3.2

With the solution shown in the picture below, find the mole percent of substance C.



Molecule	Amount Present in Box
A	7
B	6
C	5
D	6
total	24

Solution

Moles of C= (5 C molecules) x (1mol C / 6.022x10^{23} C molecules) = 8.30288941x10^{-24}mol C

Total Moles= (24 molecules) x (1mol / 6.022x10^{23} molecules)= 3.98538691x10^{-23}mol total

X_C= (8.30288941x10^{-24}mol C) / (3.98538691x10^{-23}mol) = .2083333333

Mole Percent of C

= X_C x 100%

=(o.2083333333) x 100%

=20.83333333

Mole Percent of C = 20%

Example 4.3.3

A 1.5L solution is composed of 0.25g NaCl dissolved in water. Find its molarity.

Solution

Moles of NaCl= (0.25g) / (22.99g + 35.45g) = 0.004277 mol NaCl

Molarity

=(Moles of Solute) / (Liters of Solution)

=(0.004277mol NaCl) / (1.5L)

=0.002851 M

Molarity= 0.0029M

Example 4.3.4

0.88g NaCl is dissolved in 2.0L water. Find its molality.

Solution

Moles of NaCl= (0.88g) / (22.99g + 35.45g) = 0.01506 mol NaCl

Mass of water= (2.0L) x (1000mL / 1L) x (1g / 1mL) x (1kg / 1000g) = 2.0kg water

Molality

=(Moles of Solute) / (kg of Solvent)

=(0.01506 mol NaCl) / (2.0kg)

=0.0075290897m

Molality= 0.0075m

References

1. Petrucci, Harwood, Herring. General Chemistry: Principles & Modern Applications. 8th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2002. 528-531

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4.4: Types of Chemical Reactions

Chemical reactions are the processes by which chemicals interact to form new chemicals with different compositions. Simply stated, a chemical reaction is the process where reactants are transformed into products. How chemicals react is dictated by the chemical properties of the element or compound- the ways in which a compound or element undergoes changes in composition.

Describing Reactions Quantitatively

Chemical reactions are constantly occurring in the world around us; everything from the rusting of an iron fence to the metabolic pathways of a human cell are all examples of chemical reactions. Chemistry is an attempt to classify and better understand these reactions.

Figure 4.4.0: The rusting of a chain is an example of a chemical reaction

A chemical reaction is typically represented by a chemical equation, which represents the change from reactants to products. The left hand side of the equation represents the reactants, while the right hand side represents the products. A typical chemical reaction is written with stoichiometric coefficients, which show the relative amounts of products and reactants involved in the reaction. Each compound is followed by a parenthetical note of the compound's state of 2: (l) for liquid, (s) for solid, (g) for gas. The symbol (aq) is also commonly used in order to represent an aqueous solution, in which compounds are dissolved in water. A reaction might take the following form:

$$\mathrm{A(aq) + B(g) \rightarrow C(s) + D(l)}$$

In the above example, A and B, known as the reactants, reacted to form C and D, the products.

To write an accurate chemical equation, two things must occur:

1. Each product and reactant must be written using its chemical formula, e.g., H_2
2. The number of atoms of each element must be equal on both sides of the equation. Coefficients are used in front of the chemical formulas in order to help balance the number of atoms, e.g.,

$$\mathrm{2\,Mg + O_2 \rightarrow 2\,MgO}$$

✓ Example 4.4.1: Balancing Reactions

Hydrogen and nitrogen react together in order to produce ammonia gas, write the chemical equation of this reaction.

Solution

Step 1: Write each product and reactant using its chemical formula.

$$\mathrm{H_2 + N_2 \rightarrow NH_3}$$

Step 2: Ensure the number of atoms of each element are equal on both sides of the equation.

$$\mathrm{3\,H_2 + N_2 \rightarrow 2\,NH_3}$$

In order to balance this equation, coefficients must be used. Since there are only 2 nitrogen atoms present on the left side of the equation, a coefficient of 2 must be added to NH_3.

Stoichiometry

The coefficient that used for balancing the equation is called the stoichiometric coefficient. The coefficients tell us the ratio of each element in a chemical equation. For example

$$\mathrm{2\,Mg + O_2 \rightarrow 2\,MgO}$$

means

- 2 moles of MgO is produced for every 2 moles of Mg consumed.
- 2 moles of MgO is produced for every 1 mole of O_2 consumed.

When all of the reactants of a reaction are completely consumed, the reaction is in perfect stoichiometric proportions. Often times, however, a reaction is not in perfect stoichiometric proportions, leading to a situation in which the entirety of one reactant is consumed, but there is some of another reactant remaining. The reactant that is entirely consumed is called the limiting reactant, and it determines how much of the products are produced.

✓ Example 4.4.2: Limiting Reagent

4.00 g of hydrogen gas mixed with 20.0g of oxygen gas. How many grams of water are produced?

Solution

$$n(H_2) = \frac{4g}{(1.008\times 2)g/mol} = 1.98mol$$

So theoretically, it requires 0.99 mol of O_2

$$n(O_2)=n(H_2)*(1mol\ O_2/2mol\ H_2)=0.99\ mol$$

$$m(O_2)=n(O_2)*(16g/mol\ *2) = 31.7\ g\ O_2$$

Because O_2 only has 20.0 g, less than the required mass. It is limiting.

Often, reactants do not react completely, resulting in a smaller amount of product formed than anticipated. The amount of product expected to be formed from the chemical equation is called the theoretical yield. The amount of product that is produced during a reaction is the actual yield. To determine the percent yield:

Percent yield =actual yield/theoretical yield X 100%

Chemical reactions do not only happen in the air, but also exist in solutions. In a solution, the solvent is the compound that is dissolved, and the solute is the compound that the solvent is dissolved in. The molarity of a solution is the number of moles of a solvent divided by the number of liters of solution.

$$Molarity = \frac{\text{amount of solute (mol)}}{\text{volume of solution (L)}}$$

$$M = \frac{n}{V}$$

✓ Example 4.4.3: Concentrations

100.0 g NaCl is dissolved in 50.00 ml water. What is the molarity of the solution?

Solution

a) Find the amount of solute in moles.

100.0g/(22.99 g/mol+35.45 g/mol) =1.711 moles

b) Convert mL to L.

50.00 mL=0.05000 L

c) Find the molarity

1.711 moles/0.05000L=34.22 mol/L

Physical Changes During Chemical Reactions

Physical change is the change in physical properties. Physical changes usually occur during chemical reactions, but does not change the nature of substances. The most common physical changes during reactions are the change of color, scent and evolution of gas. However, when physical changes occur, chemical reactions may not occur.

Types of Chemical Reactions

Precipitation, or double-replacement reaction

A reaction that occurs when aqueous solutions of anions (negatively charged ions) and cations (positively charged ions) combine to form a compound that is insoluble is known as precipitation. The insoluble solid is called the precipitate, and the remaining liquid is called the supernate. See Figure2.1

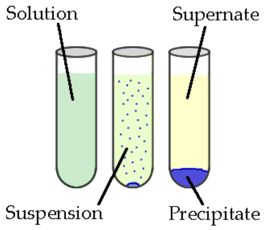


Figure 4.4.1

Real life example: The white precipitate formed by acid rain on a marble statue:

$$CaCO_3(aq) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

✓ Example 4.4.4: Precipitation

An example of a precipitation reaction is the reaction between silver nitrate and sodium iodide. This reaction is represented by the chemical equation :

$$\text{AgNO}_3\text{ (aq)+ NaI (aq)} \rightarrow \text{AgI (s) + NaNO}_3\text{ (aq)}$$

Since all of the above species are in aqueous solutions, they are written as ions, in the form:

$$\text{Ag}^{+}\text{ +NO}_3^{-}\text{ (aq)+ Na}^{+}\text{ (aq) + I}^{-}\text{ (aq)} \rightarrow \text{AgI (s) + Na}^{+}\text{ (aq) + NO}_3^{-}\text{ (aq)}$$

Ions that appear on both sides of the equation are called spectator ions. These ions do not affect the reaction and are removed from both sides of the equation to reveal the net ionic equation, as written below:

$$\text{Ag}^{+}\text{ (aq) + I}^{-}\text{ (aq)} \rightarrow \text{AgI (s)}$$

In this reaction, the solid, AgI, is known as the precipitate. The formation of a precipitate is one of the many indicators that a chemical reaction has taken place.

Acid-base, or neutralization reaction

A neutralization reaction occurs when an acid and base are mixed together. An acid is a substance that produces H^+ ions in solution, whereas a base is a substance that that produces OH^- ions in solution. A typical acid-base reaction will produce an ionic compound called a salt and water. A typical acid-base reaction is the reaction between hydrochloric acid and sodium hydroxide. This reaction is represented by the equation:

$$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)}^{+}\text{H}_2\text{O(l)}$$

In this reaction, HCl is the acid, $NaOH$ is the base, and $NaCl$ is the salt. Real life example: Baking soda reacts with vinegar is a neutralization reaction.

***Video**: Vinegar and Baking Soda Reaction with Explanation*

Oxidation-Reduction (Redox) Reactions

A redox reaction occurs when the oxidation number of atoms involved in the reaction are changed. Oxidation is the process by which an atom's oxidation number is increased, and reduction is the process by which an atom's oxidation number is decreased. If the oxidation states of any elements in a reaction change, the reaction is an oxidation-reduction reaction. An atom that undergoes oxidation is called the reducing agent, and the atom that undergoes reduction is called the oxidizing agent. An example of a redox reaction is the reaction between hydrogen gas and fluorine gas:

$$H_2(g) + F_2(g) \rightarrow 2HF(g) \tag{4.4.1}$$

In this reaction, hydrogen is oxidized from an oxidation state of 0 to +1, and is thus the reducing agent. Fluorine is reduced from 0 to -1, and is thus the oxidizing agent.

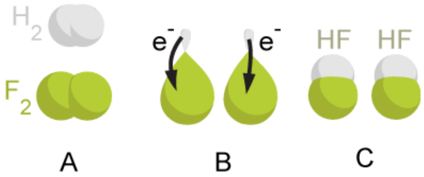


Figure 4.4.2: Figure: In redox reaction of Equation 4.4.1, a H_2 molecule donates electrons to F_2 resulting in two HF molecules

Real life example: The cut surface of an apple turns brownish after exposed to the air for a while.

Video: Why Do Apples Turn Brown?

Combustion Reaction

A combustion reaction is a type of redox reaction during which a fuel reacts with an oxidizing agent, resulting in the release of energy as heat. Such reactions are exothermic, meaning that energy is given off during the reaction. An endothermic reaction is one which absorbs heat. A typical combustion reaction has a hydrocarbon as the fuel source, and oxygen gas as the oxidizing agent. The products in such a reaction would be CO_2 and H_2O.

$$C_xH_yO_z + O_2 \rightarrow CO_2 + H_2O \quad \text{(unbalanced)}$$

Such a reaction would be the combustion of glucose in the following equation

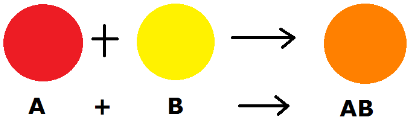
$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$$

Real life example: explosion; burning.

***Video**: Combustion reactions come in many varieties. Here's a collection of various examples, all of which require oxygen, activation energy, and of course, fuel*

Synthesis Reactions

A synthesis reaction occurs when one or more compounds combines to form a complex compound. The simplest equation of synthesis reaction is illustrated below.



An example of such a reaction is the reaction of silver with oxygen gas to form silver oxide:

$$2Ag(s) + O_2(g) \rightarrow 2AgO(s)$$

Real life example: Hydrogen gas is burned in air (reacts with oxygen) to form water:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Decomposition Reactions

A decomposition reaction is the opposite of a synthesis reaction. During a decomposition reaction, a more complex compound breaks down into multiple simpler compounds. A classic example of this type of reaction is the decomposition of hydrogen peroxide into oxygen and hydrogen gas:

$$H_2O_2(l) \rightarrow H_2(g) + O_2(g)$$

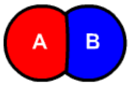
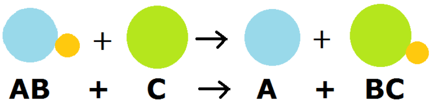


Figure 4.4.3: The molecule AB is decomposing into A and B

Single Replacement Reactions

A type of oxidation-reduction reaction in which an element in a compound is replaced by another element.



An example of such a reaction is:

$$Cu(s) + AgNO_3(aq) \rightarrow Ag(s) + Cu(NO_3)_2(aq)$$

This is also a redox reaction.

Problems

1) $C_3H_6O_3 + O_2 \rightarrow CO_2$ (g) $+H_2O$ (g)

a) What type of reaction is this?
b) Is is exothermic or endothermic? Explain.

2) Given the oxidation-reduction reaction :

Fe (s) + $CuSO_4$ (aq)→ $FeSO_4$ (aq)+ Cu (s)

a) Which element is the oxidizing agent and which is the reducing agent?
b) How do the oxidation states of these species change?

3) Given the equation:

$AgNO_3$ (aq) + KBr (aq) → AgBr (s) +KNO_3 (aq)

a) What is the net ionic reaction?
b) Which species are spectator ions?

4) 2 HNO_3 (aq) + $Sr(OH)_2$ (aq) → $Sr(NO_3)_2$ (aq) +2 H_2O (l)

a) In this reaction, which species is the acid and which is the base?
b) Which species is the salt?
c) If 2 moles of HNO3 and 1 mole of Sr(OH)2 are used, resulting in 0.85 moles of $Sr(NO_3)$2 , what is the percent yield (with respect to moles) of Sr(NO3)2 ?

5) Identify the type of the following reactions:

a) $Al(OH)_3$ (aq) + HCl (aq) → $AlCl_3$ (aq) + H_2O (l)
b) $MnO_2 + 4H^+ + 2Cl^- \rightarrow Mn^{2+} + 2H_2O$ (l) + Cl_2 (g)
c) P_4 (s) + Cl_2 (g) → PCl_3 (l)
d) Ca (s) + $2H_2O$ (l) → $Ca(OH)_2$ (aq) + H_2 (g)
e) $AgNO_3$ (aq) + NaCl (aq) → AgCl (s) + $NaNO_3$ (aq)

Solutions

1a) It is a combustion reaction

1b) It is exothermic, because combustion reactions give off heat

2a) Cu is the oxidizing agent and Fe is the reducing agent

2b) Fe changes from 0 to +2, and Cu changes from +2 to 0.

3a) Ag^+ (aq) + Br^- (aq) → AgBr (s)

3b) The spectator ions are K^+ and NO_3^-

4a) HNO_3 is the acid and $Sr(OH)_2$ is the base

4b) $Sr(NO_3)_2$ is the salt

4c) According to the stoichiometric coefficients, the theoretical yield of $Sr(NO_3)_2$ is one mole. The actual yield was 0.85 moles. Therefore the percent yield is:

(0.85/1.0) * 100% = 85%

5a) Acid-base

5b) Oxidation-reduction

5c) Synthesis

5d) Single-replacement reaction

5e) Double replacement reaction

References

1. Petrucci, Ralph H., William S. Harwood, F. G. Herring, and Jeffry D. Madura. General Chemistry. 9th ed. Upper Saddle River: Prentice Education Inc, 2007, Print.

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4.5: Precipitation Reactions

Precipitation reactions occur when cations and anions in aqueous solution combine to form an insoluble ionic solid called a **precipitate**. Whether or not such a reaction occurs can be determined by using the **solubility rules** for common ionic solids. Because not all aqueous reactions form precipitates, one must consult the solubility rules before determining the state of the products and writing a **net ionic equation.** The ability to predict these reactions allows scientists to determine which ions are present in a solution, and allows industries to form chemicals by extracting components from these reactions.

Properties of Precipitates

Precipitates are insoluble ionic solid products of a reaction, formed when certain cations and anions combine in an aqueous solution. The determining factors of the formation of a precipitate can vary. Some reactions depend on temperature, such as solutions used for buffers, whereas others are dependent only on solution concentration. The solids produced in precipitate reactions are crystalline solids, and can be suspended throughout the liquid or fall to the bottom of the solution. The remaining fluid is called supernatant liquid. The two components of the mixture (precipitate and supernate) can be separated by various methods, such as filtration, centrifuging, or decanting.

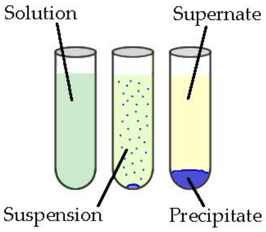

Figure 1: Above is a diagram of the formation of a precipitate in solution.

Precipitation and Double Replacement Reactions

The use of solubility rules require an understanding of the way that ions react. Most precipitation reactions are single replacement reactions or double replacement reactions. A double replacement reaction occurs when two ionic reactants dissociate and bond with the respective anion or cation from the other reactant. The ions replace each other based on their charges as either a cation or an anion. This can be thought of as "switching partners"; that is, the two reactants each "lose" their partner and form a bond with a different partner:

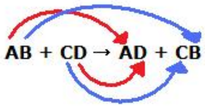

Figure 2: A double replacement reaction

A double replacement reaction is specifically classified as a **precipitation reaction** when the chemical equation in question occurs in aqueous solution and one of the of the products formed is insoluble. An example of a precipitation reaction is given below:

$$\mathrm{CdSO_4(aq) + K_2S(aq) \rightarrow CdS(s) + K_2SO_4(aq)}$$

Both reactants are aqueous and one product is solid. Because the reactants are ionic and aqueous, they dissociate and are therefore **soluble**. However, there are six solubility guidelines used to predict which molecules are insoluble in water. These molecules form a solid precipitate in solution.

Solubility Rules

Whether or not a reaction forms a precipitate is dictated by the solubility rules. These rules provide guidelines that tell which ions form solids and which remain in their ionic form in aqueous solution. The rules are to be followed from the top down, meaning that if something is insoluble (or soluble) due to rule 1, it has precedence over a higher-numbered rule.

1. Salts formed with group 1 cations and $\mathrm{NH_4^+}$ cations are **soluble**. There are some exceptions for certain $\mathrm{Li^+}$ salts.
2. Acetates ($\mathrm{C_2H_3O_2^-}$), nitrates ($\mathrm{NO_3^-}$), and perchlorates ($\mathrm{ClO_4^-}$) are **soluble.**
3. Bromides, chlorides, and iodides are **soluble.**

4. Sulfates (SO_4^{2-}) are **soluble** with the exception of sulfates formed with Ca^{2+}, Sr^{2+}, Pb^{2+}, and Ba^{2+}.
5. Salts containing silver, lead, and mercury (I) are **insoluble.**
6. Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), sulfides, oxides, and hydroxides (OH^-) are **insoluble**. Sulfides formed with group 2 cations and hydroxides formed with calcium, strontium, and barium are exceptions.

If the rules state that an ion is soluble, then it remains in its aqueous ion form. If an ion is insoluble based on the solubility rules, then it forms a solid with an ion from the other reactant. If all the ions in a reaction are shown to be soluble, then no precipitation reaction occurs.

Net Ionic Equations

To understand the definition of a **net ionic equation**, recall the equation for the double replacement reaction. Because this particular reaction is a precipitation reaction, states of matter can be assigned to each variable pair:

$$\mathbf{AB}(\mathbf{\mathit{aq}}) + \mathbf{CD}(\mathbf{\mathit{aq}}) \rightarrow \mathbf{AD}(\mathbf{\mathit{aq}}) + \mathbf{CB}(\mathbf{\mathit{s}})$$

The first step to writing a net ionic equation is to separate the soluble (aqueous) reactants and products into their respective cations and anions. Precipitates do not dissociate in water, so the solid should not be separated. The resulting equation looks like that below:

$$\mathbf{A^+}(\mathbf{\mathit{aq}}) + \mathbf{B^-}(\mathbf{\mathit{aq}}) + \mathbf{C^+}(\mathbf{\mathit{aq}}) + \mathbf{D^-}(\mathbf{\mathit{aq}}) \rightarrow \mathbf{A^+}(\mathbf{\mathit{aq}}) + \mathbf{D^-}(\mathbf{\mathit{aq}}) + \mathbf{CB}(\mathbf{\mathit{s}})$$

In the equation above, **A^+**and **D^-** ions are present on both sides of the equation. These are called **spectator ions** because they remain unchanged throughout the reaction. Since they go through the equation unchanged, they can be eliminated to show the **net ionic equation**:

$$\mathbf{C^+}\ \mathbf{(aq)} + \mathbf{B^-}\ \mathbf{(aq)} \rightarrow \mathbf{CB}\ \mathbf{(s)}$$

The net ionic equation only shows the precipitation reaction. A net ionic equation must be balanced on both sides not only in terms of atoms of elements, but also in terms of electric charge. Precipitation reactions are usually represented solely by net ionic equations. If all products are aqueous, a net ionic equation cannot be written because all ions are canceled out as spectator ions. Therefore, **no precipitation reaction occurs.**

Applications and Examples

Precipitation reactions are useful in determining whether a certain element is present in a solution. If a precipitate is formed when a chemical reacts with lead, for example, the presence of lead in water sources could be tested by adding the chemical and monitoring for precipitate formation. In addition, precipitation reactions can be used to extract elements, such as magnesium from seawater. Precipitation reactions even occur in the human body between antibodies and antigens; however, the environment in which this occurs is still being studied.

✓ Example 1

Complete the double replacement reaction and then reduce it to the net ionic equation.

$$\mathrm{NaOH(aq) + MgCl_2(aq) \rightarrow}$$

First, *predict the products* of this reaction using knowledge of double replacement reactions (remember the cations and anions "switch partners").

$$\mathrm{2\,NaOH(aq) + MgCl_2(aq) \rightarrow 2\,NaCl + Mg(OH)_2}$$

Second, *consult the solubility rules* to determine if the products are soluble. Group 1 cations ($\mathrm{Na^+}$) and chlorides are soluble from rules 1 and 3 respectively, so NaCl will be soluble in water. However, rule 6 states that hydroxides are insoluble, and thus $\mathrm{Mg(OH)_2}$ will form a precipitate. The resulting equation is the following:

$$\mathrm{2\,NaOH(aq) + MgCl_2(aq) \rightarrow 2\,NaCl(aq) + Mg(OH)_2(s)}$$

Third, *separate the reactants* into their ionic forms, as they would exist in an aqueous solution. Be sure to balance both the electrical charge and the number of atoms:

$$\mathrm{2\,Na^+(aq) + 2\,OH^-(aq) + Mg^{2+}(aq) + 2\,Cl^-(aq) \rightarrow Mg(OH)_2(s) + 2\,Na^+(aq) + 2\,Cl^-(aq)}$$

Lastly, *eliminate the spectator ions* (the ions that occur on both sides of the equation unchanged). In this case, they are the sodium and chlorine ions. The final *net ionic equation* is:

$$\mathrm{Mg^{2+}(aq) + 2\,OH^-(aq) \rightarrow Mg(OH)_2(s)}$$

Example 2

Complete the double replacement reaction and then reduce it to the net ionic equation.

$$\mathrm{CoCl_2(aq) + Na_2SO_4(aq) \rightarrow}$$

Solution

The predicted products of this reaction are $\mathrm{CoSO_4}$ and NaCl. From the solubility rules, $\mathrm{CoSO_4}$ is soluble because rule 4 states that sulfates ($\mathrm{SO_4^{2-}}$) are soluble. Similarly, we find that NaCl is soluble based on rules 1 and 3. After balancing, the resulting equation is as follows:

$$\mathrm{CoCl_2(aq) + Na_2SO_4(aq) \rightarrow CoSO_4(aq) + 2\,NaCl(aq)}$$

Separate the species into their ionic forms, as they would exist in an aqueous solution. Balance the charge and the atoms. Cancel out all spectator ions (those that appear as ions on both sides of the equation.):

$$\mathrm{Co^{2-}\cancel{(aq)} + 2\,Cl^-\cancel{(aq)} + 2\,Na^+\cancel{(aq)} + SO_4^{2-}\cancel{(aq)} \rightarrow Co^{2-}\cancel{(aq)} + SO_4^{2-}\cancel{(aq)} + 2\,Na^+\cancel{(aq)} + 2\,Cl^-\cancel{(aq)}}$$

No precipitation reaction

This particular example is important because all of the reactants and the products are aqueous, meaning they cancel out of the net ionic equation. There is no solid precipitate formed; therefore, no precipitation reaction occurs.

Exercise 4.5.1

Write the net ionic equation for this potentially double displacement reaction. Make sure to include the states of matter and balance the equations.

$$\mathrm{Fe(NO_3)_3(aq) + NaOH(aq) \rightarrow}$$

Answer

Regardless of physical state, the products of this reaction are $\mathrm{Fe(OH)_3}$ and $\mathrm{NaNO_3}$. The solubility rules predict that $\mathrm{NaNO_3}$ is soluble because all nitrates are soluble (rule 2). However, $\mathrm{Fe(OH)_3}$ is insoluble, because hydroxides are insoluble (rule 6) and Fe is not one of the cations which results in an exception. After dissociation, the ionic equation is as follows:

$$\mathrm{Fe^{3+}(aq) + NO_3^-(aq) + Na^+(aq) + 3\,OH^-(aq) \rightarrow Fe(OH)_3(s) + Na^+(aq) + NO_3^-(aq)}$$

Canceling out spectator ions

$$\mathrm{Fe^{3+}(aq) + \cancel{NO_3^-(aq)} + \cancel{Na^+(aq)} + 3\,OH^-(aq) \rightarrow Fe(OH)_3(s) + \cancel{Na^+(aq)} + \cancel{NO_3^-(aq)}}$$

leaves the net ionic equation:

$$\mathrm{Fe^{3+}(aq) + 3\,OH^-(aq) \rightarrow Fe(OH)_3(s)}$$

Exercise 4.5.2

Write the net ionic equation for this potentially double displacement reaction. Make sure to include the states of matter and balance the equations.

$$\mathrm{Al_2(SO_4)_3(aq) + BaCl_2(aq) \rightarrow}$$

Answer

From the double replacement reaction, the products are $\mathrm{AlCl_3}$ and $\mathrm{BaSO_4}$. $\mathrm{AlCl_3}$ is soluble because it contains a chloride (rule 3); however, $\mathrm{BaSO_4}$ is insoluble: it contains a sulfate, but the $\mathrm{Ba^{2+}}$ ion causes it to be insoluble because it is one of the cations that causes an exception to rule 4. The ionic equation is (after balancing):

$$\mathrm{2\,Al^{3+}(aq) + 6\,Cl^{-}(aq) + 3\,Ba^{2+}(aq) + 3\,SO_4^{2-}(aq) \rightarrow 2\,Al^{3+}(aq) + 6\,Cl^{-}(aq) + 3\,BaSO_4(s)}$$

Canceling out spectator ions leaves the following net ionic equation:

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

Exercise 4.5.3

Write the net ionic equation for this potentially double displacement reaction. Make sure to include the states of matter and balance the equations.

$$\mathrm{HI(aq) + Zn(NO_3)_2(aq) \rightarrow}$$

Answer

From the double replacement reaction, the products $\mathrm{HNO_3}$ and $\mathrm{ZnI_2}$ are formed. Looking at the solubility rules, $\mathrm{HNO_3}$ is soluble because it contains nitrate (rule 2), and $\mathrm{ZnI_2}$ is soluble because iodides are soluble (rule 3). This means that both the products are aqueous (i.e. dissociate in water), and thus no precipitation reaction occurs.

Exercise 4.5.4

Write the net ionic equation for this potentially double displacement reaction. Make sure to include the states of matter and balance the equations.

$$\mathrm{CaCl_2(aq) + Na_3PO_4(aq) \rightarrow}$$

Answer

The products of this double replacement reaction are $\mathrm{Ca_3(PO_4)_2}$ and NaCl. Rule 1 states that NaCl is soluble, and according to solubility rule 6, $\mathrm{Ca_3(PO_4)_2}$ is insoluble. The ionic equation is:

$$\mathrm{Ca^{2+}(aq) + Cl^{-}(aq) + Na^{+}(aq) + PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s) + Na^{+}(aq) + Cl^{-}(aq)}$$

After canceling out spectator ions, the net ionic equation is given below:

$$\mathrm{Ca^{2+}(aq) + PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)}$$

Exercise 4.5.5

Write the net ionic equation for this potentially double displacement reaction. Make sure to include the states of matter and balance the equations.

$$\mathrm{Pb(NO_3)_2(aq) + K_2SO_4(aq) \rightarrow}$$

Answer

The first product of this reaction, $\mathrm{PbSO_4}$, is insoluble according to rule 4 because it is a sulfate. The second product, $\mathrm{KNO_3}$, is soluble because it contains nitrate (rule 2). Therefore, $\mathrm{PbSO_3(s)}$ will precipitate.

$$\mathrm{Pb^{2+}(aq) + SO_4(aq) \longrightarrow Pb(SO_3)_2(s)}$$

References

1. Campbell, Dan, Linus Pauling, and Davis Pressman. "The Nature of the Forces Between Antigen and Antibody and of the Precipitation Reaction." *Physiological Reviews 23.3* (1943): 203-219. Online.

2. Harwood, William, F Herring, Jeffry Madura, and Ralph Petrucci. *General Chemistry*. 9th ed. Upper Saddle River: Pearson Pretence Hall, 2007. Print.
3. Freeouf, J.L, Grischkowsky, D., McInturff, D.T., Warren, A.C., & Woodall, J.M. (1990). Arsenic precipitates and the semi-insulating properties of gaas buffer layers grown by low-temperature molecular beam epitaxy. *Applied Physics Letters*, 57(13)
4. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey 2007.

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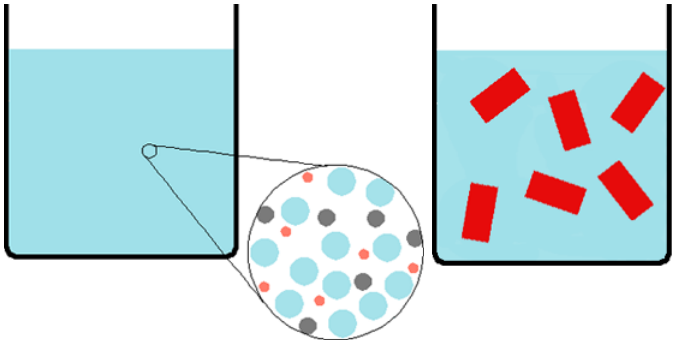
4.6: Reactions in Solution

A solution consists of two or more substances dissolved in a liquid form. Not to get confused with a *mixture*, which is heterogeneous--multiple substances exist in varying structures-- solutions are homogenous, which means that atoms of the solute are evenly dispersed throughout the solvent (ex. water, ethanol). Think of it as comparing a cup of (dissolved) sugar water and a cup of water with lego blocks in it. The solute is the substance dissolved in the solution, and the solvent is the substance doing the dissolving.

ex.

A solution of NaCl in water A mixture of lego blocks and water



Note: All solutions are mixtures but not all mixtures are solutions.

Solvents

Water (H_2O) is the most common solvent, used for dissolving many compounds or brewing coffee. Other common solvents include turpentine (a paint thinner), acetone (nail polish remover), and ethanol (used in some perfumes). Such solvents usually contain carbon and are called organic solvents. Solutions with water as the solvent are called aqueous solutions; they have special properties that are covered here.

Solutes

Different chemical compounds dissolve in solutes in varying degrees. Some compounds, such as the strong acid hydrochloric acid (HCl), dissociate completely in solution into ions. Others, like the weak base ammonia (NH_3), only partly dissociate. Yet other compounds like alcohol do not dissociate at all and remain compounds. Laboratory reactions often involve acids and bases, which are covered in more detail here.

Concentration

Concentration is the measure of the amount of solute in a certain amount of solvent. Knowing the concentration of a solution is important determining the strength of an acid or base (pH), among other things. When there is so much solute present in a concentration that it no longer dissolves, the solution is saturated.

Scientists often use **molarity** to measure concentration.

$$\text{molarity} = \text{moles/Liter}$$

Since reaction stoichiometry relies on molar ratios, molarity is the main measurement for concentration.

A less common unit for concentration is called *molality*.

$$\text{Molality} = \text{moles/Kg of solvent}$$

Scientists sometimes use molality to measure concentration because liquid volumes change slightly based on the temperature and pressure. Mass, however, stays the same and can be measured accurately using a balance. Commercial concentrated products are usually expressed in mass percent; such as commercial concentrated sulfuric acid, which is 93-98% H_2SO_4 by mass in water (Hill, Petrucci 116).

Making a Solution

Solutions used in the laboratory are usually made from either solid solutes (often salts) or stock solutions.

To make a solution from solid solutes, first calculate how many moles of solute are in the desired solutions (using the molarity). Calculate the amount of solid you need in grams using the moles needed and the molar mass of the solute and weight out the needed amount. Transfer the solute to a container (preferably a volumetric flask, which most accurately measures volume of solution labeled on the flask) and add a small amount of solvent. Mix thoroughly to dissolve the solute. Once the solute has dissolved, add the remaining solvent to make the solution of the desired volume and mix thoroughly.

For example, to make 0.5 Liters of 0.5 molar NaCl:

1. Multiply the concentration (0.5 mols/Liters) by the volume of solution you want (0.5 Liters) to find the moles of NaCl you need.

$$0.5 \text{ moles/Liter} * 0.5 \text{ Liters} = 0.25 \text{ moles of NaCl}$$

2. Multiply the moles of NaCl by its molar mass (58.44 g/mol) to find the grams of solute needed.

$$(0.25 \text{ moles NaCl})*(58.44 \text{ grams/mole}) = 14.61 \text{ grams of NaCl}$$

Making a solution of a certain concentration from a stock solution is called a dilution. When diluting a solution, keep in mind that adding a solvent to a solution changes the concentration of the solution, but not the amount of solute already present.

To dilute a solution with known concentration, first determine the number of moles of solute are in the solution by multiplying the molarity by the volume (in Liters). Then, divide by the desired molarity or volume to find the volume or concentration needed.

The equation to use is simply

$$\mathbf{M_1V_1 = M_2V_2}$$

M_1 and V_1 are the concentration and volume of the original (stock) solution to dilute; M_2 and V_2 are the desired concentration and volume of the final solution.

Solution Stoichiometry

For reactions that take place in solutions:

1. Calculate the moles of solute reacting by multiplying the concentration (molarity) by the volume of solution (Liters)
2. Determine the Limiting Reactant, if there is one
3. Follow the stoichiometric process.
4. Convert the resulting moles of solute back to molarity by dividing by the total volume, in liters, of solution used in the reaction.
5. In the case of reactions involving ions (such as in reactions between strong acids and bases), eliminate spectator ions from the net ionic equation. Spectator ions do not react in the equations.
6. If the concentration is not given but the molar mass and volume are, use density (grams/Liter) to find the amount of solute in grams, then convert it to moles.

References

1. Hill, Petrucci. General Chemistry: An integrated approach, second edition. New Jersey: Prentice Hall, 1999.
2. Petrucci, Harwood, Herring, Madura. General Chemistry: Principles and Modern Applications, ninth edition. New Jersey: Prentice Hall, 2007.

Outside Links

- en.Wikipedia.org/wiki/Solvent
- http://en.Wikipedia.org/wiki/Molar_concentration

Problems

1. A solution is prepared by dissolving 44.6 grams of acetone ($OC(CH_3)_2$) in water to produce 1.50 Liters of solution. What is the molarity of the resulting solution?
2. A certain laboratory procedure requires 0.025 M H_2SO_4. How many milliliters of 1.10 M H_2SO_4 should be diluted in water to prepare 0.500 L of 0.025 M H_2SO_4?

3. A sample of saturated $NaNO_3$ (aq) is 10.9 M at 25 degrees Celcius. How many grams of $NaNO_3$ are in 230 mL of this solution at the same temperature?
4. A beaker of 175 mL of 0.950 M NaCl is left uncovered for a period of time. If, by the end of the time period, the volume of solution in the beaker has decreased to 137 mL (the volume loss is due to water evaporation), what is the resulting concentration of the solution?
5. A student prepares a solution by dissolving 15.0 mL ethanol (C_2H_5OH) in water to make a 300.0 mL solution. Calculate the concentration (molarity) of ethanol in the solution. (density = 0.789 g/mL)

Solutions

$$44.6 gOC(CH_3)_2 \div 58.078 \frac{gOC(CH_3)_2}{mol} \div 1.50L = 0.512M$$

1.

$$M_2 = \frac{0.025MH_2SO_4 \times 0.500L}{1.10MH_2SO_4} \times \frac{1000mL}{1L} = 11.4\, mL\, H_2SO_4$$

2.

$$10.00 \frac{mol\, NaNO_3}{L} \times 230.0mL \times \frac{1L}{1000mL} \times 84.99 \frac{gNaNO_3}{mol} = 195.5\, g\, NaNO_3$$

3.

$$M_2 = \frac{0.950M\, NaCl \times 0.175L}{0.137L} = 1.21M\, NaCl$$

4.

$$15.0mL\, C_2H_5OH \times 0.789 \frac{g}{mL} \div 46.068 \frac{gC_2H_5OH}{mol} \div 300.0mL \times \frac{1L}{1000mL}$$
$$= 0.8856M\, C_2H_5OH$$

5.

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4.7: Selective Precipitation

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4.8: Stoichiometry of Precipitation Reactions

Precipitation reactions occur when cations and anions in aqueous solution combine to form an insoluble ionic solid called a **precipitate**. Whether or not such a reaction occurs can be determined by using the **solubility rules** for common ionic solids. Because not all aqueous reactions form precipitates, one must consult the solubility rules before determining the state of the products and writing a **net ionic equation.** The ability to predict these reactions allows scientists to determine which ions are present in a solution, and allows industries to form chemicals by extracting components from these reactions.

Properties of Precipitates

Precipitates are insoluble ionic solid products of a reaction, formed when certain cations and anions combine in an aqueous solution. The determining factors of the formation of a precipitate can vary. Some reactions depend on temperature, such as solutions used for buffers, whereas others are dependent only on solution concentration. The solids produced in precipitate reactions are crystalline solids, and can be suspended throughout the liquid or fall to the bottom of the solution. The remaining fluid is called supernatant liquid. The two components of the mixture (precipitate and supernate) can be separated by various methods, such as filtration, centrifuging, or decanting.

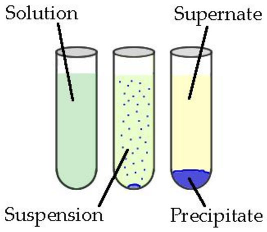

Figure 1: Above is a diagram of the formation of a precipitate in solution.

Precipitation and Double Replacement Reactions

The use of solubility rules require an understanding of the way that ions react. Most precipitation reactions are single replacement reactions or double replacement reactions. A double replacement reaction occurs when two ionic reactants dissociate and bond with the respective anion or cation from the other reactant. The ions replace each other based on their charges as either a cation or an anion. This can be thought of as "switching partners"; that is, the two reactants each "lose" their partner and form a bond with a different partner:

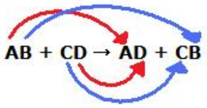

Figure 2: A double replacement reaction

A double replacement reaction is specifically classified as a **precipitation reaction** when the chemical equation in question occurs in aqueous solution and one of the of the products formed is insoluble. An example of a precipitation reaction is given below:

$$\mathrm{CdSO_4(aq) + K_2S(aq) \rightarrow CdS(s) + K_2SO_4(aq)}$$

Both reactants are aqueous and one product is solid. Because the reactants are ionic and aqueous, they dissociate and are therefore **soluble**. However, there are six solubility guidelines used to predict which molecules are insoluble in water. These molecules form a solid precipitate in solution.

Solubility Rules

Whether or not a reaction forms a precipitate is dictated by the solubility rules. These rules provide guidelines that tell which ions form solids and which remain in their ionic form in aqueous solution. The rules are to be followed from the top down, meaning that if something is insoluble (or soluble) due to rule 1, it has precedence over a higher-numbered rule.

1. Salts formed with group 1 cations and $\mathrm{NH_4^+}$ cations are **soluble**. There are some exceptions for certain $\mathrm{Li^+}$ salts.
2. Acetates $(\mathrm{C_2H_3O_2^-})$, nitrates $(\mathrm{NO_3^-})$, and perchlorates $(\mathrm{ClO_4^-})$ are **soluble.**
3. Bromides, chlorides, and iodides are **soluble.**

4. Sulfates (SO_4^{2-}) are **soluble** with the exception of sulfates formed with Ca^{2+}, Sr^{2+}, Pb^{2+}, and Ba^{2+}.
5. Salts containing silver, lead, and mercury (I) are **insoluble.**
6. Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), sulfides, oxides, and hydroxides (OH^-) are **insoluble**. Sulfides formed with group 2 cations and hydroxides formed with calcium, strontium, and barium are exceptions.

If the rules state that an ion is soluble, then it remains in its aqueous ion form. If an ion is insoluble based on the solubility rules, then it forms a solid with an ion from the other reactant. If all the ions in a reaction are shown to be soluble, then no precipitation reaction occurs.

Net Ionic Equations

To understand the definition of a **net ionic equation**, recall the equation for the double replacement reaction. Because this particular reaction is a precipitation reaction, states of matter can be assigned to each variable pair:

$$\mathbf{AB}(aq) + \mathbf{CD}(aq) \rightarrow \mathbf{AD}(aq) + \mathbf{CB}(s)$$

The first step to writing a net ionic equation is to separate the soluble (aqueous) reactants and products into their respective cations and anions. Precipitates do not dissociate in water, so the solid should not be separated. The resulting equation looks like that below:

$$\mathbf{A}^+(aq) + \mathbf{B}^-(aq) + \mathbf{C}^+(aq) + \mathbf{D}^-(aq) \rightarrow \mathbf{A}^+(aq) + \mathbf{D}^-(aq) + \mathbf{CB}(s)$$

In the equation above, $\mathbf{A}^+$and $\mathbf{D}^-$ ions are present on both sides of the equation. These are called **spectator ions** because they remain unchanged throughout the reaction. Since they go through the equation unchanged, they can be eliminated to show the **net ionic equation**:

$$\mathbf{C}^+\ (\mathbf{aq}) + \mathbf{B}^-\ (\mathbf{aq}) \rightarrow \mathbf{CB}\ (\mathbf{s})$$

The net ionic equation only shows the precipitation reaction. A net ionic equation must be balanced on both sides not only in terms of atoms of elements, but also in terms of electric charge. Precipitation reactions are usually represented solely by net ionic equations. If all products are aqueous, a net ionic equation cannot be written because all ions are canceled out as spectator ions. Therefore, **no precipitation reaction occurs.**

Applications and Examples

Precipitation reactions are useful in determining whether a certain element is present in a solution. If a precipitate is formed when a chemical reacts with lead, for example, the presence of lead in water sources could be tested by adding the chemical and monitoring for precipitate formation. In addition, precipitation reactions can be used to extract elements, such as magnesium from seawater. Precipitation reactions even occur in the human body between antibodies and antigens; however, the environment in which this occurs is still being studied.

✓ Example 1

Complete the double replacement reaction and then reduce it to the net ionic equation.

$$NaOH(aq) + MgCl_2(aq) \rightarrow$$

First, *predict the products* of this reaction using knowledge of double replacement reactions (remember the cations and anions "switch partners").

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

Second, *consult the solubility rules* to determine if the products are soluble. Group 1 cations (Na^+) and chlorides are soluble from rules 1 and 3 respectively, so $NaCl$ will be soluble in water. However, rule 6 states that hydroxides are insoluble, and thus $Mg(OH)_2$ will form a precipitate. The resulting equation is the following:

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

Third, *separate the reactants* into their ionic forms, as they would exist in an aqueous solution. Be sure to balance both the electrical charge and the number of atoms:

$$2\,Na^+(aq) + 2\,OH^-(aq) + Mg^{2+}(aq) + 2\,Cl^-(aq) \rightarrow Mg(OH)_2(s) + 2\,Na^+(aq) + 2\,Cl^-(aq)$$

Lastly, *eliminate the spectator ions* (the ions that occur on both sides of the equation unchanged). In this case, they are the sodium and chlorine ions. The final *net ionic equation* is:

$$\mathrm{Mg^{2+}(aq) + 2\,OH^{-}(aq) \rightarrow Mg(OH)_2(s)}$$

✓ Example 2

Complete the double replacement reaction and then reduce it to the net ionic equation.

$$\mathrm{CoCl_2(aq) + Na_2SO_4(aq) \rightarrow}$$

Solution

The predicted products of this reaction are $\mathrm{CoSO_4}$ and NaCl. From the solubility rules, $\mathrm{CoSO_4}$ is soluble because rule 4 states that sulfates ($\mathrm{SO_4^{2-}}$) are soluble. Similarly, we find that NaCl is soluble based on rules 1 and 3. After balancing, the resulting equation is as follows:

$$\mathrm{CoCl_2(aq) + Na_2SO_4(aq) \rightarrow CoSO_4(aq) + 2\,NaCl(aq)}$$

Separate the species into their ionic forms, as they would exist in an aqueous solution. Balance the charge and the atoms. Cancel out all spectator ions (those that appear as ions on both sides of the equation.):

$$\cancel{\mathrm{Co^{2-}(aq)}} + \cancel{\mathrm{2\,Cl^{-}(aq)}} + \cancel{\mathrm{2\,Na^{+}(aq)}} + \cancel{\mathrm{SO_4^{2-}(aq)}} \rightarrow \cancel{\mathrm{Co^{2-}(aq)}} + \cancel{\mathrm{SO_4^{2-}(aq)}} + \cancel{\mathrm{2\,Na^{+}(aq)}} + \cancel{\mathrm{2\,Cl^{-}(aq)}}$$

No precipitation reaction

This particular example is important because all of the reactants and the products are aqueous, meaning they cancel out of the net ionic equation. There is no solid precipitate formed; therefore, no precipitation reaction occurs.

? Exercise 4.8.1

Write the net ionic equation for this potentially double displacement reaction. Make sure to include the states of matter and balance the equations.

$$\mathrm{Fe(NO_3)_3(aq) + NaOH(aq) \rightarrow}$$

Answer

Regardless of physical state, the products of this reaction are $\mathrm{Fe(OH)_3}$ and $\mathrm{NaNO_3}$. The solubility rules predict that $\mathrm{NaNO_3}$ is soluble because all nitrates are soluble (rule 2). However, $\mathrm{Fe(OH)_3}$ is insoluble, because hydroxides are insoluble (rule 6) and Fe is not one of the cations which results in an exception. After dissociation, the ionic equation is as follows:

$$\mathrm{Fe^{3+}(aq) + NO_3^{-}(aq) + Na^{+}(aq) + 3\,OH^{-}(aq) \rightarrow Fe(OH)_3(s) + Na^{+}(aq) + NO_3^{-}(aq)}$$

Canceling out spectator ions

$$\mathrm{Fe^{3+}(aq)} + \cancel{\mathrm{NO_3^{-}(aq)}} + \cancel{\mathrm{Na^{+}(aq)}} + \mathrm{3\,OH^{-}(aq) \rightarrow Fe(OH)_3(s)} + \cancel{\mathrm{Na^{+}(aq)}} + \cancel{\mathrm{NO_3^{-}(aq)}}$$

leaves the net ionic equation:

$$\mathrm{Fe^{3+}(aq) + 3\,OH^{-}(aq) \rightarrow Fe(OH)_3(s)}$$

? Exercise 4.8.2

Write the net ionic equation for this potentially double displacement reaction. Make sure to include the states of matter and balance the equations.

$$\mathrm{Al_2(SO_4)_3(aq) + BaCl_2(aq) \rightarrow}$$

Answer

From the double replacement reaction, the products are $AlCl_3$ and $BaSO_4$. $AlCl_3$ is soluble because it contains a chloride (rule 3); however, $BaSO_4$ is insoluble: it contains a sulfate, but the Ba^{2+} ion causes it to be insoluble because it is one of the cations that causes an exception to rule 4. The ionic equation is (after balancing):

$$2\,Al^{3+}(aq) + 6\,Cl^{-}(aq) + 3\,Ba^{2+}(aq) + 3\,SO_4^{2-}(aq) \rightarrow 2\,Al^{3+}(aq) + 6\,Cl^{-}(aq) + 3\,BaSO_4(s)$$

Canceling out spectator ions leaves the following net ionic equation:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

? Exercise 4.8.3

Write the net ionic equation for this potentially double displacement reaction. Make sure to include the states of matter and balance the equations.

$$HI(aq) + Zn(NO_3)_2(aq) \rightarrow$$

Answer

From the double replacement reaction, the products HNO_3 and ZnI_2 are formed. Looking at the solubility rules, HNO_3 is soluble because it contains nitrate (rule 2), and ZnI_2 is soluble because iodides are soluble (rule 3). This means that both the products are aqueous (i.e. dissociate in water), and thus no precipitation reaction occurs.

? Exercise 4.8.4

Write the net ionic equation for this potentially double displacement reaction. Make sure to include the states of matter and balance the equations.

$$CaCl_2(aq) + Na_3PO_4(aq) \rightarrow$$

Answer

The products of this double replacement reaction are $Ca_3(PO_4)_2$ and $NaCl$. Rule 1 states that $NaCl$ is soluble, and according to solubility rule 6, $Ca_3(PO_4)_2$ is insoluble. The ionic equation is:

$$Ca^{2+}(aq) + Cl^{-}(aq) + Na^{+}(aq) + PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s) + Na^{+}(aq) + Cl^{-}(aq)$$

After canceling out spectator ions, the net ionic equation is given below:

$$Ca^{2+}(aq) + PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$$

? Exercise 4.8.5

Write the net ionic equation for this potentially double displacement reaction. Make sure to include the states of matter and balance the equations.

$$Pb(NO_3)_2(aq) + K_2SO_4(aq) \rightarrow$$

Answer

The first product of this reaction, $PbSO_4$, is insoluble according to rule 4 because it is a sulfate. The second product, KNO_3, is soluble because it contains nitrate (rule 2). Therefore, $PbSO_3(s)$ will precipitate.

$$Pb^{2+}(aq) + SO_4(aq) \longrightarrow Pb(SO_3)_2(s)$$

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1. Campbell, Dan, Linus Pauling, and Davis Pressman. "The Nature of the Forces Between Antigen and Antibody and of the Precipitation Reaction." *Physiological Reviews 23.3* (1943): 203-219. Online.

2. Harwood, William, F Herring, Jeffry Madura, and Ralph Petrucci. *General Chemistry*. 9th ed. Upper Saddle River: Pearson Pretence Hall, 2007. Print.
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4.9: Acid-Base Reactions

Chemical reactions are the processes by which chemicals interact to form new chemicals with different compositions. Simply stated, a chemical reaction is the process where reactants are transformed into products. How chemicals react is dictated by the chemical properties of the element or compound- the ways in which a compound or element undergoes changes in composition.

Describing Reactions Quantitatively

Chemical reactions are constantly occurring in the world around us; everything from the rusting of an iron fence to the metabolic pathways of a human cell are all examples of chemical reactions. Chemistry is an attempt to classify and better understand these reactions.

Figure 4.9.0: The rusting of a chain is an example of a chemical reaction

A chemical reaction is typically represented by a chemical equation, which represents the change from reactants to products. The left hand side of the equation represents the reactants, while the right hand side represents the products. A typical chemical reaction is written with stoichiometric coefficients, which show the relative amounts of products and reactants involved in the reaction. Each compound is followed by a parenthetical note of the compound's state of 2: (l) for liquid, (s) for solid, (g) for gas. The symbol (aq) is also commonly used in order to represent an aqueous solution, in which compounds are dissolved in water. A reaction might take the following form:

$$\mathrm{A(aq)+B(g)\rightarrow C(s)+D(l)}$$

In the above example, A and B, known as the reactants, reacted to form C and D, the products.

To write an accurate chemical equation, two things must occur:

1. Each product and reactant must be written using its chemical formula, e.g., H_2
2. The number of atoms of each element must be equal on both sides of the equation. Coefficients are used in front of the chemical formulas in order to help balance the number of atoms, e.g.,

$$\mathrm{2\,Mg+O_2\rightarrow 2\,MgO}$$

✓ Example 4.9.1: Balancing Reactions

Hydrogen and nitrogen react together in order to produce ammonia gas, write the chemical equation of this reaction.

Solution

Step 1: Write each product and reactant using its chemical formula.

$$\mathrm{H_2+N_2\rightarrow NH_3}$$

Step 2: Ensure the number of atoms of each element are equal on both sides of the equation.

$$\mathrm{3\,H_2+N_2\rightarrow 2\,NH_3}$$

In order to balance this equation, coefficients must be used. Since there are only 2 nitrogen atoms present on the left side of the equation, a coefficient of 2 must be added to NH_3.

Stoichiometry

The coefficient that used for balancing the equation is called the stoichiometric coefficient. The coefficients tell us the ratio of each element in a chemical equation. For example

$$\mathrm{2\,Mg+O_2\rightarrow 2\,MgO}$$

means

- 2 moles of MgO is produced for every 2 moles of Mg consumed.
- 2 moles of MgO is produced for every 1 mole of O_2 consumed.

When all of the reactants of a reaction are completely consumed, the reaction is in perfect stoichiometric proportions. Often times, however, a reaction is not in perfect stoichiometric proportions, leading to a situation in which the entirety of one reactant is consumed, but there is some of another reactant remaining. The reactant that is entirely consumed is called the limiting reactant, and it determines how much of the products are produced.

✓ Example 4.9.2: Limiting Reagent

4.00 g of hydrogen gas mixed with 20.0g of oxygen gas. How many grams of water are produced?

Solution

$$n(H_2) = \frac{4g}{(1.008 \times 2)g/mol} = 1.98mol$$

So theoretically, it requires 0.99 mol of O_2

$$\text{n(O}_2\text{)=n(H}_2\text{)*(1mol O}_2\text{/2mol H}_2\text{)=0.99 mol}$$

$$\text{m(O}_2\text{)=n(O}_2\text{)*(16g/mol *2) = 31.7 g O}_2$$

Because O_2 only has 20.0 g, less than the required mass. It is limiting.

Often, reactants do not react completely, resulting in a smaller amount of product formed than anticipated. The amount of product expected to be formed from the chemical equation is called the theoretical yield. The amount of product that is produced during a reaction is the actual yield. To determine the percent yield:

Percent yield =actual yield/theoretical yield X 100%

Chemical reactions do not only happen in the air, but also exist in solutions. In a solution, the solvent is the compound that is dissolved, and the solute is the compound that the solvent is dissolved in. The molarity of a solution is the number of moles of a solvent divided by the number of liters of solution.

$$Molarity = \frac{\text{amount of solute (mol)}}{\text{volume of solution (L)}}$$

$$M = \frac{n}{V}$$

✓ Example 4.9.3: Concentrations

100.0 g NaCl is dissolved in 50.00 ml water. What is the molarity of the solution?

Solution

a) Find the amount of solute in moles.

100.0g/(22.99 g/mol+35.45 g/mol) =1.711 moles

b) Convert mL to L.

50.00 mL=0.05000 L

c) Find the molarity

1.711 moles/0.05000L=34.22 mol/L

Physical Changes During Chemical Reactions

Physical change is the change in physical properties. Physical changes usually occur during chemical reactions, but does not change the nature of substances. The most common physical changes during reactions are the change of color, scent and evolution of gas. However, when physical changes occur, chemical reactions may not occur.

Types of Chemical Reactions

Precipitation, or double-replacement reaction

A reaction that occurs when aqueous solutions of anions (negatively charged ions) and cations (positively charged ions) combine to form a compound that is insoluble is known as precipitation. The insoluble solid is called the precipitate, and the remaining liquid is called the supernate. See Figure2.1

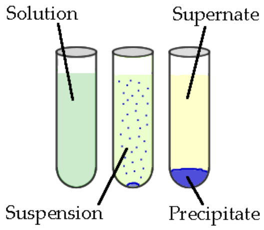


Figure 4.9.1

Real life example: The white precipitate formed by acid rain on a marble statue:

$$CaCO_3(aq) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

✓ Example 4.9.4: Precipitation

An example of a precipitation reaction is the reaction between silver nitrate and sodium iodide. This reaction is represented by the chemical equation :

$$\mathrm{AgNO_3\ (aq) + NaI\ (aq) \rightarrow AgI\ (s) + NaNO_3\ (aq)}$$

Since all of the above species are in aqueous solutions, they are written as ions, in the form:

$$\mathrm{Ag^+ + NO_3^-\ (aq) + Na^+\ (aq) + I^-\ (aq) \rightarrow AgI\ (s) + Na^+\ (aq) + NO_3^-\ (aq)}$$

Ions that appear on both sides of the equation are called spectator ions. These ions do not affect the reaction and are removed from both sides of the equation to reveal the net ionic equation, as written below:

$$\mathrm{Ag^+\ (aq) + I^-\ (aq) \rightarrow AgI\ (s)}$$

In this reaction, the solid, AgI, is known as the precipitate. The formation of a precipitate is one of the many indicators that a chemical reaction has taken place.

Acid-base, or neutralization reaction

A neutralization reaction occurs when an acid and base are mixed together. An acid is a substance that produces H^+ ions in solution, whereas a base is a substance that that produces OH^- ions in solution. A typical acid-base reaction will produce an ionic compound called a salt and water. A typical acid-base reaction is the reaction between hydrochloric acid and sodium hydroxide. This reaction is represented by the equation:

$$\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq)^+ H_2O(l)}$$

In this reaction, HCl is the acid, $NaOH$ is the base, and $NaCl$ is the salt. Real life example: Baking soda reacts with vinegar is a neutralization reaction.

***Video**: Vinegar and Baking Soda Reaction with Explanation*

Oxidation-Reduction (Redox) Reactions

A redox reaction occurs when the oxidation number of atoms involved in the reaction are changed. Oxidation is the process by which an atom's oxidation number is increased, and reduction is the process by which an atom's oxidation number is decreased. If the oxidation states of any elements in a reaction change, the reaction is an oxidation-reduction reaction. An atom that undergoes oxidation is called the reducing agent, and the atom that undergoes reduction is called the oxidizing agent. An example of a redox reaction is the reaction between hydrogen gas and fluorine gas:

$$H_2(g) + F_2(g) \rightarrow 2HF(g) \tag{4.9.1}$$

In this reaction, hydrogen is oxidized from an oxidation state of 0 to +1, and is thus the reducing agent. Fluorine is reduced from 0 to -1, and is thus the oxidizing agent.

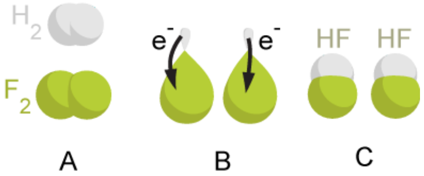


Figure 4.9.2: Figure: In redox reaction of Equation 4.9.1, a H_2 molecule donates electrons to F_2 resulting in two HF molecules

Real life example: The cut surface of an apple turns brownish after exposed to the air for a while.

Video: Why Do Apples Turn Brown?

Combustion Reaction

A combustion reaction is a type of redox reaction during which a fuel reacts with an oxidizing agent, resulting in the release of energy as heat. Such reactions are exothermic, meaning that energy is given off during the reaction. An endothermic reaction is one which absorbs heat. A typical combustion reaction has a hydrocarbon as the fuel source, and oxygen gas as the oxidizing agent. The products in such a reaction would be CO_2 and H_2O.

$$C_xH_yO_z + O_2 \rightarrow CO_2 + H_2O \quad \text{(unbalanced)}$$

Such a reaction would be the combustion of glucose in the following equation

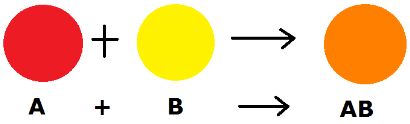
$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$$

Real life example: explosion; burning.

***Video**: Combustion reactions come in many varieties. Here's a collection of various examples, all of which require oxygen, activation energy, and of course, fuel*

Synthesis Reactions

A synthesis reaction occurs when one or more compounds combines to form a complex compound. The simplest equation of synthesis reaction is illustrated below.



An example of such a reaction is the reaction of silver with oxygen gas to form silver oxide:

$$2Ag(s) + O_2(g) \rightarrow 2AgO(s)$$

Real life example: Hydrogen gas is burned in air (reacts with oxygen) to form water:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Decomposition Reactions

A decomposition reaction is the opposite of a synthesis reaction. During a decomposition reaction, a more complex compound breaks down into multiple simpler compounds. A classic example of this type of reaction is the decomposition of hydrogen peroxide into oxygen and hydrogen gas:

$$H_2O_2(l) \rightarrow H_2(g) + O_2(g)$$

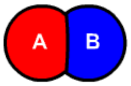
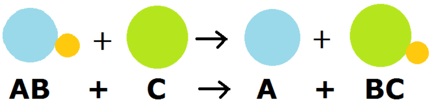


Figure 4.9.3: The molecule AB is decomposing into A and B

Single Replacement Reactions

A type of oxidation-reduction reaction in which an element in a compound is replaced by another element.



An example of such a reaction is:

$$Cu(s) + AgNO_3(aq) \rightarrow Ag(s) + Cu(NO_3)_2(aq)$$

This is also a redox reaction.

Problems

1) $C_3H_6O_3 + O_2 \rightarrow CO_2$ (g) +H_2O (g)

a) What type of reaction is this?
b) Is is exothermic or endothermic? Explain.

2) Given the oxidation-reduction reaction :

Fe (s) + $CuSO_4$ (aq)→ $FeSO_4$ (aq)+ Cu (s)

a) Which element is the oxidizing agent and which is the reducing agent?
b) How do the oxidation states of these species change?

3) Given the equation:

$AgNO_3$ (aq) + KBr (aq) → AgBr (s) +KNO_3 (aq)

a) What is the net ionic reaction?
b) Which species are spectator ions?

4) 2 HNO_3 (aq) + $Sr(OH)_2$ (aq) → $Sr(NO_3)_2$ (aq) +2 H_2O (l)

a) In this reaction, which species is the acid and which is the base?
b) Which species is the salt?
c) If 2 moles of HNO3 and 1 mole of Sr(OH)2 are used, resulting in 0.85 moles of Sr(NO₃)2 , what is the percent yield (with respect to moles) of Sr(NO3)2 ?

5) Identify the type of the following reactions:

a) $Al(OH)_3$ (aq) + HCl (aq) → $AlCl_3$ (aq) + H_2O (l)
b) $MnO_2 + 4H^+ + 2Cl^- \rightarrow Mn^{2+} + 2H_2O$ (l) + Cl_2 (g)
c) P_4 (s) + Cl_2 (g) → PCl_3 (l)
d) Ca (s) + $2H_2O$ (l) → $Ca(OH)_2$ (aq) + H_2 (g)
e) $AgNO_3$ (aq) + NaCl (aq) → AgCl (s) + $NaNO_3$ (aq)

Solutions

1a) It is a combustion reaction

1b) It is exothermic, because combustion reactions give off heat

2a) Cu is the oxidizing agent and Fe is the reducing agent

2b) Fe changes from 0 to +2, and Cu changes from +2 to 0.

3a) Ag^+ (aq) + Br^- (aq) → AgBr (s)

3b) The spectator ions are K^+ and NO_3^-

4a) HNO_3 is the acid and $Sr(OH)_2$ is the base

4b) $Sr(NO_3)_2$ is the salt

4c) According to the stoichiometric coefficients, the theoretical yield of $Sr(NO_3)_2$ is one mole. The actual yield was 0.85 moles. Therefore the percent yield is:

(0.85/1.0) * 100% = 85%

5a) Acid-base

5b) Oxidation-reduction

5c) Synthesis

5d) Single-replacement reaction

5e) Double replacement reaction

References

1. Petrucci, Ralph H., William S. Harwood, F. G. Herring, and Jeffry D. Madura. General Chemistry. 9th ed. Upper Saddle River: Prentice Education Inc, 2007, Print.

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4.10: Oxidation-Reduction Reactions

An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

Rules for Assigning Oxidation States

The oxidation state (OS) of an element corresponds to the number of electrons, e$^-$, that an atom loses, gains, or appears to use when joining with other atoms in compounds. In determining the oxidation state of an atom, there are seven guidelines to follow:

1. The oxidation state of an individual atom is 0.
2. The total oxidation state of all atoms in: a *neutral species* is 0 and in an *ion* is equal to the ion charge.
3. Group 1 metals have an oxidation state of +1 and Group 2 an oxidation state of +2
4. The oxidation state of fluorine is -1 in compounds
5. Hydrogen generally has an oxidation state of +1 in compounds
6. Oxygen generally has an oxidation state of -2 in compounds
7. In binary metal compounds, Group 17 elements have an oxidation state of -1, Group 16 elements of -2, and Group 15 elements of -3.

> *The **sum** of the oxidation states is equal to zero for neutral compounds and equal to the **charge** for polyatomic ion species.*

Example 4.10.1: Assigning Oxidation States

Determine the Oxidation States of each element in the following reactions:

a. $\mathrm{Fe(s) + O_2(g) \longrightarrow Fe_2O_3(g)}$
b. $\mathrm{Fe^{2+}(aq)}$
c. $\mathrm{Ag(s) + H_2S \longrightarrow Ag_2S(g) + H_2(g)}$

Solutions

A. Fe and O_2 are free elements; therefore, they each have an oxidation state of 0 according to Rule #1. The product has a total oxidation state equal to 0, and following Rule #6, O has an oxidation state of -2, which means Fe has an oxidation state of +3.
B. The oxidation state of Fe ions just corresponds to its charge since it is a single element species; therefore, the oxidation state is +2.
C. Ag has an oxidation state of 0, H has an oxidation state of +1 according to Rule #5, H_2 has an oxidation state of 0, S has an oxidation state of -2 according to Rule #7, and hence Ag in Ag_2S has an oxidation state of +1.

Example 4.10.2: Assigning Oxidation States

Determine the oxidation states of the phosphorus atom bold element in each of the following species:

a. $\mathrm{Na_3PO_3}$
b. $\mathrm{H_2PO_4^-}$

Solutions

a. The oxidation numbers of Na and O are +1 and -2. Because sodium phosphite is neutral species, the sum of the oxidation numbers must be zero. Letting x be the oxidation number of phosphorus, 0= 3(+1) + x + 3(-2). x=oxidation number of P= +3.
b. Hydrogen and oxygen have oxidation numbers of +1 and -2. The ion has a charge of -1, so the sum of the oxidation numbers must be -1. Letting y be the oxidation number of phosphorus, -1= y + 2(+1) +4(-2), y= oxidation number of P= +5.

✓ Example 4.10.3: Identifying Reduced and Oxidized Elements

Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the oxidation state of each):

a. $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$
b. $2Al + 3Cu^{2+} \longrightarrow 2Al^{3+} + 3Cu$
c. $CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$

Solutions

a. Zn is oxidized (Oxidation number: 0 → +2); H^+ is reduced (Oxidation number: +1 → 0)
b. Al is oxidized (Oxidation number: 0 → +3); Cu^{2+} is reduced (+2 → 0)
c. This is not a redox reaction because each element has the same oxidation number in both reactants and products: O= -2, H= +1, C= +4.

An atom is oxidized if its oxidation number increases, the reducing agent, and an atom is reduced if its oxidation number decreases, the oxidizing agent. The atom that is oxidized is the reducing agent, and the atom that is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound).

Oxidation-Reduction Reactions

Redox reactions are comprised of two parts, a reduced half and an oxidized half, that *always* occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases. Simple ways to remember this include the mnemonic devices **OIL RIG,** meaning "*oxidation is loss*" and "*reduction is gain*." There is no net change in the number of electrons in a redox reaction. Those given off in the oxidation half reaction are taken up by another species in the reduction half reaction.

The two species that exchange electrons in a redox reaction are given special names:

1. The ion or molecule that accepts electrons is called the **oxidizing agent -** by accepting electrons it oxidizes other species.
2. The ion or molecule that donates electrons is called the **reducing agent -** by giving electrons it reduces the other species.

Hence, what is oxidized is the reducing agent and what is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound, as in disproportionation reactions discussed below).

A good example of a redox reaction is the thermite reaction, in which iron atoms in ferric oxide lose (or give up) O atoms to Al atoms, producing Al_2O_3.

$$Fe_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Fe(l)$$

✓ Example 4.10.4: Identifying Oxidizing and Reducing Agents

Determine what is the oxidizing and reducing agents in the following reaction.

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

Solution

The oxidation state of H changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2. Hence, Zn is oxidized and acts as the *reducing agent*. H^+ ion is reduced and acts as the *oxidizing agent*.

Combination Reactions

Combination reactions are among the simplest redox reactions and, as the name suggests, involves "combining" elements to form a chemical compound. As usual, oxidation and reduction occur together. The general equation for a combination reaction is given below:

$$A + B \longrightarrow AB$$

✓ Example 4.10.5: Combination Reaction

Consider the combination reaction of hydrogen and oxygen

$$H_2 + O_2 \longrightarrow H_2O$$

Solution

$$0 + 0 \rightarrow \mathbf{(2)(+1) + (-2) = 0}$$

In this reaction both H_2 and O_2 are free elements; following Rule #1, their oxidation states are 0. The product is H_2O, which has a total oxidation state of 0. According to Rule #6, the oxidation state of oxygen is usually -2. Therefore, the oxidation state of H in H_2O must be +1.

Decomposition Reactions

A **decomposition** reaction is the reverse of a combination reaction, the breakdown of a chemical compound into individual elements:

$$AB \longrightarrow A + B$$

✓ Example 4.10.6: Decomposition Reaction

Consider the following reaction:

$$H_2O \longrightarrow H_2 + O_2$$

This follows the definition of the decomposition reaction, where water is "decomposed" into hydrogen and oxygen.

$$(2)(+1) + (-2) = 0 \rightarrow 0 + 0$$

As in the previous example the H_2O has a total oxidation state of 0; thus, according to Rule #6 the oxidation state of oxygen is usually -2, so the oxidation state of hydrogen in H_2O must be +1.

Note that the autoionization reaction of water is **not** a redox nor decomposition reaction since the oxidation states do not change for any element:

$$H_2O \longrightarrow H^+ + OH^-$$

Single Replacement Reactions

A **single replacement** reaction involves the "replacing" of an element in the reactants with another element in the products:

$$A + BC \longrightarrow AB + C$$

✓ Example 4.10.7: Single Replacement Reaction

Equation:

$$Cl_2 + Na\underline{Br} \rightarrow Na\underline{Cl} + Br_2$$

Calculation:

$$(0) + ((+1) + (-1) = 0) \text{ -> } ((+1) + (-1) = 0) + 0$$

In this equation, Br is replaced with Cl, and the Cl atoms in Cl_2 are reduced, while the Br ion in NaBr is oxidized.

Double Replacement Reactions

A double replacement reaction is similar to a single replacement reaction, but involves "replacing" two elements in the reactants, with two in the products:

$$AB + CD \longrightarrow AD + CB$$

An example of a double replacement reaction is the reaction of magnesium sulfate with sodium oxalate

$$\mathrm{MgSO_4(aq) + Na_2C_2O_4(aq) \longrightarrow MgC_2O_4(s) + Na_2SO_4(aq)}$$

Combustion Reactions

Combustion is the formal terms for "burning" and typically involves a substance reacts with oxygen to transfer energy to the surroundings as light and heat. Hence, combustion reactions are almost always exothermic. For example, internal combustion engines rely on the combustion of organic hydrocarbons $\mathrm{C_xH_y}$ to generate $\mathrm{CO_2}$ and $\mathrm{H_2O}$:

$$\mathrm{C_xH_y + O_2 \longrightarrow CO_2 + H_2O}$$

Although combustion reactions typically involve redox reactions with a chemical being oxidized by oxygen, many chemicals can "burn" in other environments. For example, both titanium and magnesium metals can burn in nitrogen as well:

$$\mathrm{2\,Ti(s) + N_2(g) \longrightarrow 2\,TiN(s)}$$

$$\mathrm{3\,Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)}$$

Moreover, chemicals can be oxidized by other chemicals than oxygen, such as $\mathrm{Cl_2}$ or $\mathrm{F_2}$; these processes are also considered combustion reactions.

✓ Example 4.10.8: Identifying Combustion Reactions

Which of the following are combustion reactions?

a. $\mathrm{2\,H_2O \rightarrow 2\,H_2 + O_2}$
b. $\mathrm{4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3}$
c. $\mathrm{2\,AgNO_3 + H_2S \rightarrow Ag_2S + 2\,NHO_3}$
d. $\mathrm{2\,Al + N_2 \rightarrow 2\,AlN_4}$

Solution

Both reaction b and reaction d are combustion reactions, although with different oxidizing agents. Reaction b is the conventional combustion reaction using $\mathrm{O_2}$ and reaction uses $\mathrm{N_2}$ instead.

Disproportionation Reactions

In disproportionation reactions, a single substance can be both oxidized and reduced. These are known as disproportionation reactions, with the following general equation:

$$\mathrm{2\,A \longrightarrow A^{+n} + A^{-n}}$$

where n is the number of electrons transferred. Disproportionation reactions do not need begin with neutral molecules, and can involve more than two species with differing oxidation states (but rarely).

✓ Example 4.10.9: Disproportionation Reaction

Disproportionation reactions have some practical significance in everyday life, including the reaction of hydrogen peroxide, $\mathrm{H_2O_2}$ poured over a cut. This a decomposition reaction of hydrogen peroxide, which produces oxygen and water. Oxygen is present in all parts of the chemical equation and as a result it is both oxidized and reduced. The reaction is as follows:

$$\mathrm{2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)}$$

Dicussion

On the reactant side, H has an oxidation state of +1 and O has an oxidation state of -1, which changes to -2 for the product $\mathrm{H_2O}$ (oxygen is reduced), and 0 in the product $\mathrm{O_2}$ (oxygen is oxidized).

? Exercise 4.10.9

Which element undergoes a bifurcation of oxidation states in this disproportionation reaction:

$$\mathrm{HNO_2 \longrightarrow HNO_3 + NO + H_2O}$$

Answer

The N atom undergoes disproportionation. You can confirm that by identifying the oxidation states of each atom in each species.

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1. Petrucci, et al. *General Chemistry: Principles & Modern Applications*. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.
2. Sadava, et al. *Life: The Science of Biology*. 8th ed. New York, NY. W.H. Freeman and Company, 2007

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4.11: Balancing Redox Equations

Oxidation-Reduction Reactions, or redox reactions, are reactions in which one reactant is oxidized and one reactant is reduced simultaneously. This module demonstrates how to balance various redox equations.

Identifying Redox Reactions

The first step in balancing any redox reaction is determining whether or not it is even an oxidation-reduction reaction. This requires that one and typically more species changing oxidation states during the reaction. To maintain charge neutrality in the sample, the redox reaction will entail both a reduction component and an oxidation components. These are often separated into independent two hypothetical **half-reactions** to aid in understanding the reaction. This requires identifying which element is oxidized and which element is reduced. For example, consider this reaction:

$$\mathrm{Cu(s) + 2\,Ag^{+}(aq) \rightarrow Cu^{2\,+}(aq) + 2\,Ag(s)}$$

The first step in determining whether the reaction is a redox reaction is to split the equation into two hypothetical *half-reactions*. Let's start with the half-reaction involving the copper atoms:

$$\mathrm{Cu(s) \rightarrow Cu^{2\,+}(aq)}$$

The oxidation state of copper on the left side is 0 because it is an element on its own. The oxidation state of copper on the right hand side of the equation is +2. The copper in this half-reaction is oxidized as the oxidation states increases from 0 in Cu to +2 in $\mathrm{Cu^{2\,+}}$. Now consider the silver atoms

$$\mathrm{2\,Ag^{+}(aq) \rightarrow 2\,Ag(s)}$$

In this half-reaction, the oxidation state of silver on the left side is a +1. The oxidation state of silver on the right is 0 because it is an pure element. Because the oxidation state of silver decreases from +1 to 0, this is the reduction half-reaction.

Consequently, this reaction is a redox reaction as both reduction and oxidation half-reactions occur (via the transfer of electrons, that are not explicitly shown in equations 2). Once confirmed, it often necessary to balance the reaction (the reaction in equation 1 is balanced already though), which can be accomplished in two ways because the reaction could take place in neutral, acidic or basic conditions.

Balancing Redox Reactions

Balancing redox reactions is slightly more complex than balancing standard reactions, but still follows a relatively simple set of rules. One major difference is the necessity to know the half-reactions of the involved reactants; a half-reaction table is very useful for this. Half-reactions are often useful in that two half reactions can be added to get a total net equation. Although the half-reactions must be known to complete a redox reaction, it is often possible to figure them out without having to use a half-reaction table. This is demonstrated in the acidic and basic solution examples. Besides the general rules for neutral conditions, additional rules must be applied for aqueous reactions in acidic or basic conditions.

One method used to balance redox reactions is called the **Half-Equation Method**. In this method, the equation is separated into two half-equations; one for oxidation and one for reduction.

Half-Equation Method to Balance redox Reactions in **Acidic** Aqueous Solutions

Each reaction is balanced by adjusting coefficients and adding $\mathrm{H_2O}$, $\mathrm{H^+}$, and $\mathrm{e^-}$ in this order:

1. Balance elements in the equation other than O and H.
2. Balance the oxygen atoms by adding the appropriate number of water ($\mathrm{H_2O}$) molecules to the opposite side of the equation.
3. Balance the hydrogen atoms (including those added in step 2 to balance the oxygen atom) by adding $\mathrm{H^+}$ ions to the opposite side of the equation.
4. Add up the charges on each side. Make them equal by adding enough electrons ($\mathrm{e^-}$) to the more positive side. (Rule of thumb: $\mathrm{e^-}$ and $\mathrm{H^+}$ are almost always on the same side.)
5. The $\mathrm{e^-}$ on each side must be made equal; if they are not equal, they must be multiplied by appropriate integers (the lowest common multiple) to be made the same.
6. The half-equations are added together, canceling out the electrons to form one balanced equation. Common terms should also be canceled out.

The equation can now be checked to make sure that it is balanced.

Half-Equation Method to Balance redox Reactions in **Basic** Aqueous Solutions

If the reaction is being balanced in a basic solution, the above steps are modified with the the addition of one step between #3 and #4:

3b Add the appropriate number of $\mathrm{OH^-}$ to neutralize all $\mathrm{H^+}$ and to convert into water molecules.

The equation can now be checked to make sure that it is balanced.

Neutral Conditions

The first step to balance any redox reaction is to separate the reaction into half-reactions. The substance being reduced will have electrons as reactants, and the oxidized substance will have electrons as products. (Usually all reactions are written as reduction reactions in half-reaction tables. To switch to oxidation, the whole equation is reversed and the voltage is multiplied by -1.) Sometimes it is necessary to determine which half-reaction will be oxidized and which will be reduced. In this case, whichever half-reaction has a higher reduction potential will by reduced and the other oxidized.

Example 4.11.1: Balancing in a Neutral Solution

Balance the following reaction

$$\mathrm{Cu^+(aq) + Fe(s) \rightarrow Fe^{3+}(aq) + Cu(s)}$$

Solution

Step 1: Separate the half-reactions. By searching for the reduction potential, one can find two separate reactions:

$$\mathrm{Cu^+(aq) + e^- \rightarrow Cu(s)}$$

and

$$\mathrm{Fe^{3+}(aq) + 3\,e^- \rightarrow Fe(s)}$$

The copper reaction has a higher potential and thus is being reduced. Iron is being oxidized so the half-reaction should be flipped. This yields:

$$\mathrm{Cu^+(aq) + e^- \rightarrow Cu(s)}$$

and

$$\mathrm{Fe(s) \rightarrow Fe^{3+}(aq) + 3\,e^-}$$

Step 2: Balance the electrons in the equations. In this case, the electrons are simply balanced by multiplying the entire $Cu^+(aq) + e^- \rightarrow Cu(s)$ half-reaction by 3 and leaving the other half reaction as it is. This gives:

$$\mathrm{3\,Cu^+(aq) + 3\,e^- \rightarrow 3\,Cu(s)}$$

and

$$\mathrm{Fe(s) \rightarrow Fe^{3+}(aq) + 3\,e^-}$$

Step 3: Adding the equations give:

$$\mathrm{3\,Cu^+(aq) + 3\,e^- + Fe(s) \rightarrow 3\,Cu(s) + Fe^{3+}(aq) + 3\,e^-}$$

The electrons cancel out and the balanced equation is left.

$$\mathrm{3\,Cu^+(aq) + Fe(s) \rightarrow 3\,Cu(s) + Fe^{3+}(aq)}$$

Acidic Conditions

Acidic conditions usually implies a solution with an excess of $\mathrm{H^+}$ concentration, hence making the solution acidic. The balancing starts by separating the reaction into half-reactions. However, instead of immediately balancing the electrons, balance all the elements in the half-reactions that are not hydrogen and oxygen. Then, add $\mathrm{H_2O}$ molecules to balance any oxygen atoms. Next, balance the hydrogen atoms by adding protons ($\mathrm{H^+}$). Now, balance the *charge* by adding electrons and scale the electrons (multiply by the lowest common multiple) so that they will cancel out when added together. Finally, add the two half-reactions and cancel out common terms.

✓ Example 4.11.2: Balancing in a Acid Solution

Balance the following redox reaction in acidic conditions.

$$\mathrm{Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3^-(aq)}$$

Solution

Step 1: Separate the half-reactions. The table provided does not have acidic or basic half-reactions, so just write out what is known.

$$\mathrm{Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)}$$

$$\mathrm{HNO_2(aq) \rightarrow NO_3^-(aq)}$$

Step 2: Balance elements other than O and H. In this example, only chromium needs to be balanced. This gives:

$$\mathrm{Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq)}$$

and

$$\mathrm{HNO_2(aq) \rightarrow NO_3^-(aq)}$$

Step 3: Add H_2O to balance oxygen. The chromium reaction needs to be balanced by adding 7 $\mathrm{H_2O}$ molecules. The other reaction also needs to be balanced by adding one water molecule. This yields:

$$\mathrm{Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)}$$

and

$$\mathrm{HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq)}$$

Step 4: Balance hydrogen by adding protons (H^+). 14 protons need to be added to the left side of the chromium reaction to balance the 14 (2 per water molecule * 7 water molecules) hydrogens. 3 protons need to be added to the right side of the other reaction.

$$\mathrm{14\,H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)}$$

and

$$\mathrm{HNO_2(aq) + H_2O(l) \rightarrow 3\,H^+(aq) + NO_3^-(aq)}$$

Step 5: Balance the charge of each equation with electrons. The chromium reaction has (14+) + (2-) = 12+ on the left side and (2 * 3+) = 6+ on the right side. To balance, add 6 electrons (each with a charge of -1) to the left side:

$$\mathrm{6\,e^- + 14\,H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)}$$

For the other reaction, there is no charge on the left and a (3+) + (-1) = 2+ charge on the right. So add 2 electrons to the right side:

$$\mathrm{HNO_2(aq) + H_2O(l) \rightarrow 3\,H^+(aq) + NO_3^-(aq) + 2\,e^-}$$

Step 6: Scale the reactions so that the electrons are equal. The chromium reaction has $6e^-$ and the other reaction has $2e^-$, so it should be multiplied by 3. This gives:

$$\mathrm{6\,e^- + 14\,H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)}\cdot$$

and

$$\begin{aligned} 3 \times \left[\mathrm{HNO_2(aq) + H_2O(l)}\right. &\left.\mathrm{\rightarrow 3\,H^+(aq) + NO_3^-(aq) + 2\,e^-}\right] \\ \mathrm{3\,HNO_2(aq) + 3\,H_2O(l)} &\mathrm{\rightarrow 9\,H^+(aq) + 3\,NO_3^-(aq) + 6\,e^-} \end{aligned}$$

Step 7: Add the reactions and cancel out common terms.

$$\begin{array}{c} \mathrm{3\,HNO_2(aq) + 3\,H_2O(l) \rightarrow 9\,H^+(aq) + 3\,NO_3^-(aq) + 6\,e^-} \\ \mathrm{6\,e^- + 14\,H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)} \\ \hline \mathrm{3\,HNO_2(aq) + 3\,\cancel{H_2O(l)} + 6\cancel{e^-} + 14\,H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 9\,H^+(aq) + 3\,NO_3^-(aq) + 6\cancel{e^-} + 2\,Cr^{3+}(aq) + \overset{4}{\cancel{7}}\,H_2O(l)} \end{array}$$

The electrons cancel out as well as 3 water molecules and 9 protons. This leaves the balanced net reaction of:

$$3\,HNO_2(aq) + 5\,H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 3\,NO_3^-(aq) + 2\,Cr^{3+}(aq) + 4\,H_2O(l)$$

Basic Conditions

Bases dissolve into OH^- ions in solution; hence, balancing redox reactions in basic conditions requires OH^-. Follow the same steps as for acidic conditions. The only difference is adding hydroxide ions to each side of the net reaction to balance any H^+. OH^- and H^+ ions on the same side of a reaction should be added together to form water. Again, any common terms can be canceled out.

✓ Example 4.11.1: Balancing in Basic Solution

Balance the following redox reaction in basic conditions.

$$Ag(s) + Zn^{2+}(aq) \rightarrow Ag_2O(aq) + Zn(s)$$

Solution

Go through all the same steps as if it was in acidic conditions.

Step 1: Separate the half-reactions.

$$Ag(s) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 2: Balance elements other than O and H.

$$2\,Ag(s) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 3: Add H_2O to balance oxygen.

$$H_2O(l) + 2\,Ag(s) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 4: Balance hydrogen with protons.

$$H_2O(l) + 2\,Ag(s) \rightarrow Ag_2O(aq) + 2\,H^+(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 5: Balance the charge with e^-.

$$H_2O(l) + 2\,Ag(s) \rightarrow Ag_2O(aq) + 2\,H^+(aq) + 2\,e^-$$

$$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$$

Step 6: Scale the reactions so that they have an equal amount of electrons. In this case, it is already done.

Step 7: Add the reactions and cancel the electrons.

$$H_2O(l) + 2\,Ag(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2\,H^+(aq).$$

Step 8: Add OH^- to balance H^+. There are 2 net protons in this equation, so add 2 OH^- ions to each side.

$$H_2O(l) + 2\,Ag(s) + Zn^{2+}(aq) + 2\,OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2\,H^+(aq) + 2\,OH^-(aq).$$

Step 9: Combine OH^- ions and H^+ ions that are present on the same side to form water.

$$\cancel{H_2O(l)} + 2\,Ag(s) + Zn^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Zn(s) + Ag_2O(aq) + \cancel{2}\,H_2O(l)$$

Step 10: Cancel common terms.

$$2\,Ag(s) + Zn^{2+}(aq) + 2\,OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + H_2O(l)$$

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4.12: Redox Titrations

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CHAPTER OVERVIEW

5: Gases

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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5.1: Early Efforts to Understand Gases

Learning Objectives

- To describe the characteristics of a gas.

The three common phases (or states) of matter are gases, liquids, and solids. Gases have the lowest density of the three, are highly compressible, and completely fill any container in which they are placed. Gases behave this way because their intermolecular forces are relatively weak, so their molecules are constantly moving independently of the other molecules present. Solids, in contrast, are relatively dense, rigid, and incompressible because their intermolecular forces are so strong that the molecules are essentially locked in place. Liquids are relatively dense and incompressible, like solids, but they flow readily to adapt to the shape of their containers, like gases. We can therefore conclude that the sum of the intermolecular forces in liquids are between those of gases and solids. Figure 5.1.1 compares the three states of matter and illustrates the differences at the molecular level.

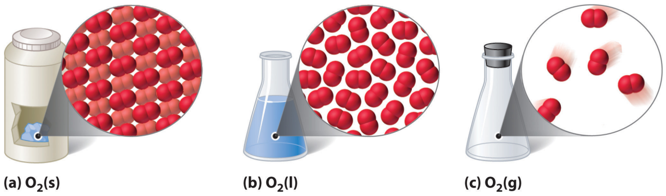

Figure 5.1.1: A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States: (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

The state of a given substance depends strongly on conditions. For example, H_2O is commonly found in all three states: solid ice, liquid water, and water vapor (its gaseous form). Under most conditions, we encounter water as the liquid that is essential for life; we drink it, cook with it, and bathe in it. When the temperature is cold enough to transform the liquid to ice, we can ski or skate on it, pack it into a snowball or snow cone, and even build dwellings with it. Water vapor (the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions so nitrogen (N_2) and oxygen (O_2) are referred to as gases, but gaseous water in the atmosphere is called water vapor) is a component of the air we breathe, and it is produced whenever we heat water for cooking food or making coffee or tea. Water vapor at temperatures greater than 100°C is called steam. Steam is used to drive large machinery, including turbines that generate electricity. The properties of the three states of water are summarized in Table 5.1.1.

Table 5.1.1: Properties of Water at 1.0 atm

Temperature	State	Density (g/cm^3)
≤0°C	solid (ice)	0.9167 (at 0.0°C)
0°C–100°C	liquid (water)	0.9997 (at 4.0°C)
≥100°C	vapor (steam)	0.005476 (at 127°C)

The geometric structure and the physical and chemical properties of atoms, ions, and molecules usually do *not* depend on their physical state; the individual water molecules in ice, liquid water, and steam, for example, are all identical. In contrast, the macroscopic properties of a substance depend strongly on its physical state, which is determined by intermolecular forces and conditions such as temperature and pressure.

Figure 5.1.2 shows the locations in the periodic table of those elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble gases (group 18) are monatomic gases, whereas the other gaseous elements are diatomic molecules (**H_2, N_2, O_2, F_2, and Cl_2**). Oxygen can also form a second allotrope, the highly reactive triatomic molecule ozone (**O_3**), which is also a gas. In contrast, bromine (as Br_2) and mercury (Hg) are liquids under normal conditions (25°C and 1.0 atm, commonly referred to as "room temperature and pressure"). Gallium (Ga), which melts at only 29.76°C, can be converted to a liquid simply by holding a container of it in your hand or keeping it in a non-air-conditioned room on a hot summer day. The rest of the elements are all solids under normal conditions.

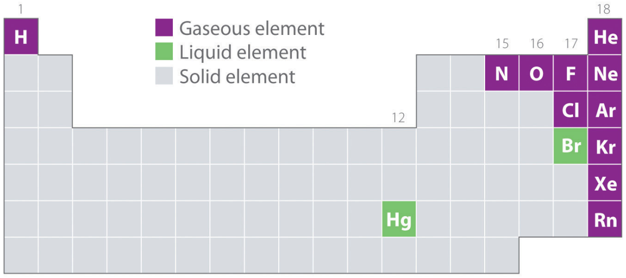

Figure 5.1.2: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

All of the gaseous elements (other than the monatomic noble gases) are molecules. Within the same group (1, 15, 16 and 17), the lightest elements are gases. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms.

Defining Gas Pressure: https://youtu.be/_CRn3cFs2CI

Summary

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2, O_2).

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5.2: The Gas Laws of Boyle, Charles, and Avogadro

Learning Objectives

- To understand the relationships among pressure, temperature, volume, and the amount of a gas.

Early scientists explored the relationships among the pressure of a gas (*P*) and its temperature (*T*), volume (*V*), and amount (*n*) by holding two of the four variables constant (amount and temperature, for example), varying a third (such as pressure), and measuring the effect of the change on the fourth (in this case, volume). The history of their discoveries provides several excellent examples of the scientific method.

The Relationship between Pressure and Volume: Boyle's Law

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

The Irish chemist Robert Boyle (1627–1691) carried out some of the earliest experiments that determined the quantitative relationship between the pressure and the volume of a gas. Boyle used a J-shaped tube partially filled with mercury, as shown in Figure $5.2.1$. In these experiments, a small amount of a gas or air is trapped above the mercury column, and its volume is measured at atmospheric pressure and constant temperature. More mercury is then poured into the open arm to increase the pressure on the gas sample. The pressure on the gas is atmospheric pressure plus the difference in the heights of the mercury columns, and the resulting volume is measured. This process is repeated until either there is no more room in the open arm or the volume of the gas is too small to be measured accurately. Data such as those from one of Boyle's own experiments may be plotted in several ways (Figure $5.2.2$). A simple plot of V versus P gives a curve called a hyperbola and reveals an inverse relationship between pressure and volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the two quantities is described as follows:

$$PV = \text{constant} \tag{5.2.1}$$

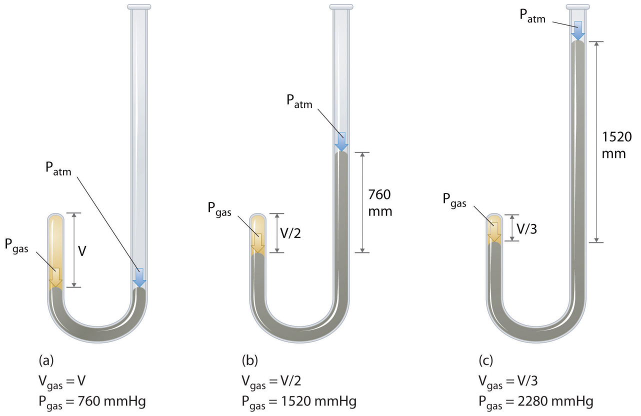


Figure 5.2.1: Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is *V*. (b) If enough mercury is added to the right side to give a difference in height of 760 mmHg between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is *V*/2. (c) If an additional 760 mmHg is added to the column on the right, the total pressure on the gas increases to 2280 mmHg, and the volume of the gas decreases to *V*/3.

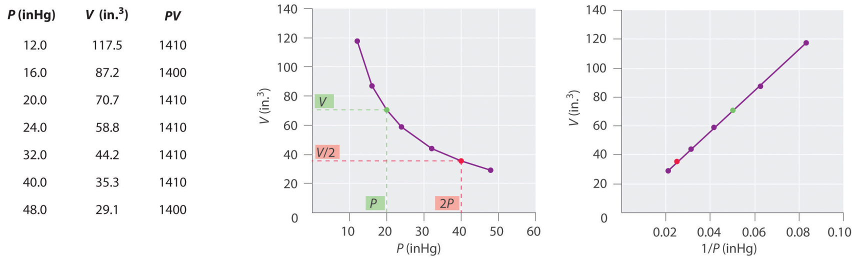
Dividing both sides by P gives an equation illustrating the inverse relationship between P and V:

$$V = \frac{\text{const.}}{P} = \text{const.}\left(\frac{1}{P}\right) \tag{5.2.2}$$

or

$$V \propto \frac{1}{P} \tag{5.2.3}$$

where the ∝ symbol is read "is proportional to." A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equation 6.2.1 and Equation 6.2.3. Dividing both sides of Equation 6.2.1 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of the constant depends on the amount of gas used in the experiment and on the temperature at which the experiments are carried out. This relationship between pressure and volume is known as Boyle's law, after its discoverer, and can be stated as follows: *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.*



P (inHg)	V (in.^{3})	PV
12.0	117.5	1410
16.0	87.2	1400
20.0	70.7	1410
24.0	58.8	1410
32.0	44.2	1410
40.0	35.3	1410
48.0	29.1	1400

(a) Data from Boyle's experiment (b) Volume vs. pressure (c) Volume vs. 1/pressure

Figure 5.2.2: Plots of Boyle's Data. (a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.^{3} rather than cm^3) and the pressure (in. Hg rather than mmHg). (b) This plot of pressure versus volume is a hyperbola. Because PV is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) A plot of volume versus 1/pressure for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation V = constant/P.

Boyle's Law: https://youtu.be/lu86VSupPO4

The Relationship between Temperature and Volume: Charles's Law

Hot air rises, which is why hot-air balloons ascend through the atmosphere and why warm air collects near the ceiling and cooler air collects at ground level. Because of this behavior, heating registers are placed on or near the floor, and vents for air-conditioning are placed on or near the ceiling. The fundamental reason for this behavior is that gases expand when they are heated. Because the same amount of substance now occupies a greater volume, hot air is less dense than cold air. The substance with the lower density—in this case hot air—rises through the substance with the higher density, the cooler air.

The first experiments to quantify the relationship between the temperature and the volume of a gas were carried out in 1783 by an avid balloonist, the French chemist Jacques Alexandre César Charles (1746–1823). Charles's initial experiments showed that a plot of the volume of a given sample of gas versus temperature (in degrees Celsius) at constant pressure is a straight line. Similar but more precise studies were carried out by another balloon enthusiast, the Frenchman Joseph-Louis Gay-Lussac (1778–1850), who showed that a plot of V versus T was a straight line that could be extrapolated to a point at zero volume, a theoretical condition now known to correspond to −273.15°C (Figure 5.2.3).A sample of gas cannot really have a volume of zero because any sample of matter must have some volume. Furthermore, at 1 atm pressure all gases liquefy at temperatures well above −273.15°C. Note from part (a) in Figure 5.2.3 that the slope of the plot of V versus T varies for the same gas at different pressures but that the intercept remains constant at −273.15°C. Similarly, as shown in part (b) in Figure 5.2.3, plots of V versus T for different amounts of varied gases are straight lines with different slopes but the same intercept on the T axis.

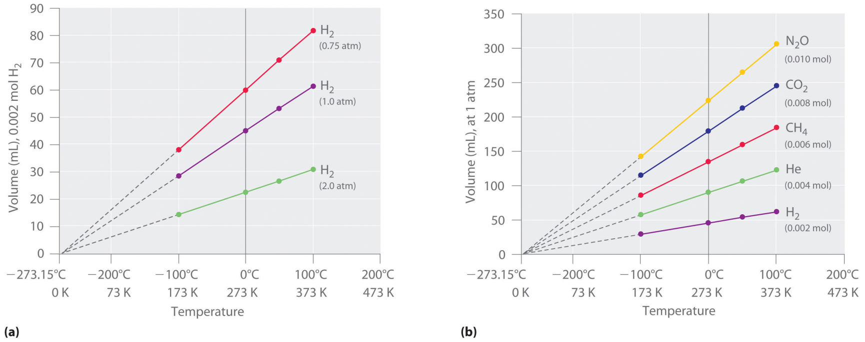


Figure 5.2.3: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data to $V = 0$. The temperature scale is given in both degrees Celsius and kelvins. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at $V = 0$ (−273.15°C = 0 K). (b) In these plots of volume versus temperature for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of $V = 0$ at −273.15°C, regardless of the identity or the amount of the gas.

The significance of the invariant T intercept in plots of V versus T was recognized in 1848 by the British physicist William Thomson (1824–1907), later named Lord Kelvin. He postulated that −273.15°C was the lowest possible temperature that could theoretically be achieved, for which he coined the term absolute zero (0 K).

We can state Charles's and Gay-Lussac's findings in simple terms: At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in kelvins). This relationship, illustrated in part (b) in Figure 5.2.3 is often referred to as Charles's law and is stated mathematically as

$$V = \text{const. } T \tag{5.2.4}$$

or

$$V \propto T \tag{5.2.5}$$

with *temperature expressed in kelvins*, not *in degrees Celsius*. Charles's law is valid for virtually all gases at temperatures well above their boiling points.

Charles's Law: https://youtu.be/NBf510ZnlR0

The Relationship between Amount and Volume: Avogadro's Law

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac's work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles (Figure 5.2.4). This is the historic "Avogadro's hypothesis."

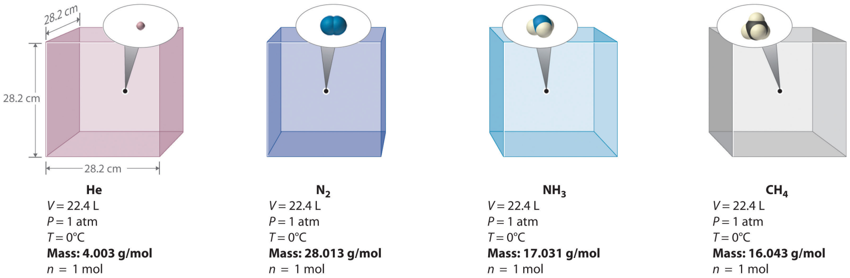


Figure $5.2.4$: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas.

A logical corollary to Avogadro's hypothesis (sometimes called Avogadro's law) describes the relationship between the volume and the amount of a gas: *At constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.* Stated mathematically,

$$V = \text{const.}\ (n) \tag{5.2.6}$$

or

$$V \propto . n @ \text{constant T and P} \tag{5.2.7}$$

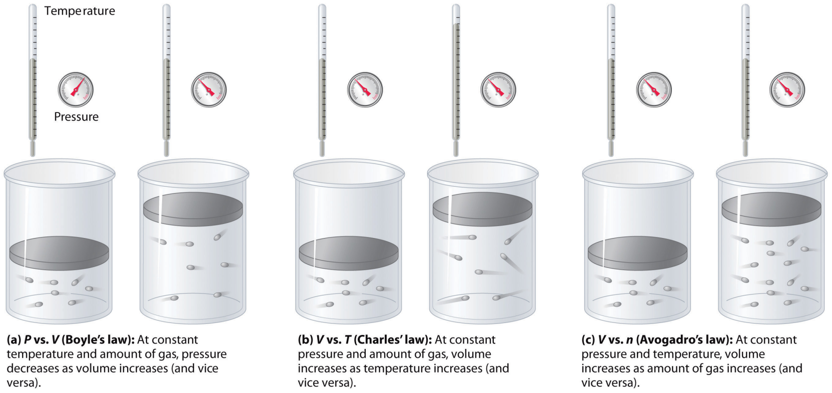
This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.

Note

For a sample of gas,

- V increases as P decreases (and vice versa)
- V increases as T increases (and vice versa)
- V increases as n increases (and vice versa)

The relationships among the volume of a gas and its pressure, temperature, and amount are summarized in Figure $5.2.5$. Volume *increases* with increasing temperature or amount but *decreases* with increasing pressure.



(a) *P* vs. *V* (Boyle's law): At constant temperature and amount of gas, pressure decreases as volume increases (and vice versa).

(b) *V* vs. *T* (Charles' law): At constant pressure and amount of gas, volume increases as temperature increases (and vice versa).

(c) *V* vs. *n* (Avogadro's law): At constant pressure and temperature, volume increases as amount of gas increases (and vice versa).

Figure $5.2.5$: The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas. The thermometer and pressure gauge indicate the temperature and the pressure qualitatively, the level in the flask indicates the volume, and the number of particles in each flask indicates relative amounts.

Avogadro’s Law: https://youtu.be/dRY3Trl4T24

Summary

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to its pressure (**Boyle’s law**), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature (in kelvins) at constant pressure (**Charles’s law**), and Avogadro postulated that the volume of a gas is directly proportional to the number of moles of gas present (**Avogadro’s law**). Plots of the volume of gases versus temperature extrapolate to zero volume at −273.15°C, which is **absolute zero (0 K)**, the lowest temperature possible. Charles’s law implies that the volume of a gas is directly proportional to its absolute temperature.

5.2: The Gas Laws of Boyle, Charles, and Avogadro is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

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5.3: The Ideal Gas Law

Learning Objectives

- To use the ideal gas law to describe the behavior of a gas.

In this module, the relationship between Pressure, Temperature, Volume, and Amount of a gas are described and how these relationships can be combined to give a general expression that describes the behavior of a gas.

Deriving the Ideal Gas Law

Any set of relationships between a single quantity (such as V) and several other variables (P, T, and n) can be combined into a single expression that describes all the relationships simultaneously. The three individual expressions are as follows:

- **Boyle's law**

$$V \propto \frac{1}{P} \quad \text{@ constant n and T} \tag{5.3.1}$$

- **Charles's law**

$$V \propto T \quad \text{@ constant n and P} \tag{5.3.2}$$

- **Avogadro's law**

$$V \propto n \quad \text{@ constant T and P} \tag{5.3.3}$$

Combining these three expressions gives

$$V \propto \frac{nT}{P} \tag{6.3.1}$$

which shows that the volume of a gas is proportional to the number of moles and the temperature and inversely proportional to the pressure. This expression can also be written as

$$V = \text{Cons.} \left(\frac{nT}{P}\right) \tag{6.3.2}$$

By convention, the proportionality constant in Equation 6.3.1 is called the gas constant, which is represented by the letter R. Inserting R into Equation 6.3.2 gives

$$V = \frac{Rnt}{P} = \frac{nRT}{P} \tag{6.3.3}$$

Clearing the fractions by multiplying both sides of Equation 6.3.4 by P gives

$$PV = nRT \tag{6.3.4}$$

This equation is known as the **ideal gas law**.

An ideal gas is defined as a hypothetical gaseous substance whose behavior is independent of attractive and repulsive forces and can be completely described by the ideal gas law. In reality, there is no such thing as an ideal gas, but an ideal gas is a useful conceptual model that allows us to understand how gases respond to changing conditions. As we shall see, under many conditions, most real gases exhibit behavior that closely approximates that of an ideal gas. The ideal gas law can therefore be used to predict the behavior of real gases under most conditions. The ideal gas law does not work well at very low temperatures or very high pressures, where deviations from ideal behavior are most commonly observed.

Note

Significant deviations from ideal gas behavior commonly occur at low temperatures and very high pressures.

Before we can use the ideal gas law, however, we need to know the value of the gas constant R. Its form depends on the units used for the other quantities in the expression. If V is expressed in liters (L), P in atmospheres (atm), T in kelvins (K), and n in moles (mol), then

$$R = 0.08206 \frac{\mathrm{L \cdot atm}}{\mathrm{K \cdot mol}} \tag{6.3.5}$$

Because the product PV has the units of energy, R can also have units of J/(K•mol):

$$R = 8.3145 \frac{\mathrm{J}}{\mathrm{K \cdot mol}} \tag{6.3.6}$$

Standard Conditions of Temperature and Pressure

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and $1\ \mathrm{bar} = 100\ \mathrm{kPa} = 10^5\ \mathrm{Pa}$ pressure, referred to as standard temperature and pressure (**STP**).

$$\text{STP:} \qquad T = 273.15\ \mathrm{K} \text{ and } P = 1\ \mathrm{bar} = 10^5\ \mathrm{Pa} \tag{5.3.4}$$

Please note that STP was defined differently in the part. The old definition was based on a standard pressure of 1 atm.

We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the ideal gas law given in Equation 6.3.4:

$$V = \frac{nRT}{P} \tag{6.3.7}$$

Thus the volume of 1 mol of an ideal gas is **22.71 L at STP** and **22.41 L at 0°C and 1 atm**, approximately equivalent to the volume of three basketballs. The molar volumes of several real gases at 0°C and 1 atm are given in Table 10.3, which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at 0°C and 1 atm. The relationships described in Section 10.3 as Boyle's, Charles's, and Avogadro's laws are simply special cases of the ideal gas law in which two of the four parameters (P, V, T, and n) are held fixed.

Table 5.3.1: Molar Volumes of Selected Gases at 0°C and 1 atm

Gas	Molar Volume (L)
He	22.434
Ar	22.397
H_2	22.433
N_2	22.402
O_2	22.397
CO_2	22.260
NH_3	22.079

Applying the Ideal Gas Law

The ideal gas law allows us to calculate the value of the fourth variable for a gaseous sample if we know the values of any three of the four variables (P, V, T, and n). It also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (P, V, T, and n) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same equation—the ideal gas law—and then determine which quantities are given and which need to be calculated. Let's begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

✓ Example 5.3.1

The balloon that Charles used for his initial flight in 1783 was destroyed, but we can estimate that its volume was 31,150 L (1100 ft^3), given the dimensions recorded at the time. If the temperature at ground level was 86°F (30°C) and the atmospheric pressure was 745 mmHg, how many moles of hydrogen gas were needed to fill the balloon?

Given: volume, temperature, and pressure

Asked for: amount of gas

Strategy:

A. Solve the ideal gas law for the unknown quantity, in this case *n*.
B. Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

Solution:

A We are given values for *P*, *T*, and *V* and asked to calculate *n*. If we solve the ideal gas law (Equation 6.3.4) for *n*, we obtain

$$745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.980 \text{ atm} \tag{5.3.5}$$

B *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.08206 (L•atm)/(K•mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$T = 273 + 30 = 303\text{K} \tag{5.3.6}$$

Substituting these values into the expression we derived for *n*, we obtain

$$n = \frac{PV}{RT} = \frac{0.980 \text{ atm} \times 31150 \text{ L}}{0.08206 \dfrac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 303 \text{ K}} = 1.23 \times 10^3 \text{ mol} \tag{5.3.7}$$

Exercise 5.3.1

Suppose that an “empty” aerosol spray-paint can has a volume of 0.406 L and contains 0.025 mol of a propellant gas such as CO_2. What is the pressure of the gas at 25°C?

Answer: 1.5 atm

In Example 5.3.1, we were given three of the four parameters needed to describe a gas under a particular set of conditions, and we were asked to calculate the fourth. We can also use the ideal gas law to calculate the effect of *changes* in any of the specified conditions on any of the other parameters, as shown in Example 5.3.5.

The Ideal Gas Law: https://youtu.be/rHGs23368mE

General Gas Equation

When a gas is described under two different conditions, the ideal gas equation must be applied twice - to an initial condition and a final condition. This is:

$$\begin{array}{cc}\text{Initial condition }(i) & \text{Final condition}(f)\\ P_iV_i = n_iRT_i & P_fV_f = n_fRT_f\end{array} \tag{5.3.8}$$

Both equations can be rearranged to give:

$$R = \frac{P_iV_i}{n_iT_i} \qquad R = \frac{P_fV_f}{n_fT_f} \tag{5.3.9}$$

The two equations are equal to each other since each is equal to the same constant R. Therefore, we have:

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f} \tag{6.3.8}$$

The equation is called the **general gas equation**. The equation is particularly useful when one or two of the gas properties are held constant between the two conditions. In such cases, the equation can be simplified by eliminating these constant gas properties.

✓ Example $5.3.2$

Suppose that Charles had changed his plans and carried out his initial flight not in August but on a cold day in January, when the temperature at ground level was −10°C (14°F). How large a balloon would he have needed to contain the same amount of hydrogen gas at the same pressure as in Example $5.3.1$?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A. Use the results from Example $5.3.1$ for August as the initial conditions and then calculate the *change in volume* due to the change in temperature from 30°C to −10°C. Begin by constructing a table showing the initial and final conditions.
B. Simplify the general gas equation by eliminating the quantities that are held constant between the initial and final conditions, in this case P and n.
C. Solve for the unknown parameter.

Solution:

A To see exactly which parameters have changed and which are constant, prepare a table of the initial and final conditions:

Initial (August)	Final (January)
$T_i =$ 30°C = 303 K	$T_f =$−10°C = 263 K
$P_i =$0.980 atm	$P_f =$0.980 atm
$n_i =$1.23 × 103 mol	$n_f =$1.23 × 103 mol
$V_i =$ 31150 L	$V_f =$?

B Both n and P are the same in both cases ($n_i = n_f, P_i = P_f$). Therefore, Equation can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f} \tag{5.3.10}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$V_f = V_i \times \frac{T_f}{T_i} = 31150 \text{ L} \times \frac{263 \text{ K}}{303 \text{ K}} = 2.70 \times 10^4 \text{ L} \tag{5.3.11}$$

It is important to check your answer to be sure that it makes sense, just in case you have accidentally inverted a quantity or multiplied rather than divided. In this case, the temperature of the gas decreases. Because we know that gas volume decreases with decreasing temperature, the final volume must be less than the initial volume, so the answer makes sense. We could have calculated the new volume by plugging all the given numbers into the ideal gas law, but it is generally much easier and faster to focus on only the quantities that change.

? Exercise 5.3.2

At a laboratory party, a helium-filled balloon with a volume of 2.00 L at 22°C is dropped into a large container of liquid nitrogen (T = −196°C). What is the final volume of the gas in the balloon?

Answer: 0.52 L

Example 5.3.1 illustrates the relationship originally observed by Charles. We could work through similar examples illustrating the inverse relationship between pressure and volume noted by Boyle (PV = constant) and the relationship between volume and amount observed by Avogadro (V/n = constant). We will not do so, however, because it is more important to note that the historically important gas laws are only special cases of the ideal gas law in which two quantities are varied while the other two remain fixed. The method used in Example 5.3.1 can be applied in *any* such case, as we demonstrate in Example 5.3.2 (which also shows why heating a closed container of a gas, such as a butane lighter cartridge or an aerosol can, may cause an explosion).

✓ Example 5.3.3

Aerosol cans are prominently labeled with a warning such as “Do not incinerate this container when empty.” Assume that you did not notice this warning and tossed the “empty” aerosol can in Exercise 5 (0.025 mol in 0.406 L, initially at 25°C and 1.5 atm internal pressure) into a fire at 750°C. What would be the pressure inside the can (if it did not explode)?

Given: initial volume, amount, temperature, and pressure; final temperature

Asked for: final pressure

Strategy:

Follow the strategy outlined in Example 5.3.5.

Solution:

Prepare a table to determine which parameters change and which are held constant:

Initial	Final
$V_i = 0.406\text{ L}$	$V_f = 0.406\text{ L}$
$n_i = 0.025\text{ mol}$	$n_f = 0.025\text{ mol}$
$T_i = 25\ ^\circ\text{C} = 298\text{ K}$	$T_i = 750\ ^\circ\text{C} = 1023\text{ K}$
$P_i = 1.5\text{ atm}$	$P_f = ?$

Both V and n are the same in both cases ($V_i = V_f, n_i = n_f$). Therefore, Equation can be simplified to:

$$P_i T_i = P_f T_f \tag{5.3.12}$$

By solving the equation for P_f, we get:

$$P_f = P_i \times \frac{T_i}{T_f} = 1.5\text{ atm} \times \frac{1023\text{ K}}{298\text{ K}} = 5.1\text{ atm} \tag{5.3.13}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

? Exercise 5.3.3

Suppose that a fire extinguisher, filled with CO_2 to a pressure of 20.0 atm at 21°C at the factory, is accidentally left in the sun in a closed automobile in Tucson, Arizona, in July. The interior temperature of the car rises to 160°F (71.1°C). What is the internal pressure in the fire extinguisher?

Answer: 23.4 atm

In Example $5.3.1$ and Example $5.3.2$, two of the four parameters (P, V, T, and n) were fixed while one was allowed to vary, and we were interested in the effect on the value of the fourth. In fact, we often encounter cases where two of the variables P, V, and T are allowed to vary for a given sample of gas (hence n is constant), and we are interested in the change in the value of the third under the new conditions.

✓ Example $5.3.4$

We saw in Example $5.3.1$ that Charles used a balloon with a volume of 31,150 L for his initial ascent and that the balloon contained 1.23×10^3 mol of H_2 gas initially at 30°C and 745 mmHg. Suppose that Gay-Lussac had also used this balloon for his record-breaking ascent to 23,000 ft and that the pressure and temperature at that altitude were 312 mmHg and −30°C, respectively. To what volume would the balloon have had to expand to hold the same amount of hydrogen gas at the higher altitude?

Given: initial pressure, temperature, amount, and volume; final pressure and temperature

Asked for: final volume

Strategy:

Follow the strategy outlined in Example $5.3.5$.

Solution:

Begin by setting up a table of the two sets of conditions:

Initial	Final
$P_i = 745 \text{ mmHg} = 0.980 \text{ atm}$	$P_f = 312 \text{ mmHg} = 0.411 \text{ atm}$
$T_i = 30 \text{ °C} = 303 \text{ K}$	$T_f = 750 - 30 \text{ °C} = 243 \text{ K}$
$n_i = 1.2 \times 10^3 \text{ mol}$	$n_i = 1.2 \times 10^3 \text{ mol}$
$V_i = 31150 \text{ L}$	$V_f = ?$

By eliminating the constant property (n) of the gas, Equation 6.3.8 is simplified to:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \tag{5.3.14}$$

By solving the equation for V_f, we get:

$$V_f = V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i} = 3.115 \times 10^4 \text{ L} \times \frac{0.980 \text{ atm}}{0.411 \text{ atm}}\frac{243 \text{ K}}{303 \text{ K}} = 5.96 \times 10^4 \text{ L} \tag{5.3.15}$$

Does this answer make sense? Two opposing factors are at work in this problem: decreasing the pressure tends to *increase* the volume of the gas, while decreasing the temperature tends to *decrease* the volume of the gas. Which do we expect to predominate? The pressure drops by more than a factor of two, while the absolute temperature drops by only about 20%. Because the volume of a gas sample is directly proportional to both T and $1/P$, the variable that changes the most will have the greatest effect on V. In this case, the effect of decreasing pressure predominates, and we expect the volume of the gas to increase, as we found in our calculation.

We could also have solved this problem by solving the ideal gas law for V and then substituting the relevant parameters for an altitude of 23,000 ft:

Except for a difference caused by rounding to the last significant figure, this is the same result we obtained previously. *There is often more than one "right" way to solve chemical problems.*

Exercise 5.3.4

A steel cylinder of compressed argon with a volume of 0.400 L was filled to a pressure of 145 atm at 10°C. At 1.00 atm pressure and 25°C, how many 15.0 mL incandescent light bulbs could be filled from this cylinder? (Hint: find the number of moles of argon in each container.)

Answer: 4.07×10^3

Second Type of Ideal Gas Law Problems: https://youtu.be/WQDJOqddPI0

Using the Ideal Gas Law to Calculate Gas Densities and Molar Masses

The ideal gas law can also be used to calculate molar masses of gases from experimentally measured gas densities. To see how this is possible, we first rearrange the ideal gas law to obtain

$$\frac{n}{V} = \frac{P}{RT} \tag{6.3.9}$$

The left side has the units of moles per unit volume (mol/L). The number of moles of a substance equals its mass (m, in grams) divided by its molar mass (M, in grams per mole):

$$n = \frac{m}{M} \tag{6.3.10}$$

Substituting this expression for n into Equation 6.3.9 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{6.3.11}$$

Because m/V is the density d of a substance, we can replace m/V by d and rearrange to give

$$\rho = \frac{m}{V} = \frac{MP}{RT} \tag{6.3.12}$$

The distance between particles in gases is large compared to the size of the particles, so their densities are much lower than the densities of liquids and solids. Consequently, gas density is usually measured in grams per liter (g/L) rather than grams per milliliter (g/mL).

✓ Example 5.3.5

Calculate the density of butane at 25°C and a pressure of 750 mmHg.

Given: compound, temperature, and pressure

Asked for: density

Strategy:

A. Calculate the molar mass of butane and convert all quantities to appropriate units for the value of the gas constant.
B. Substitute these values into Equation 6.3.12 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$M = (4)(12.011) + (10)(1.0079) = 58.123 \text{g/mol} \tag{5.3.16}$$

Using 0.08206 (L•atm)/(K•mol) for R means that we need to convert the temperature from degrees Celsius to kelvins (T = 25 + 273 = 298 K) and the pressure from millimeters of mercury to atmospheres:

$$P = 750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.987 \text{ atm} \tag{5.3.17}$$

B Substituting these values into Equation 6.3.12 gives

$$\rho = \frac{58.123 \text{ g/mol} \times 0.987 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} = 2.35 \text{ g/L} \tag{5.3.18}$$

? Exercise 5.3.5

Radon (Rn) is a radioactive gas formed by the decay of naturally occurring uranium in rocks such as granite. It tends to collect in the basements of houses and poses a significant health risk if present in indoor air. Many states now require that houses be tested for radon before they are sold. Calculate the density of radon at 1.00 atm pressure and 20°C and compare it with the density of nitrogen gas, which constitutes 80% of the atmosphere, under the same conditions to see why radon is found in basements rather than in attics.

Answer: radon, 9.23 g/L; N_2, 1.17 g/L

A common use of Equation 6.3.12 is to determine the molar mass of an unknown gas by measuring its density at a known temperature and pressure. This method is particularly useful in identifying a gas that has been produced in a reaction, and it is not difficult to carry out. A flask or glass bulb of known volume is carefully dried, evacuated, sealed, and weighed empty. It is then filled with a sample of a gas at a known temperature and pressure and reweighed. The difference in mass between the two readings is the mass of the gas. The volume of the flask is usually determined by weighing the flask when empty and when filled with a liquid of known density such as water. The use of density measurements to calculate molar masses is illustrated in Example 5.3.6.

✓ Example 5.3.6

The reaction of a copper penny with nitric acid results in the formation of a red-brown gaseous compound containing nitrogen and oxygen. A sample of the gas at a pressure of 727 mmHg and a temperature of 18°C weighs 0.289 g in a flask with a volume of 157.0 mL. Calculate the molar mass of the gas and suggest a reasonable chemical formula for the compound.

Given: pressure, temperature, mass, and volume

Asked for: molar mass and chemical formula

Strategy:

A. Solve Equation 6.3.12 for the molar mass of the gas and then calculate the density of the gas from the information given.
B. Convert all known quantities to the appropriate units for the gas constant being used. Substitute the known values into your equation and solve for the molar mass.
C. Propose a reasonable empirical formula using the atomic masses of nitrogen and oxygen and the calculated molar mass of the gas.

Solution:

A Solving Equation 6.3.12 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P} \tag{5.3.19}$$

Density is the mass of the gas divided by its volume:

$$\rho=\frac{m}{V}=\frac{0.289\text{g}}{0.17\text{L}}=1.84\text{g/L} \tag{5.3.20}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T=18+273=291K \tag{5.3.21}$$

$$P=727\text{mmHg}\times\frac{1\text{atm}}{760\text{mmHg}}=0.957\text{atm} \tag{5.3.22}$$

The molar mass of the unknown gas is thus

$$\rho=\frac{1.84\text{ g/L}\times 0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\times 291\text{ K}}{0.957\text{ atm}}=45.9\text{g/mol} \tag{5.3.23}$$

C The atomic masses of N and O are approximately 14 and 16, respectively, so we can construct a list showing the masses of possible combinations:

$$M(\text{NO})=14+16=30\text{ g/mol} \tag{5.3.24}$$

$$M(\text{N}_2\text{O})=(2)(14)+16=44\text{ g/mol} \tag{5.3.25}$$

$$M(\text{NO}_2)=14+(2)(16)=46\text{ g/mol} \tag{5.3.26}$$

The most likely choice is NO_2 which is in agreement with the data. The red-brown color of smog also results from the presence of NO_2 gas.

? Exercise 5.3.6

You are in charge of interpreting the data from an unmanned space probe that has just landed on Venus and sent back a report on its atmosphere. The data are as follows: pressure, 90 atm; temperature, 557°C; density, 58 g/L. The major constituent of the atmosphere (>95%) is carbon. Calculate the molar mass of the major gas present and identify it.

Answer: 44 g/mol; CO_2

Density and the Molar Mass of Gases: https://youtu.be/gnkGBsvUFVk

Summary

The ideal gas law is derived from empirical relationships among the pressure, the volume, the temperature, and the number of moles of a gas; it can be used to calculate any of the four properties if the other three are known.

Ideal gas equation: $PV=nRT$,

where $R = 0.08206 \frac{\mathrm{L \cdot atm}}{\mathrm{K \cdot mol}} = 8.3145 \frac{\mathrm{J}}{\mathrm{K \cdot mol}}$

General gas equation: $\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f}$

Density of a gas: $\rho = \frac{MP}{RT}$

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the **ideal gas law**, $PV = nRT$. The proportionality constant, R, is called the **gas constant** and has the value 0.08206 (L•atm)/(K•mol), 8.3145 J/(K•mol), or 1.9872 cal/(K•mol), depending on the units used. The ideal gas law describes the behavior of an **ideal gas**, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. **Standard temperature and pressure (STP)** is 0°C and 1 atm. The volume of 1 mol of an ideal gas at STP is 22.41 L, the **standard molar volume**. All of the empirical gas relationships are special cases of the ideal gas law in which two of the four parameters are held constant. The ideal gas law allows us to calculate the value of the fourth quantity (P, V, T, or n) needed to describe a gaseous sample when the others are known and also predict the value of these quantities following a change in conditions if the original conditions (values of P, V, T, and n) are known. The ideal gas law can also be used to calculate the density of a gas if its molar mass is known or, conversely, the molar mass of an unknown gas sample if its density is measured.

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5.4: Gas Stoichiometry

What you Should Know

Before beginning this section, you should know and understand:

- The concept of Stoichiometric proportions in reactions
- Avogadro's Constant and its uses in converting grams to moles
- The Ideal Gas Law: $PV = nRT$
- Dalton's Law of Partial Pressure

Chemical reactions between gaseous materials are quite similar to reactions between solids and liquids, except the Ideal Gas Law ($PV = nRT$) can now be included in the calculations. If a chemical reaction is reversible (such as the decay and formation of dinitrogen tetraoxide), then Dalton's Law of Partial Pressure may be used to determine the moles of reactants and products at which the reaction ceases (and subsequently, the temperature, pressure and volume of each gas can be determined as well).

Non-Reversible Reactions

A non-reversible reaction uses the reactants to form the products. The reaction goes in one direction; that is, using the product to recreate the reactants has greatly different requirements. One of the most common forms of non-reversible reactions is combustion (once an organic molecule has been converted to water and hydrogen gas, it is extremely difficult to reform). Other non-reversible reactions produce a state change, such as Hydrogen Peroxide (the gaseous material produces water, a liquid). To understand how the Ideal Gas Law applies to reactions, we shall use a nonreversible reaction as an example.

Example 5.4.1: the decomposition of Hydrogen Peroxide to water and oxygen gas

If 4.000 grams of hydrogen peroxide is placed within a sealed 250 milliliter container at 500 K. What is the pressure of the oxygen gas produced in atmospheres?

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

Solution

First, we need to determine the moles of O_2 produced, just like any other stoichiometric problem.

$$(4g\ \ H_2\cancel{O_2}) \times \left(\frac{1\ mol\ \ H_2\cancel{O_2}}{34.016\ g\ \ H_2\cancel{O_2}}\right)\left(\frac{1\ mol\ O_2}{2\ mol\ \ H_2\cancel{O_2}}\right) = 0.0588\ mol\ O_2$$

With the moles of oxygen determined, we can now use the Ideal Gas Law to determine the pressure.

$$PV = nRT$$

The volume (250 mL = 0.25 L) and temperature (500 K) are already given to us, and R (0.0820574 Latm mol^{-1}K^{-1}) is a constant.

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(0.0588\ mol\ O_2) \times (0.0820\ L\ atm\ mol^{-1}\ K^{-1}) \times (500\ K)}{0.25\ L} \\ &= 9.65\ atm \end{aligned}$$

By using the Ideal Gas Law for unit conversions, properties such as the pressure, volume, moles, and temperature of a gas involved in a reaction can be determined. However, a different approach is needed to solve reversible reactions.

For further clarification, when solving equations with gases, we must remember that gases behave differently under different conditions. For example, if we have a certain temperature or pressure, this can change the number of moles produced or the volume. This is unlike regular solids where we only had to account for the mass of the solids and solve for the mass of the product by stoichiometry. In order to solve for the temperature, pressure, or volume of a gas using chemical reactions, we often need to have information on two out of three of these variables. So we need either the temperature and volume, temperature and pressure, or pressure and volume. The mass we can find using stoichiometric conversions we have learned before.

The reason why gases require additional information is because gases behave as ideal gases and ideal gases behave differently under different conditions. To account for these conditions, we use the ideal gas equation PV=nRT where P is the pressure measured in atmosphere(atm), V is the volume measured in liters (L), n is the number of moles, R is the gas constant with a value of .08206 L atm mol^{-1} K^{-1}, and T is the temperature measured in kelvin (K).

Example 5.4.2

Suppose we have the following combustion reaction (below). If we are given 2 moles of ethane at STP, how many liters of CO_2 are produced?

$$2\,C_2H_6(s) + 7\,O_2(g) \longrightarrow 6\,H_2O(l) + 4\,CO_2(g) \tag{5.4.1}$$

Solution

Step 1

First use stoichiometry to solve for the number of moles of CO_2 produced.

$$(2\,mol\,C_2H_6)\left(\frac{4\,mol CO_2}{2\,mol\,C_2H_6}\right) = 4 mol\,CO_2$$

So 4 moles of Carbon Dioxide are produced if we react 2 moles of ethane gas.

Step 2

Now we simply need to manipulate the ideal gas equation to solve for the variable of interest. In this case we are solving for the number of liters.

Since we are told ethane is at STP, we know that the temperature is 273 K and the pressure is 1 atm.

So the variables we have are:

- V = ?
- T = 273K
- P = 1 atm
- n = 4 moles CO_2
- R (gas constant) = 0.08206 L atm mol^{-1} K^{-1}

Isolating the variable of interest from $PV = nRT$, we get

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{4\,mol \times 0.08206\,L\,atm\,mol^{-1}K^{-1} \times 273\,K}{1\,atm} \\ &= 89.61\,L \end{aligned}$$

So we have a volume of 89.61 liters.

Reversible Reactions in Gases

A reversible reaction is a chemical reaction in which reactants produces a product, which then decays back to the reactants. This continues until the products and reactants are in equilibrium. In other words, the final state of the gas includes both the reactants and the products. For example, Reactant A combines with Reactant B to form Product AB, which then breaks apart into A and B, until an equilibrium of the three is reached. In a reaction between gases, determining gas properties such as partial pressure and moles can be quite difficult. For this example, we consider the theral decomposition of Dinitrogen Tetraoxide into Nitrogen Dioxide.

✓ Example 5.4.3

For this example, we shall use Dinitrogen Tetraoxide, which decomposes to form Nitrogen Dioxide.

$$N_2O_4 \rightleftharpoons 2\,NO_2$$

2 atm of dinitrogen tetraoxide is added to a 500 mL container at 273 K. After several minutes, the total pressure of N_2O_4 and $2NO_2$ at equilibrium is found to be 3.2 atm. Find the partial pressures of both gases.

Solution

The simplest way of solving this problem is to begin with an ICE table.

	N_2O_4	$2\,NO_2$	Description of Each Letter
Initial	2atm	0atm	The initial amounts of reactants and products
Change	-X	+2X	The unknown change, X, each one multiplied by their stoichiometric factor
Equilibrium	2-Xatm	2x atm	The initial + the change

With this data, a simple equation can be derived to determine the value of X.

$$P_{total} = (2 - X) + 2X = 3.2\ atm \tag{5.4.2}$$

$$X = 1.2\ atm \tag{5.4.3}$$

$$P_{NO_2} = 2x = 2.4\ atm \tag{5.4.4}$$

$$P_{N_{2}0_{4}} = 2 - x = 0.8\ atm \tag{5.4.5}$$

Law of Combining Volumes

This law of combining volumes was first discovered by the famous scientist Gay-Lussac who noticed this relationship. He determined that if certain gases that are products and reactions in a chemical reaction are measured at the same conditions, temperature and pressure, then the volume of gas consumed/produced is equal to the ratio between the gases or the ratio of the coefficients.

✓ Example 5.4.4

If ozone, hydrogen, and oxygen were all measured at 35^{o}C and at 753 mmHg, then how many liters of ozone was consumed if you had 5 liters of oxygen gas?

$$O_3(g) + H_2O(l) \longrightarrow H_2(g) + 2\,O_2(g)$$

Solution

Step 1

Identify what we are looking for and if any relationships can be spotted. In this case, we can see that there are three gases all at the same temperature and pressure, which follows Gay-Lussac's Law of Combining Volumes. We can now proceed to use his law.

Step 2

We simply change the coefficients to volumetric ratios. So for every 1 Liter of Ozone gas we have, we produce 1 Liter of H_2gas and 2 Liter of O_2 gas.

We are given 5 liters of Oxygen gas and want to solve for the amount of liters of ozone consumed. We simply use the 2:1 stoichiometry of the reaction.

$$5LO_2\left(\frac{1\ L\ O_3}{2\ L\ O_2}\right)=2.5\ L\ O_3 \tag{5.4.6}$$

Problems

1. A 450 mL container of oxygen gas is at STP. Hydrogen gas is pumped into the container, producing water. What is the least amount of mL of Hydrogen gas needed in order to react the oxygen to completion?

$$2H_{2(g)}+O_{2(g)}\rightarrow 2H_2O_{(l)} \tag{5.4.7}$$

2. This reaction occurred at 427 Kelvin, with 37 g of CH_4 and an excess of oxygen. The carbon dioxide produced was captured in a 30L sealed container. What is the pressure of the carbon dioxide within the container?

$$CH_4+2O_2\rightarrow CO_2+2H_2O \tag{5.4.8}$$

Solution

1. $900\ mL\ H_2$: To solve this question you simply use Gay-Lussac's law of combining volume because both gases are at the same temperature at pressure.

$$450\ mL\ O_2\left(\frac{2\ mL\ H_2}{1\ mL\ O_2}\right)=900\ mL\ H_2 \tag{5.4.9}$$

2. $2.7\ atm$: For a question like this, you want to first determine the number of moles of the compound in interest first using stoichiometry and then using the ideal gas law to solve for the variable of interest.

$$37\ g\ CH_4\left(\frac{1\ mol\ CH_4}{16\ g\ CH_4}\right)\left(\frac{1\ mol\ CO_2}{1\ mol\ CH_4}\right)=2.3\ mol\ CO_2 \tag{5.4.10}$$

Now use the ideal gas law to solve for the pressure of CO_2.

- PV=nRT
- P = ?
- V = 30L
- n= 2.3 mol CO_2
- T = 427 K
- P = nRT/V

$$P = (2.3\text{ mol} * .08206\text{ L atm mol}^{-1}\text{ K}^{-1} * 427\text{ K})/(30\text{ L})$$

$$P=2.7\text{ atm}$$

References

1. Petrucci, Harwood, Herring, Madura. General Chemistry: Principles and Modern Applications. Prentice Hall, New Jersey 2007.

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5.5: Dalton's Law of Partial Pressures

Learning Objectives

- To determine the contribution of each component gas to the total pressure of a mixture of gases

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{5.5.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressure, the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, ***the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases***. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as *Dalton's law of partial pressures*. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots = \sum_{i=1}^{n} P_i \tag{5.5.2}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

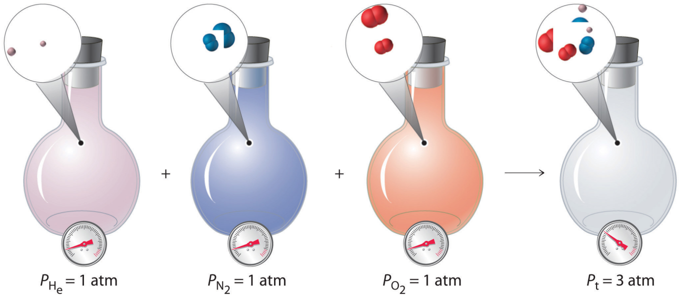

Figure 5.5.1: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right) \tag{5.5.3}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{5.5.4}$$

$$P_{tot} = \sum_{i=1}^{n} n_i \left(\frac{RT}{V}\right) \tag{5.5.5}$$

Equation 6.6.4 restates Equation 6.6.3 in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on only the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For Equation 6.6.4 to be valid, the identity of the particles present cannot have an effect. Thus an ideal gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 5.5.1.

✓ Example 5.5.1

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called “the bends.” At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of components, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A. Calculate the number of moles of He and O_2 present.
B. Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of He is

$$n_{\text{He}} = \frac{326.4 \text{ g}}{4.003 \text{ g/mol}} = 81.54 \text{ mol} \tag{5.5.6}$$

The number of moles of O_2 is

$$n_{\text{O}_2} = \frac{51.2 \text{ g}}{32.00 \text{ g/mol}} = 1.60 \text{ mol} \tag{5.5.7}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}} RT}{V} = \frac{81.54 \text{ mol} \times 0.08206 \dfrac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15 \text{ K}}{10.0 \text{ L}} = 196.2 \text{ atm} \tag{5.5.8}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2} RT}{V} = \frac{1.60 \text{ mol} \times 0.08206 \dfrac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15 \text{ K}}{10.0 \text{ L}} = 3.85 \text{ atm} \tag{5.5.9}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85) \text{ atm} = 200.1 \text{ atm} \tag{5.5.10}$$

? Exercise 5.5.1

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer: $P_{CH_4} = 137\ atm; P_{C_2H_6} = 13.4\ atm; P_{tot} = 151\ atm$

Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction (X) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_{tot}):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{5.5.11}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $x_A = 1.0$, then the sample is pure A, not a mixture. If $x_A = 0$, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let’s evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the ideal gas law to describe the pressures of both gas A and the mixture: $P_A = n_A RT/V$ and $P_{tot} = n_t RT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = x_A \tag{5.5.12}$$

Rearranging this equation gives

$$P_A = x_A P_{tot} \tag{5.5.13}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. By volume, Earth’s atmosphere is about 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of gases such as CO_2, H_2O, and others. This means that 78% of the particles present in the atmosphere are N_2; hence the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using Equation 6.6.7, we therefore know that the partial pressure of N_2 is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of O_2 and Ar are 0.21 and 0.009 atm, respectively.

✓ Example 5.5.2

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

	Inhaled Air / mmHg	**Exhaled Air / mmHg**
$P_{\mathrm{N_2}}$	597	568
$P_{\mathrm{O_2}}$	158	116
$P_{\mathrm{H_2O}}$	0.3	28
$P_{\mathrm{CO_2}}$	5	48
P_{Ar}	8	8
P_{tot}	767	767

Given: pressures of gases in inhaled and exhaled air

Asked for: mole fractions of gases in exhaled air

Strategy:

Calculate the mole fraction of each gas using Equation 6.6.7.

Solution:

The mole fraction of any gas A is given by

$$x_A = \frac{P_A}{P_{tot}} \tag{5.5.14}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of CO_2 is given as:

$$x_{\text{CO}_2} = \frac{48\text{ mmHg}}{767\text{ mmHg}} = 0.063 \tag{5.5.15}$$

The following table gives the values of x_A for the gases in the exhaled air.

Gas	Mole Fraction
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

? Exercise 5.5.2

Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.

Answer

$$P_{\text{CO}_2} = 86\text{ atm},\ P_{\text{N}_2} = 2.7\text{ atm}$$

Dalton’s Law of Partial Pressures: https://youtu.be/y5-SbspyvBA

Summary

- The partial pressure of each gas in a mixture is proportional to its mole fraction.

The pressure exerted by each gas in a gas mixture (its **partial pressure**) is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (**Dalton’s law of partial pressures**). The amount of gas present in a mixture may be described by its partial pressure or its mole fraction. The **mole fraction** of any component of a mixture is the ratio of the number of moles of that substance to the total number of moles of all substances present. In a mixture of gases, the partial pressure of each gas is the product of the total pressure and the mole fraction of that gas.

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5.6: The Kinetic Molecular Theory of Gases

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

A Molecular Description

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

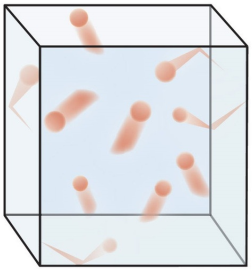

Figure 5.6.1 Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In Section 10.8, we explain how this theory must be modified to account for the behavior of real gases.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 5.6.2).

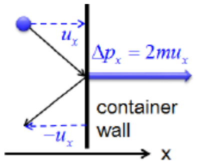

Figure 5.6.2 Momentum transfer (Impulse) from a molecule to the container wall as it bounces off the wall. u_x and Δp_x are the x component of the molecular velocity and the momentum transfered to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity u_x in x direction hits is expressed as:

$$\Delta p_x = 2mu_x \tag{5.6.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (u_x) \times \left(\frac{N}{V}\right) \tag{5.6.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mu_x^2 \tag{5.6.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace u_x^2 in the expression above with the average value of u_x^2, which is denoted by $\overline{u_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\overline{u_x^2} \tag{5.6.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that $\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{u^2}$. Here the quantity $\overline{u^2}$ is called the **mean-square speed** defined as the average value of square-speed (u^2) over all molecules. Since $u^2 = u_x^2 + u_y^2 + u_z^2$ for each molecule, $\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}$. By substituting $\frac{1}{3}\overline{u^2}$ for $\overline{u_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2} \tag{5.6.5}$$

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Postulate 5 refers to the *average translational* kinetic energy of the molecules of a gas $(\overline{e_K})$, which can be represented as *and states that at a given Kelvin temperature* (T), *all gases have the same value of*

$$\overline{e_K} = \frac{1}{2}m\overline{u^2} = \frac{3}{2}\frac{R}{N_A}T \tag{5.6.6}$$

where N_A is the Avogadro's constant. The total translational kinetic energy of 1 mole of molecules can be obtained by multiplying the equation by N_A:

$$N_A\overline{e_K} = \frac{1}{2}M\overline{u^2} = \frac{3}{2}RT \tag{5.6.7}$$

where M is the molar mass of the gas molecules and is related to the molecular mass by $M = N_A m$.

By rearranging the equation, we can get the relationship between the root-mean square speed (u_{rms}) and the temperature.

The rms speed (u_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{5.6.8}$$

where N is the number of particles and u_i is the speed of particle i.

The relationship between u_{rms} and the temperature is given by:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{5.6.9}$$

In this equation, u_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol).

The equation shows that u_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however, because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, not the same average speed. In contrast, the most probable speed (v_p) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then Equation 6.7.8 tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and v_p increases.

Note

At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.

✓ Example 5.6.1

The speeds of eight particles were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{av}) root mean square speed (v_{rms}), and most probable speed (v_{m}).

Given: particle speeds

Asked for: average speed (v_{av}), root mean square speed (v_{rms}), and most probable speed (v_{m})

Strategy:

Use Equation 6.7.6 to calculate the average speed and Equation 6.7.8 to calculate the rms speed. Find the most probable speed by determining the speed at which the greatest number of particles is moving.

Solution:

The average speed is the sum of the speeds divided by the number of particles:

$$v_{\text{av}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s} \tag{5.6.10}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\text{rms}} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}} = 6.2\ \text{m/s} \tag{5.6.11}$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence $v_{\text{m}} = 6.0$ m/s. The v_{rms} of the particles, which is related to the average kinetic energy, is greater than their average speed.

Boltzmann Distributions

At any given time, what fraction of the molecules in a particular sample has a given speed? Some of the molecules will be moving more slowly than average, and some will be moving faster than average, but how many in each situation? Answers to questions such as these can have a substantial effect on the amount of product formed during a chemical reaction, as you will learn in Chapter 14. This problem was solved mathematically by Maxwell in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature. Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in Figure $5.6.1$. Increasing the temperature has two effects. First, the peak of the curve moves to the right because the most probable speed increases. Second, the curve becomes broader because of the increased spread of the speeds. Thus increased temperature increases the *value* of the most probable speed but decreases the relative number of molecules that have that speed. Although the mathematics behind curves such as those in Figure $5.6.1$ were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributions, after one of the other major figures responsible for the kinetic molecular theory of gases.

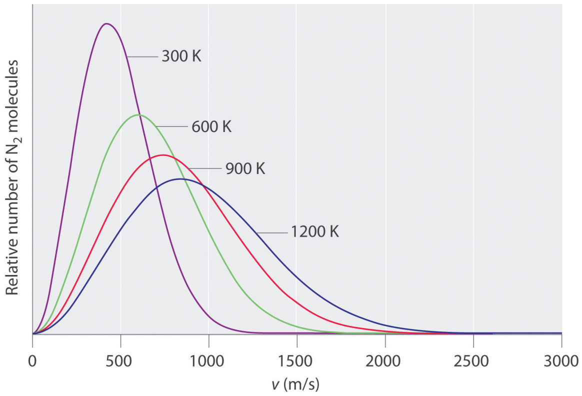

Figure $5.6.2$ The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

The Relationships among Pressure, Volume, and Temperature

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

- **Pressure versus Volume**: At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.
- **Volume versus Temperature**: Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the pressure, as we have just seen. Thus an increase in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.
- **Pressure of Gas Mixtures**: Postulate 3 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton’s law of partial pressures holds.

✓ Example $5.6.2$

The temperature of a 4.75 L container of N_2 gas is increased from 0°C to 117°C. What is the qualitative effect of this change on the

1. average kinetic energy of the N_2 molecules?
2. rms speed of the N_2 molecules?

3. average speed of the N_2 molecules?
4. impact of each N_2 molecule on the wall of the container during a collision with the wall?
5. total number of collisions per second of N_2 molecules with the walls of the entire container?
6. number of collisions per second of N_2 molecules with each square centimeter of the container wall?
7. pressure of the N_2 gas?

Given: temperatures and volume

Asked for: effect of increase in temperature

Strategy:

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

Solution:

1. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
2. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
3. If the rms speed of the N_2 molecules increases, the average speed also increases.
4. If, on average, the particles are moving faster, then they strike the container walls with more energy.
5. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
6. The number of collisions per second of N_2 molecules with each square centimeter of container wall increases because the total number of collisions has increased, but the volume occupied by the gas and hence the total area of the walls are unchanged.
7. The pressure exerted by the N_2 gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law.

? Exercise 5.6.2

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at constant temperature. What is the qualitative effect of this change on the

1. average kinetic energy of the He atoms?
2. rms speed of the He atoms?
3. average speed of the He atoms?
4. impact of each He atom on the wall of the container during a collision with the wall?
5. total number of collisions per second of He atoms with the walls of the entire container?
6. number of collisions per second of He atoms with each square centimeter of the container wall?
7. pressure of the He gas?

Answer: a. no change; b. no change; c. no change; d. no change; e. decreases; f. decreases; g. decreases

Kinetic-Molecular Theory of Gases: https://youtu.be/9f83XAYfXAg

Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T, \tag{5.6.12}$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}, \tag{5.6.13}$$

- **Kinetic molecular theory of gases:**

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \tag{5.6.14}$$

The behavior of ideal gases is explained by the **kinetic molecular theory of gases**. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same **root mean square (rms) speed (v_{rms})**. The actual values of speed and kinetic energy are not the same for all particles of a gas but are given by a **Boltzmann distribution**, in which some molecules have higher or lower speeds (and kinetic energies) than average.

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5.7: Effusion and Diffusion

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

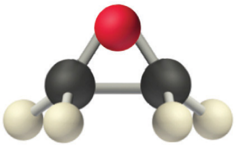
Diffusion and Effusion

As you have learned, the molecules of a gas are *not* stationary but in constant and random motion. If someone opens a bottle of perfume in the next room, for example, you are likely to be aware of it soon. Your sense of smell relies on molecules of the aromatic substance coming into contact with specialized olfactory cells in your nasal passages, which contain specific receptors (protein molecules) that recognize the substance. How do the molecules responsible for the aroma get from the perfume bottle to your nose? You might think that they are blown by drafts, but, in fact, molecules can move from one place to another even in a draft-free environment.

Diffusion is the gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with uniform composition. Diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. The related process, effusion, is the escape of gaseous molecules through a small (usually microscopic) hole, such as a hole in a balloon, into an evacuated space.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass. This relationship *is referred to as Graham's law*, after the Scottish chemist Thomas Graham (1805–1869). The ratio of the effusion rates of two gases is the square root of the inverse ratio of their molar masses*:*

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}} \tag{5.7.1}$$



Ethylene oxide

Figure 5.7.1 for ethylene oxide and helium. Helium (M = 4.00 g/mol) effuses much more rapidly than ethylene oxide (M = 44.0 g/mol). Because helium is less dense than air, helium-filled balloons "float" at the end of a tethering string. Unfortunately, rubber balloons filled with helium soon lose their buoyancy along with much of their volume. In contrast, rubber balloons filled with air tend to retain their shape and volume for a much longer time. Because helium has a molar mass of 4.00 g/mol, whereas air has an average molar mass of about 29 g/mol, pure helium effuses through the microscopic pores in the rubber balloon $\sqrt{\frac{29}{4.00}} = 2.7$ times faster than air. For this reason, high-quality helium-filled balloons are usually made of Mylar, a dense, strong, opaque material with a high molecular mass that forms films that have many fewer pores than rubber. Hence, mylar balloons can retain their helium for days.

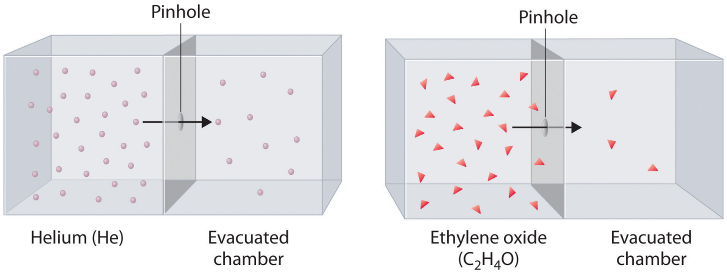


Figure 5.7.1: The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law.

Note

At a given temperature, heavier molecules move more slowly than lighter molecules.

Example 5.7.1

During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of ^{235}U. Naturally occurring uranium is only 0.720% ^{235}U, whereas most of the rest (99.275%) is ^{238}U, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

1. Calculate the ratio of the rates of effusion of $^{235}UF_6$ and $^{238}UF_6$ for a single step in which UF_6 is allowed to pass through a porous barrier. (The atomic mass of ^{235}U is 235.04, and the atomic mass of ^{238}U is 238.05.)
2. If n identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the nth power. How many effusion steps are needed to obtain 99.0% pure $^{235}UF_6$?

Given: isotopic content of naturally occurring uranium and atomic masses of ^{235}U and ^{238}U

Asked for: ratio of rates of effusion and number of effusion steps needed to obtain 99.0% pure $^{235}UF_6$

Strategy:

A. Calculate the molar masses of $^{235}UF_6$ and $^{238}UF_6$, and then use Graham's law to determine the ratio of the effusion rates. Use this value to determine the isotopic content of $^{235}UF_6$ after a single effusion step.
B. Divide the final purity by the initial purity to obtain a value for the number of separation steps needed to achieve the desired purity. Use a logarithmic expression to compute the number of separation steps required.

Solution:

1. The molar mass of $^{238}UF_6$ is 238.05 + (6)(18.998) = 352.04 g/mol

   The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law using Equation 6.8.1:

$$\frac{\text{rate } ^{235}\text{UF}_6}{\text{rate } ^{238}\text{UF}_6}=\sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}}=1.0043 \tag{5.7.2}$$

2.

   Thus passing UF_6 containing a mixture of the two isotopes through a single porous barrier gives an enrichment of 1.0043, so after one step the isotopic content is (0.720%)(1.0043) = 0.723% $^{235}UF_6$.

3. **B** To obtain 99.0% pure $^{235}UF_6$ requires many steps. We can set up an equation that relates the initial and final purity to the number of times the separation process is repeated: final purity = (initial purity)(separation)^n

   In this case, 0.990 = (0.00720)(1.0043)^n, which can be rearranged to give

$$1.0043^n = \frac{0.990}{0.00720} = 137.50 \tag{5.7.3}$$

4. Taking the logarithm of both sides gives

$$n \ln(1.0043) = \ln(137.50) \tag{5.7.4}$$

$$n = \frac{\ln(137.50)}{\ln(1.0043)} = 1148 \tag{5.7.5}$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched ^{235}U. Figure 5.7.2 shows a small part of a system that is used to prepare enriched uranium on a large scale.

Figure 5.7.2: A Portion of a Plant for Separating Uranium Isotopes by Effusion of UF_6. The large cylindrical objects (note the human for scale) are so-called diffuser (actually effuser) units, in which gaseous UF_6 is pumped through a porous barrier to partially separate the isotopes. The UF_6 must be passed through multiple units to become substantially enriched in ^{235}U.

? Exercise 5.7.1

Helium consists of two isotopes: ^3He (natural abundance = 0.000134%) and ^4He (natural abundance = 99.999866%). Their atomic masses are 3.01603 and 4.00260, respectively. Helium-3 has unique physical properties and is used in the study of ultralow temperatures. It is separated from the more abundant ^4He by a process of gaseous effusion.

a. Calculate the ratio of the effusion rates of ^3He and ^4He and thus the enrichment possible in a single effusion step.
b. How many effusion steps are necessary to yield 99.0% pure ^3He?

Answer: a. ratio of effusion rates = 1.15200; one step gives 0.000154% ^3He; b. 96 steps

Rates of Diffusion or Effusion

Graham’s law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have the same average kinetic energy. We can write the expression for the average kinetic energy of two gases with different molar masses:

$$KE = \frac{1}{2}\frac{M_\text{A}}{N_A}v^2_\text{rms,A} = \frac{1}{2}\frac{M_\text{B}}{N_A}v^2_\text{rms,B} \tag{5.7.6}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v^2_\text{rms,B}}{v^2_\text{rms,A}} = \frac{M_\text{A}}{M_\text{B}} \tag{5.7.7}$$

Taking the square root of both sides gives

$$\frac{v_\text{rms,B}}{v_\text{rms,A}} = \sqrt{\frac{M_\text{A}}{M_\text{B}}} \tag{5.7.8}$$

Thus the rate at which a molecule, or a mole of molecules, diffuses or effuses is directly related to the speed at which it moves. Equation 6.8.4 shows that Graham's law is a direct consequence of the fact that gaseous molecules at the same temperature have the same average kinetic energy.

Typically, gaseous molecules have a speed of hundreds of meters per second (hundreds of miles per hour). The effect of molar mass on these speeds is dramatic, as illustrated in Figure 5.7.3 for some common gases. Because all gases have the same average kinetic energy, according to the Boltzmann distribution, molecules with lower masses, such as hydrogen and helium, have a wider distribution of speeds.

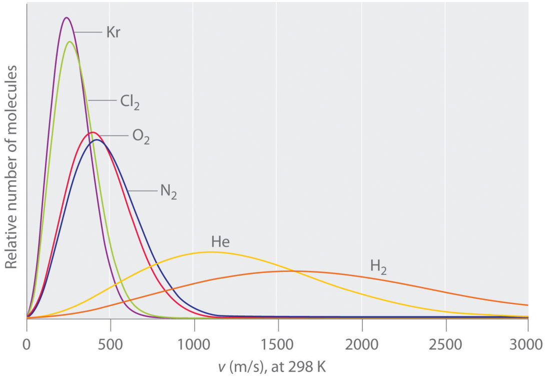


Figure 5.7.3: The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses

The lightest gases have a wider distribution of speeds and the highest average speeds.

Note

Molecules with lower masses have a wider distribution of speeds and a higher average speed.

Gas molecules do not diffuse nearly as rapidly as their very high speeds might suggest. If molecules actually moved through a room at hundreds of miles per hour, we would detect odors faster than we hear sound. Instead, it can take several minutes for us to detect an aroma because molecules are traveling in a medium with other gas molecules. Because gas molecules collide as often as 10^{10} times per second, changing direction and speed with each collision, they do not diffuse across a room in a straight line, as illustrated schematically in Figure 5.7.4.

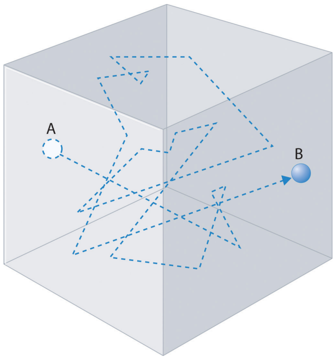


Figure 5.7.4: The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

The average distance traveled by a molecule between collisions is the mean free path. The denser the gas, the shorter the mean free path; conversely, as density decreases, the mean free path becomes longer because collisions occur less frequently. At 1 atm pressure and 25°C, for example, an oxygen or nitrogen molecule in the atmosphere travels only about 6.0×10^{-8} m (60 nm) between collisions. In the upper atmosphere at about 100 km altitude, where gas density is much lower, the mean free path is about 10 cm; in space between galaxies, it can be as long as 1×10^{10} m (about 6 million miles).

Note

The **denser** the gas, the **shorter** the mean free path.

Example 5.7.2

Calculate the rms speed of a sample of *cis*-2-butene (C_4H_8) at 20°C.

Given: compound and temperature

Asked for: rms speed

Strategy:

Calculate the molar mass of cis-2-butene. Be certain that all quantities are expressed in the appropriate units and then use Equation 6.8.5 to calculate the rms speed of the gas.

Solution:

To use Equation 6.8.4, we need to calculate the molar mass of *cis*-2-butene and make sure that each quantity is expressed in the appropriate units. Butene is C_4H_8, so its molar mass is 56.11 g/mol. Thus

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.3145 \ \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (20 + 273) \ \text{K}}{56.11 \times 10^{-3} \ \text{kg}}} = 361 \ \text{m/s} \tag{5.7.9}$$

or approximately 810 mi/h.

Exercise 5.7.2

Calculate the rms speed of a sample of radon gas at 23°C.

Answer: 1.82×10^2 m/s (about 410 mi/h)

The kinetic molecular theory of gases demonstrates how a successful theory can explain previously observed empirical relationships (laws) in an intuitively satisfying way. Unfortunately, the actual gases that we encounter are not “ideal,” although their behavior usually approximates that of an ideal gas. In Section 10.8, we explore how the behavior of real gases differs from that of ideal gases.

Graham’s law of Diffusion and Effusion: https://youtu.be/9HO-qgh-iGI

Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T, \tag{5.7.10}$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}, \tag{5.7.11}$$

- **Kinetic molecular theory of gases**:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \tag{5.7.12}$$

- **Graham's law for effusion:**

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_{\text{A}}}{M_{\text{B}}}} \tag{5.7.13}$$

Diffusion is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, **effusion** is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (**Graham's law**), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases. The **mean free path** of a molecule is the average distance it travels between collisions.

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5.10: Real Gases

Learning Objectives

- To recognize the differences between the behavior of an ideal gas and a real gas.
- To understand how molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (part (a) in Figure $5.10.1$). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (part (b) in Figure $5.10.1$).

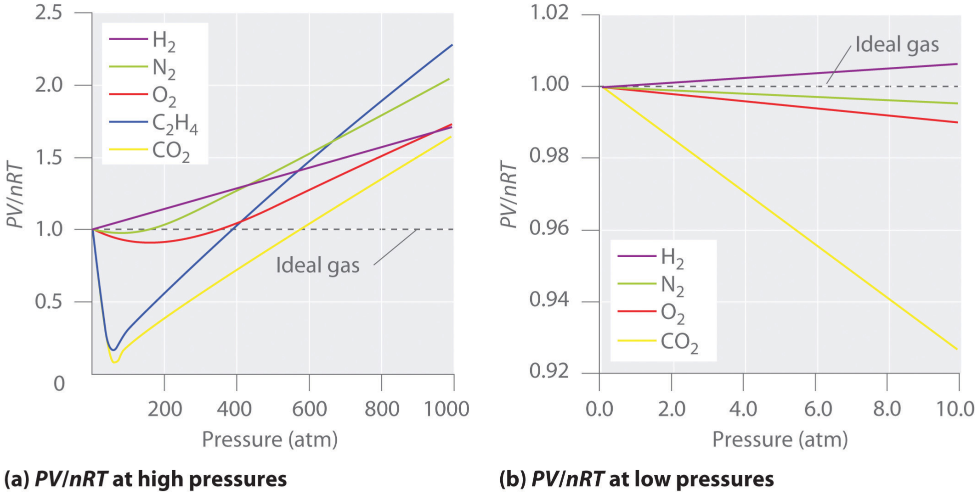


Figure 5.10.1: Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures. (a) In these plots of *PV*/*nRT* versus *P* at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.

Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure $5.10.2$ for N_2. Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

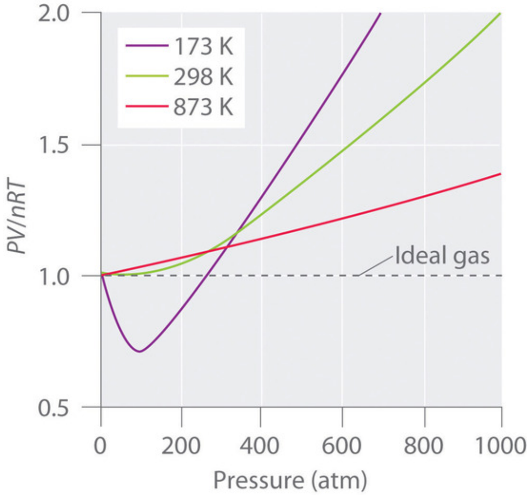


Figure 5.10.2: The Effect of Temperature on the Behavior of Real Gases. A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure $5.10.3$). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of *PV*/*nRT* is greater than the value predicted by the ideal gas law.

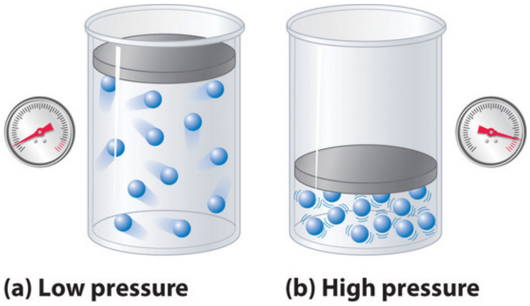


Figure 5.10.3: The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected. Thus as shown in Figure $5.10.2$, at low temperatures, the ratio of \(PV/nRT\) is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

> *Nonzero molecular volume makes the actual volume greater than predicted at high pressures; intermolecular attractions make the pressure less than predicted.*

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas behavior, the so-called *van der Waals* equation,

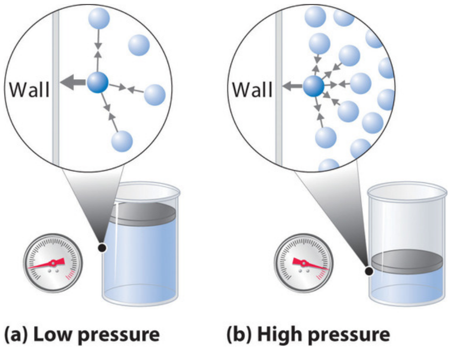
$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT \tag{5.10.1}$$

a and b are empirical constants that are different for each gas. The values of a and b are listed in Table $5.10.1$ for several common gases.

Table 5.10.1: van der Waals Constants for Some Common Gases (see Table A8 for more complete list)

Gas	a ((L^2·atm)/mol^2)	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

The pressure term in Equation 5.10.1 —$P+(an^2/V^2)$—corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure $5.10.4$. The volume term—$V-nb$—corrects for the volume occupied by the gaseous molecules.



(a) Low pressure **(b) High pressure**

Figure 5.10.4: The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on V and P, respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the an^2/V^2 term must be added to the measured pressure to correct for these effects.

✓ Example 5.10.1

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.00 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain *a* and *b* values for Cl_2 from Table $5.10.1$. Use the van der Waals equation to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$n=\frac{m}{M}=\frac{500\text{ g}}{70.906\text{ g/mol}}=7.052\text{ mol} \tag{5.10.2}$$

Using the ideal gas law and the temperature in kelvins (298 K), we calculate the pressure:

$$P=\frac{nRT}{V}=\frac{7.052\text{ mol}\times 0.08206\dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\times 298\text{ K}}{4.00\text{ L}}=43.1\text{ atm} \tag{5.10.3}$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the *a* and *b* values for Cl_2 from Table $5.10.1$. Solving for *P* gives

$$\begin{aligned}P&=\frac{nRT}{V-nb}-\frac{an^2}{V^2}\\&=\frac{7.052\text{ mol}\times 0.08206\dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\times 298\text{ K}}{4.00\text{ L}-7.052\text{ mol}\times 0.0542\dfrac{\text{L}}{\text{mol}}}-\frac{6.260\dfrac{\text{L}^2\text{atm}}{\text{mol}^2}\times(7.052\text{ mol})^2}{(4.00\text{ L})^2}\\&=28.2\text{ atm}\end{aligned}$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

? Exercise 5.10.1

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

a. ideal gas law.
b. van der Waals equation.

Answer: a. 77 atm; b. 67 atm

Liquefaction of Gases

Liquefaction of gases is the condensation of gases into a liquid form, which is neither anticipated nor explained by the kinetic molecular theory of gases. Both the theory and the ideal gas law predict that gases compressed to very high pressures and cooled to very low temperatures should still behave like gases, albeit cold, dense ones. As gases are compressed and cooled, however, they invariably condense to form liquids, although very low temperatures are needed to liquefy light elements such as helium (for He, 4.2 K at 1 atm pressure).

Liquefaction can be viewed as an extreme deviation from ideal gas behavior. It occurs when the molecules of a gas are cooled to the point where they no longer possess sufficient kinetic energy to overcome intermolecular attractive forces. The precise combination of temperature and pressure needed to liquefy a gas depends strongly on its molar mass and structure, with heavier and more complex molecules usually liquefying at higher temperatures. In general, substances with large van der Waals a coefficients are relatively easy to liquefy because large a coefficients indicate relatively strong intermolecular attractive interactions. Conversely, small molecules with only light elements have small a coefficients, indicating weak intermolecular interactions, and they are relatively difficult to liquefy. Gas liquefaction is used on a massive scale to separate O_2, N_2, Ar, Ne, Kr, and Xe. After a sample of air is liquefied, the mixture is warmed, and the gases are separated according to their boiling points.

> *A large value of a indicates the presence of relatively strong intermolecular attractive interactions.*

The ultracold liquids formed from the liquefaction of gases are called cryogenic liquids, from the Greek *kryo*, meaning “cold,” and *genes*, meaning “producing.” They have applications as refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.

Figure 5.10.5: A Liquid Natural Gas Transport Ship

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure $5.10.5$). Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are liquefied forms of hydrocarbons produced from natural gas or petroleum reserves. LNG consists mostly of methane, with small amounts of heavier hydrocarbons; it is prepared by cooling natural gas to below about −162°C. It can be stored in double-walled, vacuum-insulated containers at or slightly above atmospheric pressure. Because LNG occupies only about 1/600 the volume of natural gas, it is easier and more economical to transport. LPG is typically a mixture of propane, propene, butane, and butenes and is primarily used as a fuel for home heating. It is also used as a feedstock for chemical plants and as an inexpensive and relatively nonpolluting fuel for some automobiles.

Summary

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Deviations from ideal gas behavior can be seen in plots of PV/nRT versus P at a given temperature; for an ideal gas, PV/nRT versus $P = 1$ under all conditions. At high pressures, most real gases exhibit larger PV/nRT values than predicted by the ideal gas law, whereas at low pressures, most real gases exhibit PV/nRT values close to those predicted by the ideal gas law. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the **van der Waals equation**, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces. If the temperature of a gas is decreased sufficiently, **liquefaction** occurs, in which the gas condenses into a liquid form. Liquefied gases have many commercial applications, including the transport of large amounts of gases in small volumes and the uses of ultracold **cryogenic liquids**.

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5.11: Characteristics of Several Real Gases

Gases that deviate from ideality are known as Real Gases, which originate from two factors: (1) First, the theory assumes that as pressure increases, the volume of a gas becomes very small and approaches zero. While it does approach a small number, it will not be zero because molecules do occupy space (i.e. have volume) and cannot be compressed. (2) Intermolecular forces do exist in gases. These become increasingly important in low temperatures, when translational (definition of translational, please) molecular motion slows down, almost to a halt. However, at high temperatures, or even normal, every day temperatures, the intermolecular forces are very small and tend to be considered negligible.

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5.12: Chemistry in the Atmosphere

The earth's stratospheric ozone layer plays a critical role in absorbing ultraviolet radiation emitted by the sun. In the last thirty years, it has been discovered that stratospheric ozone is depleting as a result of anthropogenic pollutants. There are a number of chemical reactions that can deplete stratospheric ozone; however, some of the most significant of these involves the catalytic destruction of ozone by halogen radicals such as chlorine and bromine.

Introduction

The atmosphere of the Earth is divided into five layers. In order of closest and thickest to farthest and thinnest the layers are listed as follows: troposphere, stratosphere, mesosphere, thermosphere and exosphere. The majority of the ozone in the atmosphere resides in the stratosphere, which extends from six miles above the Earth's surface to 31 miles. Humans rely heavily on the absorption of ultraviolet B rays by the ozone layer because UV-B radiation causes skin cancer and can lead to genetic damage. The ozone layer has historically protected the Earth from the harmful UV rays, although in recent decades this protection has diminished due to stratospheric ozone depletion.

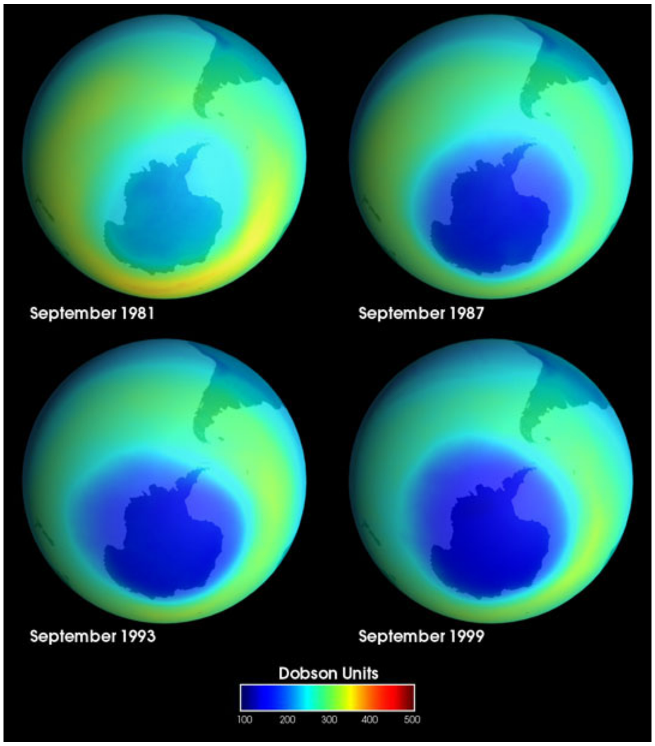

Figure courtesy of NASA.

Ozone depletion is largely a result of man-made substances. Humans have introduced gases and chemicals into the atmosphere that have rapidly depleted the ozone layer in the last century. This depletion makes humans more vulnerable to the UV-B rays which are known to cause skin cancer as well as other genetic deformities. The possibility of ozone depletion was first introduced by scientists in the late 1960's as dreams of super sonic transport began to become a reality. Scientists had long been aware that nitric oxide (NO) can catalytically react with ozone (O_3) to produce O_2 molecules; however, NO molecules produced at ground level have a half life far too short to make it into the stratosphere. It was not until the advent of commercial super sonic jets (which fly in the stratosphere and at an altitude much higher then conventional jets) that the potential for NO to react with stratospheric ozone became a possibility. The threat of ozone depletion from commercial super sonic transport was so great that it is often cited as the main reason why the US federal government pulled support for its development in 1971. Fear of ozone depletion was abated until 1974 when Sherwood Rowland and Mario Molina discovered that chlorofluorocarbons could be photolyzed by high energy photons in the stratosphere. They discovered that this process could releasing chlorine radicals that would catalytically react with O_3 and destroy the molecule. This process is called the Rowland-Molina theory of O_3 depletion.

The Chapman Cycle

The stratosphere is in a constant cycle with oxygen molecules and their interaction with ultraviolet rays. This process is considered a cycle because of its constant conversion between different molecules of oxygen. The ozone layer is created when ultraviolet rays react with oxygen molecules (O_2) to create ozone (O_3) and atomic oxygen (O). This process is called the *Chapman cycle*.

Step 1: An oxygen molecules is photolyzed by solar radiation, creating two oxygen radicals:

$$h\nu + O_2 \rightarrow 2O^{\cdot}$$

Step 2: Oxygen radicals then react with molecular oxygen to produce ozone:

$$O_2 + O^{\cdot} \rightarrow O_3$$

Step 3: Ozone then reacts with an additional oxygen radical to form molecular oxygen:

$$O_3 + O^{\cdot} \rightarrow 2O_2$$

Step 4: Ozone can also be recycled into molecular oxygen by reacting with a photon:

$$O_3 + h\nu \rightarrow O_2 + O^{\cdot}$$

It is important to keep in mind that ozone is constantly being created and destroyed by the Chapman cycle and that these reactions are natural processes, which have been taking place for millions of years. Because of this, the thickness the ozone layer at any particular time can vary greatly. It is also important to know that O_2 is constantly being introduced into the atmosphere through photosynthesis, so the ozone layer has the capability of regenerating itself.

Chemistry of Ozone Depletion

CFC molecules are made up of chlorine, fluorine and carbon atoms and are extremely stable. This extreme stability allows CFC's to slowly make their way into the stratosphere (most molecules decompose before they can cross into the stratosphere from the troposphere). This prolonged life in the atmosphere allows them to reach great altitudes where photons are more energetic. When the CFC's come into contact with these high energy photons, their individual components are freed from the whole. The following reaction displays how Cl atoms have an ozone destroying cycle:

$$Cl + O_3 \rightarrow ClO + O_2 \tag{step 1}$$

$$ClO + O^{\cdot} \rightarrow Cl + O_2 \tag{step 2}$$

$$O_3 + O^{\cdot} \rightarrow 2O_2 \tag{Overall reaction}$$

Chlorine is able to destroy so much of the ozone because it acts as a catalyst. Chlorine initiates the breakdown of ozone and combines with a freed oxygen to create two oxygen molecules. After each reaction, chlorine begins the destructive cycle again with another ozone molecule. One chlorine atom can thereby destroy thousands of ozone molecules. Because ozone molecules are being broken down they are unable to absorb any ultraviolet light so we experience more intense UV radiation at the earths surface.

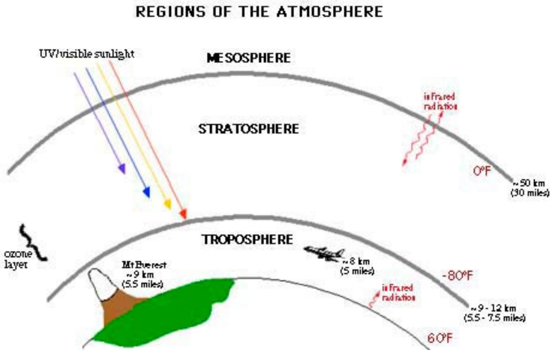

Figure courtesy of NOAA.

From 1985 to 1988, researchers studying atmospheric properties over the south pole continually noticed significantly reduced concentrations of ozone directly over the continent of Antarctica. For three years it was assumed that the ozone data was incorrect and was due to some type of instrument malfunction. In 1988, researchers finally realized their error and concluded that an enormous hole in the ozone layer had indeed developed over Antarctica. Examination of NASA satellite data later showed that the hole had begun to develop in the mid 1970's.

The ozone hole over Antarctica is formed by a slew of unique atmospheric conditions over the continent that combine to create an ideal environment for ozone destruction.

- Because Antarctica is surrounded by water, winds over the continent blow in a unique clockwise direction creating a so called "polar vortex" that effectively contains a single static air mass over the continent. As a result, air over Antarctica does not mix with air in the rest of the earth's atmosphere.
- Antarctica has the coldest winter temperatures on earth, often reaching -110 F. These chilling temperatures result in the formation of polar stratospheric clouds (PSC's) which are a conglomeration of frozen H_2O and HNO_3. Due to their extremely cold temperatures, PSC's form an electrostatic attraction with CFC molecules as well as other halogenated compounds

As spring comes to Antarctica, the PSC's melt in the stratosphere and release all of the halogenated compounds that were previously absorbed to the cloud. In the antarctic summer, high energy photons are able to photolyze the halogenated compounds, freeing halogen radicals that then catalytically destroy O_3. Because Antarctica is constantly surrounded by a polar vortex, radical halogens are not able to be diluted over the entire globe. The ozone hole develops as result of this process.

Resent research suggests that the strength of the polar vortex from any given year is directly correlated to the size of the ozone hole. In years with a strong polar vortex, the ozone hole is seen to expand in diameter, whereas in years with a weaker polar vortex, the ozone hole is noted to shrink

Ozone Depleting Substances

The following substances are listed as ozone depleting substances under Title VI of the United State Clean Air Act:

Table 5.12.1: Ozone Depleting Substances And Their Ozone-Depletion Potential. Taken directly from the Clean Air Act, as of June 2010.

Substance	Ozone- depletion potential
chlorofluorocarbon-11 (CFC–11)	1.0
chlorofluorocarbon-12 (CFC–12)	1.0
chlorofluorocarbon-13 (CFC–13)	1.0
chlorofluorocarbon-111 (CFC–111)	1.0
chlorofluorocarbon-112 (CFC–112)	1.0
chlorofluorocarbon-113 (CFC–113)	0.8
chlorofluorocarbon-114 (CFC–114)	1.0
chlorofluorocarbon-115 (CFC–115)	0.6
chlorofluorocarbon-211 (CFC–211)	1.0
chlorofluorocarbon-212 (CFC–212)	1.0
chlorofluorocarbon-213 (CFC–213)	1.0
chlorofluorocarbon-214 (CFC–214)	1.0
chlorofluorocarbon-215 (CFC–215)	1.0
chlorofluorocarbon-216 (CFC–216)	1.0
chlorofluorocarbon-217 (CFC–217)	1.0
halon-1211	3.0
halon-1301	10.0
halon-2402	6.0
carbon tetrachloride	1.1

Substance	Ozone- depletion potential
methyl chloroform	0.1
hydrochlorofluorocarbon-22 (HCFC–22)	0.05
hydrochlorofluorocarbon-123 (HCFC–123)	0.02
hydrochlorofluorocarbon-124 (HCFC–124)	0.02
hydrochlorofluorocarbon-141(b) (HCFC–141(b))	0.1
hydrochlorofluorocarbon-142(b) (HCFC–142(b))	0.06

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General Questions

- What are the causes of the depletion of our ozone layer?
  - the release of free radicals, the use of CFC's, the excessive burning of fossil fuels
- What is the chemical reaction that displays how ozone is created?
  - UV + O_2 -> 2O + heat, O_2 + O -> O_3, O_3 + O -> $2O_2$
- Which reactions demonstrate the destruction of the ozone layer?
  - Cl + O_3 ------> ClO + O_2 and ClO + O ------> Cl + O
- How do CFC's destroy the ozone layer?
  - the atomic chlorine freed from CFC reacts in a catalytic manner with ozone and atomic oxygen to make more oxygen molecules
- Why should regulations be enforced now in regards to pollution and harmful chemicals?
  - without regulation, the production and use of chemicals will run out of hand and do irreversible damage to the stratosphere
- What type of atom in the CFC molecule is most destructive to the ozone?
  - chlorine
- In which layer of the atmosphere does the ozone layer?
  - the stratosphere, the second closest to the Earth's surface
- What cycle is responsible for ozone in the stratosphere?
  - the Chapman cycle
- What factor is responsible for breaking up stable molecules?
  - ultraviolet rays from the sun

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CHAPTER OVERVIEW

9: Thermochemistry

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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9.1: The Nature of Energy

What is Energy?

Energy is one of the most fundamental and universal concepts of physical science, but one that is remarkably difficult to define in a way that is meaningful to most people. This perhaps reflects the fact that energy is not a “thing” that exists by itself, but is rather an attribute of matter (and also of electromagnetic radiation) that can manifest itself in different ways. It can be observed and measured only indirectly through its effects on matter that acquires, loses, or possesses it.

The concept that we call energy was very slow to develop; it took more than a hundred years just to get people to agree on the definitions of many of the terms we use to describe energy and the interconversion between its various forms. But even now, most people have some difficulty in explaining what it is; somehow, the definition we all learned in elementary science ("the capacity to do work") seems less than adequate to convey its meaning.

Although the term "energy" was not used in science prior to 1802, it had long been suggested that certain properties related to the motions of objects exhibit an endurance which is incorporated into the modern concept of "conservation of energy". In the 17th Century, the great mathematician Gottfried Leibnitz (1646-1716) suggested the distinction between *vis viva* ("live force") and *vis mortua* ("dead force"), which later became known as kinetic energy (1829) and potential energy (1853).

Kinetic energy and potential energy

Whatever energy may be, there are basically two kinds.

Kinetic energy is associated with the **motion** of an object, and its direct consequences are part of everyone's daily experience; the faster the ball you catch in your hand, and the heavier it is, the more you feel it. Quantitatively, a body with a mass m and moving at a velocity v possesses the kinetic energy $mv^2/2$.

✓ Example 1

A rifle shoots a 4.25 g bullet at a velocity of 965 m s^{-1}. What is its kinetic energy?

Solution

The only additional information you need here is that

$$1\text{ J} = 1\text{ kg m}^2\text{ s}^{-2}:$$

$$\text{KE} = ½ \times (.00425\text{ kg})\ (965\text{ m s}^{-1})^2 = 1980\text{ J}$$

Potential energy is energy a body has by virtue of its *location*. But there is more: the body must be subject to a "restoring force" of some kind that tends to move it to a location of lower potential energy. Think of an arrow that is subjected to the force from a stretched bowstring; the more tightly the arrow is pulled back against the string, the more potential energy it has.

More generally, the restoring force comes from what we call a *force field*— a gravitational, electrostatic, or magnetic field. We observe the consequences of *gravitational* potential energy all the time, such as when we walk, but seldom give it any thought.

If an object of mass m is raised off the floor to a height h, its potential energy increases by mgh, where g is a proportionality constant known as the *acceleration of gravity*; its value at the earth's surface is 9.8 m s^{-2}.

✓ Example 2

Find the change in potential energy of a 2.6 kg textbook that falls from the 66-cm height of a table top onto the floor.

Solution

$$\text{PE} = m\,g\,h = (2.6\text{ kg})(9.8\text{ m s}^{-2})(0.66\text{ m}) = 16.8\text{ kg m}^2\text{ s}^{-2} = 16.8\text{ J}$$

Similarly, the potential energy of a particle having an electric charge $q$depends on its location in an electrostatic field.

"Chemical energy"

Electrostatic potential energy plays a major role in chemistry; the potential energies of electrons in the force field created by atomic nuclei lie at the heart of the chemical behavior of atoms and molecules. "Chemical energy" usually refers to the energy that is stored in the chemical bonds of molecules. These bonds form when electrons are able to respond to the force fields created by two or more atomic nuclei, so they can be regarded as manifestations of electrostatic potential energy. In an **exothermic** chemical reaction, the electrons and nuclei within the reactants undergo rearrangement into products possessing lower energies, and the difference is released to the environment in the form of heat.

Interconversion of potential and kinetic energy

Transitions between potential and kinetic energy are such an intimate part of our daily lives that we hardly give them a thought. It happens in walking as the body moves up and down. Our bodies utilize the chemical energy in glucose to keep us warm and to move our muscles. In fact, life itself depends on the conversion of chemical energy to other forms.

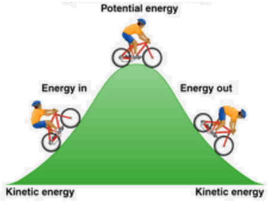

Figure: Conservation of energy applied to a bicyclist and a hill.

Energy is conserved: it can neither be created nor destroyed. So when you go uphill, your kinetic energy is transformed into potential energy, which gets changed back into kinetic energy as you coast down the other side. And where did the kinetic energy you expended in peddling uphill come from? By conversion of some of the chemical potential energy in your breakfast cereal.

- When drop a book, its potential energy is transformed into kinetic energy. When it strikes the floor, this transformation is complete. What happens to the energy then? The kinetic energy that at the moment of impact was formerly situated exclusively in the moving book, now becomes shared between the book and the floor, and in the form of randomized thermal motions of the molecular units of which they are made; we can observe this effect as a rise in temperature.
- Much of the potential energy of falling water can be captured by a water wheel or other device that transforms the kinetic energy of the exit water into kinetic energy. The output of a hydroelectric power is directly proportional to its height above the level of the generator turbines in the valley below. At this point, the kinetic energy of the exit water is transferred to that of the turbine, most of which (up to 90 percent in the largest installations) is then converted into electrical energy.
- Will the temperature of the water at the bottom of a water fall be greater than that at the top? James Joule himself predicted that it would be. It has been calculated that at Niagara falls, that complete conversion of the potential energy of 1 kg of water at the top into kinetic energy when it hits the plunge pool 58 meters below will result in a temperature increase of about 0.14 C°. (But there are lots of complications. For example, some of the water breaks up into tiny droplets as it falls, and water evaporates from droplets quite rapidly, producing a cooling effect.)
- Chemical energy can also be converted, at least partially, into electrical energy: this is what happens in a battery. If a highly exothermic reaction also produces gaseous products, the latter may expand so rapidly that the result is an explosion — a net conversion of chemical energy into kinetic energy (including sound).

Thermal energy

Kinetic energy is associated with motion, but in two different ways. For a macroscopic object such as a book or a ball, or a parcel of flowing water, it is simply given by $\frac{1}{2} mv^2$. However, as we mentioned above, when an object is dropped onto the floor, or when an exothermic chemical reaction heats surrounding matter, the kinetic energy gets dispersed into the molecular units in the environment. This "microscopic" form of kinetic energy, unlike that of a speeding bullet, is completely random in the kinds of motions it exhibits and in its direction. We refer to this as "thermalized" kinetic energy, or more commonly simply as *thermal energy*. We observe the effects of this as a rise in the temperature of the surroundings. The temperature of a body is direct measure of the quantity of thermal energy is contains.

Thermal energy is never completely recoverable

Once kinetic energy is thermalized, only a portion of it can be converted back into potential energy. The remainder simply gets dispersed and diluted into the environment, and is effectively lost.

To summarize, then:

- Potential energy can be converted entirely into kinetic energy..
- Potential energy can also be converted, with varying degrees of efficiency,into electrical energy.

- The kinetic energy of macroscopic objects can be transferred between objects (barring the effects of friction).
- Once kinetic energy becomes thermalized, only a portion of it can be converted back into either potential energy or be concentrated back into the kinetic energy of a macroscopic. This limitation, which has nothing to do with technology but is a fundamental property of nature, is the subject of the second law of thermodynamics.
- A device that is intended to accomplish the partial transformation of thermal energy into organized kinetic energy is known as a *heat engine*.

Energy scales are always arbitrary

You might at first think that a book sitting on the table has zero kinetic energy since it is not moving. But if you think about it, the earth itself is moving; it is spinning on its axis, it is orbiting the sun, and the sun itself is moving away from the other stars in the general expansion of the universe. Since these motions are normally of no interest to us, we are free to adopt an arbitrary scale in which the velocity of the book is measured with respect to the table; on this so-called *laboratory coordinate system*, the kinetic energy of the book can be considered zero.

We do the same thing with potential energy. If the book is on the table, its potential energy with respect to the surface of the table will be zero. If we adopt this as our zero of potential energy, and then push the book off the table, its potential energy will be negative after it reaches the floor.

Energy units

Energy is measured in terms of its ability to perform work or to transfer heat. Mechanical work is done when a force f displaces an object by a distance *d*:

$$w = f \times d \tag{9.1.1}$$

The basic unit of energy is the *joule*. One joule is the amount of work done when a force of 1 newton acts over a distance of 1 m; thus 1 J = 1 N-m. The newton is the amount of force required to accelerate a 1-kg mass by 1 m/sec^2, so the basic dimensions of the joule are kg m^2 s^{-2}. The other two units in wide use. the *calorie* and the *BTU* (British thermal unit) are defined in terms of the heating effect on water. Because of the many forms that energy can take, there are a correspondingly large number of units in which it can be expressed, a few of which are summarized below.

1 calorie will raise the temperature of 1 g of water by 1 C°. The “dietary” calorie is actually 1 kcal. An average young adult expends about 1800 kcal per day just to stay alive. (you should know this definition)	1 cal = 4.184 J
1 BTU (British Thermal Unit) will raise the temperature of 1 lb of water by 1F°.	1 BTU = 1055 J
The erg is the c.g.s. unit of energy and a very small one; the work done when a 1-dyne force acts over a distance of 1 cm.	1 J = 10^7 ergs 1 erg = 1 d-cm = 1 g cm^2 s^{-2}
The electron-volt is even tinier: 1 eV is the work required to move a unit electric charge (1 C) through a potential difference of 1 volt.	1 J = 6.24 × 1018 eV
The watt is a unit of power, which measures the rate of energy flow in J sec^{-1}. Thus the watt-hour is a unit of energy. An average human consumes energy at a rate of about 100 watts; the brain alone runs at about 5 watts.	1 J = 2.78 × 10^{-4}watt-hr 1 w-h = 3.6 kJ
The liter-atmosphere is a variant of force-displacement work associated with volume changes in gases.	1 L-atm = 101.325 J
The huge quantities of energy consumed by cities and countries are expressed in quads; the therm is a similar but smaller unit.	1 quad = 1015 Btu = 1.05 × 10^{18} J
If the object is to obliterate cities or countries with nuclear weapons, the energy unit of choice is the ton of TNT equivalent.	1 ton of TNT = 4.184 GJ (by definition)

In terms of fossil fuels, we have barrel-of-oil equivalent, cubic-meter-of-natural gas equivalent, and ton-of-coal equivalent.	1 bboe = 6.1 GJ 1 cmge = 37-39 mJ 1 toce = 29 GJ

Heat and Work

Heat and work are both measured in energy units, so they must both represent energy. How do they differ from each other, and from just plain “energy” itself? In our daily language, we often say that "this object contains a lot of heat", but this is gibberish in thermodynamics terms, although it is ok to say that the object is "hot", indicating that its temperature is high. The term "heat" has a special meaning in thermodynamics: it is a *process* in which a body (the contents of a tea kettle, for example) acquires or loses energy as a direct consequence of its having a *different temperature* than its surroundings. Hence, thermal energy can only flow from a higher temperature to a lower temperature. It is this flow that constitutes "heat". Use of the term "flow" of heat recalls the incorrect 18th-century notion that heat is an actual substance called “caloric” that could flow like a liquid.

Note: Heat

We often say that "this object contains a lot of heat," however, this makes no sense since heat represents an energy transfer.

Transfer of thermal energy can be accomplished by bringing two bodies into physical contact (the kettle on top of the stove, or through an electric heating element inside the kettle). Another mechanism of thermal energy transfer is by radiation; a hot object will convey energy to any body in sight of it via electromagnetic radiation in the infrared part of the spectrum. In many cases, both modes will be active.

Work refers to the transfer of energy some means that does not depend on temperature difference. Work, like energy, can take various forms, the most familiar being mechanical and electrical.

- *Mechanical work* arises when an object moves a distance Δx against an opposing force f:

$$w = f \, \Delta x \tag{9.1.2}$$

- *Electrical work* is done when a body having a charge q moves through a potential difference ΔV.

Note: Work

A transfer of energy to or from a system by any means other than heat is called “work”.

Work can be completely converted into heat (by friction, for example), but heat can only be partially converted to work. **Conversion of heat into work** is accomplished by means of a *heat engine*, the most common example of which is an ordinary gasoline engine. The science of thermodynamics developed out of the need to understand the limitations of steam-driven heat engines at the beginning of the Industrial Age. The Second Law of Thermodynamics, states that the complete conversion of heat into work is impossible. Something to think about when you purchase fuel for your car!

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9.2: Enthalpy

the-mole-and-avogadro-s-number

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9.3: Calorimetry

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9.5: Hess's Law

Hess's Law of Constant Heat Summation (or just **Hess's Law**) states that regardless of the multiple stages or steps of a reaction, the total enthalpy change for the reaction is the sum of all changes. This law is a manifestation that enthalpy is a state function.

Introduction

Hess's Law is named after Russian Chemist and Doctor Germain Hess. Hess helped formulate the early principles of thermochemistry. His most famous paper, which was published in 1840, included his law on thermochemistry. Hess's law is due to enthalpy being a state function, which allows us to calculate the overall change in enthalpy by simply summing up the changes for each step of the way, until product is formed. All steps have to proceed at the same temperature and the equations for the individual steps must balance out. The principle underlying Hess's law does not just apply to Enthalpy and can be used to calculate other state functions like changes in Gibbs' Energy and Entropy.

Definition: Hess's Law

The heat of any reaction ΔH°_{f} for a specific reaction is equal to the sum of the heats of reaction for any set of reactions which in sum are equivalent to the overall reaction:

(Although we have not considered the restriction, applicability of this law requires that all reactions considered proceed under similar conditions: we will consider all reactions to occur at constant pressure.)

Application

Hydrogen gas, which is of potential interest nationally as a clean fuel, can be generated by the reaction of carbon (coal) and water:

$$C_{(s)} + 2H_2O_{(g)} \rightarrow CO_{2\,(g)} + 2H_{2\,(g)} \tag{2}$$

Calorimetry reveals that this reaction requires the input of 90.1 kJ of heat for every mole of $C_{(s)}$ consumed. By convention, when heat is absorbed during a reaction, we consider the quantity of heat to be a positive number: in chemical terms, $q > 0$ for an endothermic reaction. When heat is evolved, the reaction is exothermic and $q < 0$ by convention.

It is interesting to ask where this input energy goes when the reaction occurs. One way to answer this question is to consider the fact that the reaction converts one fuel, $C_{(s)}$, into another, $H_{2(g)}$. To compare the energy available in each fuel, we can measure the heat evolved in the combustion of each fuel with one mole of oxygen gas. We observe that

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{3}$$

produces $393.5\,kJ$ for one mole of carbon burned; hence $q = -393.5\,kJ$. The reaction

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{4}$$

produces 483.6 kJ for two moles of hydrogen gas burned, so q=-483.6 kJ. It is evident that more energy is available from combustion of the hydrogen fuel than from combustion of the carbon fuel, so it is not surprising that conversion of the carbon fuel to hydrogen fuel requires the input of energy. Of considerable importance is the observation that the heat input in equation [2], 90.1 kJ, is exactly equal to the difference between the heat evolved, -393.5 kJ, in the combustion of carbon and the heat evolved, -483.6 kJ, in the combustion of hydrogen. This is not a coincidence: if we take the combustion of carbon and add to it the reverse of the combustion of hydrogen, we get

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{9.5.1}$$

$$2H_2O_{(g)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{9.5.2}$$

$$C_{(s)} + O_{2(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 2H_{2(g)} + O_{2(g)} \tag{5}$$

Canceling the $O_{2(g)}$ from both sides, since it is net neither a reactant nor product, equation [5] is equivalent to equation [2]. Thus, taking the combustion of carbon and "subtracting" the combustion of hydrogen (or more accurately, adding the reverse of the combustion of hydrogen) yields equation [2]. And, the heat of the combustion of carbon minus the heat of the combustion of hydrogen equals the heat of equation [2]. By studying many chemical reactions in this way, we discover that this result, known as Hess's Law, is general.

Why it works

A pictorial view of Hess's Law as applied to the heat of equation [2] is illustrative. In figure 1, the reactants C(s) + 2 H_2O(g) are placed together in a box, representing the state of the materials involved in the reaction prior to the reaction. The products CO_2(g) + 2 H_2(g) are placed together in a second box representing the state of the materials involved after the reaction. The reaction arrow connecting these boxes is labeled with the heat of this reaction. Now we take these same materials and place them in a third box containing C(s), O_2(g), and 2 H_2(g). This box is connected to the reactant and product boxes with reaction arrows, labeled by the heats of reaction in equation [3] and equation [4].

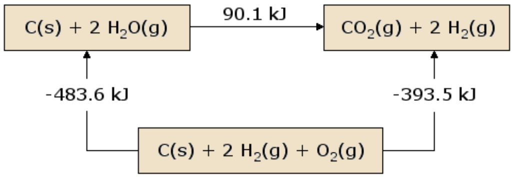

Figure 1: A Pictorial View of Hess's Law.

This picture of Hess's Law reveals that the heat of reaction along the "path" directly connecting the reactant state to the product state is exactly equal to the total heat of reaction along the alternative "path" connecting reactants to products via the intermediate state containing $C_{(s)}$, $O_{2(g)}$, and 2 $H_{2(g)}$. A consequence of our observation of Hess's Law is therefore that the net heat evolved or absorbed during a reaction is independent of the path connecting the reactant to product (this statement is again subject to our restriction that all reactions in the alternative path must occur under constant pressure conditions).

A slightly different view of figure 1 results from beginning at the reactant box and following a complete circuit through the other boxes leading back to the reactant box, summing the net heats of reaction as we go. We discover that the net heat transferred (again provided that all reactions occur under constant pressure) is exactly zero. This is a statement of the conservation of energy: the energy in the reactant state does not depend upon the processes which produced that state. Therefore, we cannot extract any energy from the reactants by a process which simply recreates the reactants. Were this not the case, we could endlessly produce unlimited quantities of energy by following the circuitous path which continually reproduces the initial reactants.

By this reasoning, we can define an energy function whose value for the reactants is independent of how the reactant state was prepared. Likewise, the value of this energy function in the product state is independent of how the products are prepared. We choose this function, H, so that the change in the function, $\Delta H = H_{products} - H_{reactants}$, is equal to the heat of reaction q under constant pressure conditions. H, which we call the enthalpy, is a state function, since its value depends only on the state of the materials under consideration, that is, the temperature, pressure and composition of these materials.

The concept of a state function is somewhat analogous to the idea of elevation. Consider the difference in elevation between the first floor and the third floor of a building. This difference is independent of the path we choose to get from the first floor to the third floor. We can simply climb up two flights of stairs, or we can climb one flight of stairs, walk the length of the building, then walk a second flight of stairs. Or we can ride the elevator. We could even walk outside and have a crane lift us to the roof of the building, from which we climb down to the third floor. Each path produces exactly the same elevation gain, even though the distance traveled is significantly different from one path to the next. This is simply because the elevation is a "state function". Our elevation, standing on the third floor, is independent of how we got to the third floor, and the same is true of the first floor. Since the elevation thus a state function, the elevation gain is independent of the path. Now, the existence of an energy state function H is of considerable importance in calculating heats of reaction. Consider the prototypical reaction in subfigure 2.1, with reactants R being converted to products P. We wish to calculate the heat absorbed or released in this reaction, which is ΔH. Since H is a state function, we can follow any path from R to P and calculate ΔH along that path. In subfigure 2.2, we consider one such possible path, consisting of two reactions passing through an intermediate state containing all the atoms involved in the reaction, each in elemental form. This is a useful intermediate state since it can be used for any possible chemical reaction. For example, in figure 1, the atoms involved in the reaction are C, H, and O, each of which are represented in the intermediate state in elemental form. We can see in subfigure 2.2 that the ΔH for the overall reaction is now the difference between the ΔH in the formation of the products P from the elements and the ΔH in the formation of the reactants R from the elements.

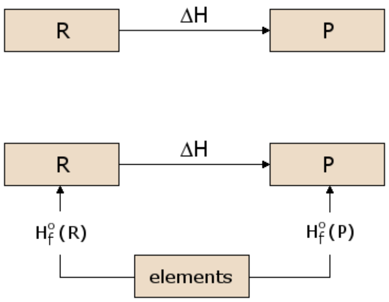

Figure 2: Calculation of ΔH.

The ΔH values for formation of each material from the elements are thus of general utility in calculating ΔH for any reaction of interest. We therefore define the standard formation reaction for reactant R, as

elements in standard state → R

and the heat involved in this reaction is the standard enthalpy of formation, designated by $\Delta H_f°$. The subscript f, standing for "formation," indicates that the ΔH is for the reaction creating the material from the elements in standard state. The superscript ° indicates that the reactions occur under constant standard pressure conditions of 1 atm. From subfigure 2.2, we see that the heat of any reaction can be calculated from

$$\Delta H_f^\circ = \Delta H^\circ_{f,products} - \Delta H^\circ_{f,reactants} \tag{6}$$

Extensive tables of $\Delta H°_f$ values (Table T1) have been compiled that allows us to calculate with complete confidence the heat of reaction for any reaction of interest, even including hypothetical reactions which may be difficult to perform or impossibly slow to react.

✓ Example 1

The enthalpy of a reaction does not depend on the elementary steps, but on the final state of the products and initial state of the reactants. Enthalpy is an extensive property and hence changes when the size of the sample changes. This means that the enthalpy of the reaction scales proportionally to the moles used in the reaction. For instance, in the following reaction, one can see that doubling the molar amounts simply doubles the enthalpy of the reaction.

$$H_2\ (g) + 1/2O_2\ (g) \rightarrow H_2O\ (g)\ \Delta H° = -572\ kJ$$

$$2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (g)\ \Delta H° = -1144kJ$$

The sign of the reaction enthalpy changes when a process is reversed.

$$H_2\ (g) + 1/2O_2\ (g) \rightarrow H_2O\ (g)\ \Delta H° = -572\ kJ$$

When switched:

$$H_2O\ (g) \rightarrow H_2\ (g) + 1/2O_2\ (g)\ \Delta H° = +572\ kJ$$

Since enthalpy is a state function, it is path independent. Therefore, it does not matter what reactions one uses to obtain the final reaction.

Contributors and Attributions

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9.6: Standard Enthalpies of Formation

Standard Enthalpy Of Formation?highlight=standard enthalpy

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9.7: Present Sources of Energy

Wikipedia Link: Energy Development

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CHAPTER OVERVIEW

12: Atomic Theory and Quantum Mechanics

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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12.1: Electromagnetic Radiation

As you read the print off this computer screen now, you are reading pages of fluctuating energy and magnetic fields. Light, electricity, and magnetism are all different forms of electromagnetic radiation.

Introduction

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. The electric and magnetic fields come at right angles to each other and combined wave moves perpendicular to both magnetic and electric oscillating fields thus the disturbance. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum. These electric and magnetic waves travel perpendicular to each other and have certain characteristics, including amplitude, wavelength, and frequency.

General Properties of all electromagnetic radiation:

1. Electromagnetic radiation can travel through empty space. Most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through in order to be heard.
2. The speed of light is always a constant. (Speed of light : 2.99792458 x 10^8 m s^{-1})
3. Wavelengths are measured between the distances of either crests or troughs. It is usually characterized by the Greek symbol λ.

Waves and their Characteristics

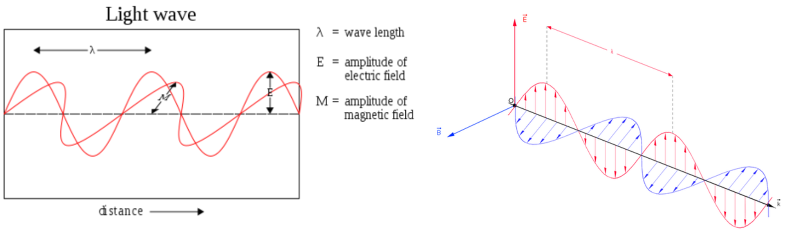

Fig. 1 & 2: Electromagnetic Waves

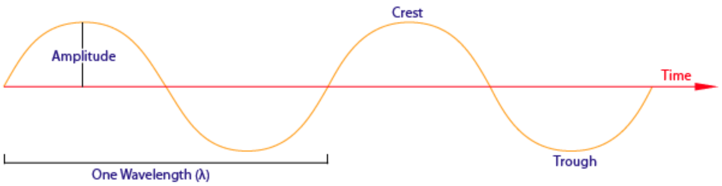

Fig. 3: An EM Wave

Amplitude

Amplitude is the distance from the maximum vertical displacement of the wave to the middle of the wave. This measures the magnitude of oscillation of a particular wave. In short, the amplitude is basically the height of the wave. Larger amplitude means higher energy and lower amplitude means lower energy. Amplitude is important because it tells you the intensity or brightness of a wave in comparison with other waves.

Wavelength

Wavelength (λ) is the distance of one full cycle of the oscillation. Longer wavelength waves such as radio waves carry low energy; this is why we can listen to the radio without any harmful consequences. Shorter wavelength waves such as x-rays carry higher energy that can be hazardous to our health. Consequently lead aprons are worn to protect our bodies from harmful radiation when we undergo x-rays. This wavelength frequently relationship is characterized by:

$$c = \lambda \nu \tag{12.1.1}$$

where

- c is the speed of light,
- λ is wavelength, and
- ν is frequency.

Shorter wavelength means greater frequency, and greater frequency means higher energy. Wavelengths are important in that they tell one what type of wave one is dealing with.

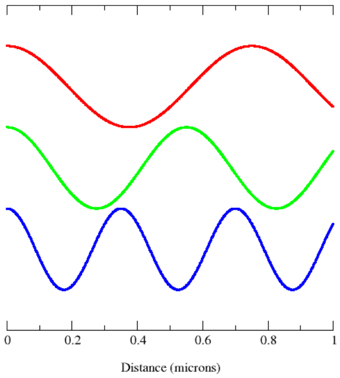

Fig. 4: Different Wavelengths and Frequencies

Remember, **Wavelength tells you the type of light** and **Amplitude tells you about the intensity of the light**

Frequency

Frequency is defined as the number of cycles per second, and is expressed as sec^{-1} or Hertz (Hz). Frequency is directly proportional to energy and can be express as:

$$E = h\nu \tag{12.1.2}$$

where

- E is energy,
- h is Planck's constant, (h= 6.62607 x 10^{-34} J), and
- ν is frequency.

Period

Period (T) is the amount of time a wave takes to travel one wavelength; it is measured in seconds (s).

Velocity

The velocity of wave in general is expressed as:

$$velocity = \lambda\nu \tag{12.1.3}$$

For Electromagnetic wave, the velocity in vacuum is $2.99 \times 10^8\ m/s$ or $186,282$miles/second.

Electromagnetic spectrum

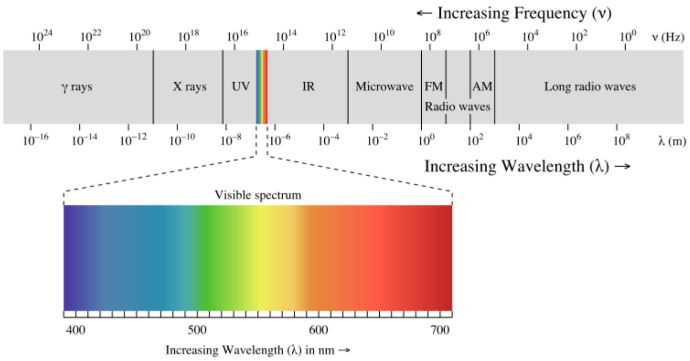

***Figure 24.5.1**: Electromagnetic spectrum with light highlighted. from Wikipedia.*

As a wave’s wavelength increases, the frequency decreases, and as wave’s wavelength decreases, the frequency increases. When electromagnetic energy is released as the energy level increases, the wavelength decreases and frequency decreases. Thus, electromagnetic radiation is then grouped into categories based on its wavelength or frequency into the electromagnetic spectrum. The different types of electromagnetic radiation shown in the electromagnetic spectrum consists of radio waves, microwaves, infrared waves, visible light, ultraviolet radiation, X-rays, and gamma rays. The part of the electromagnetic spectrum that we are able to see is the visible light spectrum.

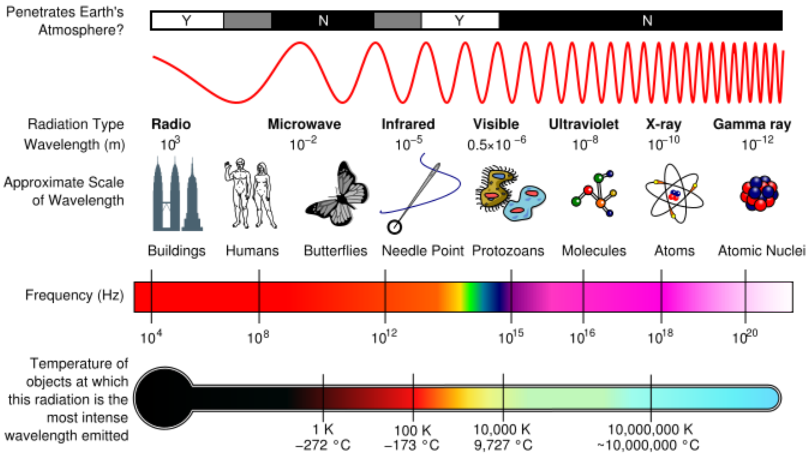

Fig. 6: Electromagnetic Spectrum with Radiation Types

Radiation Types

Radio Waves are approximately 10^3 m in wavelength. As the name implies, radio waves are transmitted by radio broadcasts, TV broadcasts, and even cell phones. Radio waves have the lowest energy levels. Radio waves are used in remote sensing, where hydrogen gas in space releases radio energy with a low frequency and is collected as radio waves. They are also used in radar systems, where they release radio energy and collect the bounced energy back. Especially useful in weather, radar systems are used to can illustrate maps of the surface of the Earth and predict weather patterns since radio energy easily breaks through the atmosphere. ;

Microwaves can be used to broadcast information through space, as well as warm food. They are also used in remote sensing in which microwaves are released and bounced back to collect information on their reflections.

Microwaves can be measured in centimeters. They are good for transmitting information because the energy can go through substances such as clouds and light rain. Short microwaves are sometimes used in Doppler radars to predict weather forecasts.

Infrared radiation can be released as heat or thermal energy. It can also be bounced back, which is called near infrared because of its similarities with visible light energy. Infrared Radiation is most commonly used in remote sensing as infrared sensors collect thermal energy, providing us with weather conditions.

This picture represents a snap shot in mid-infrared light.

Visible Light is the only part of the electromagnetic spectrum that humans can see with an unaided eye. This part of the spectrum includes a range of different colors that all represent a particular wavelength. Rainbows are formed in this way; light passes through matter in which it is absorbed or reflected based on its wavelength. Thus, some colors are reflected more than other, leading to the creation of a rainbow.

Color Region	Wavelength (nm)

Violet	380-435
Blue	435-500
Cyan	500-520
Green	520-565
Yellow	565-590
Orange	590-625
Red	625-740

Fig. 7: The color regions of the Visible Spectrum

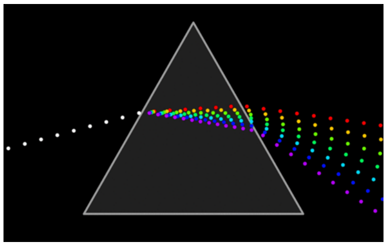

Fig. 8: Dispersion of Light Through A Prism

Ultraviolet, Radiation, X-Rays, and Gamma Rays are all related to events occurring in space. UV radiation is most commonly known because of its severe effects on the skin from the sun, leading to cancer. X-rays are used to produce medical images of the body. Gamma Rays can used in chemotherapy in order to rid of tumors in a body since it has such a high energy level. The shortest waves, Gamma rays, are approximately 10^{-12} m in wavelength. Out this huge spectrum, the human eyes can only detect waves from 390 nm to 780 nm.

Equations of Waves

The mathematical description of a wave is:

$$y = A\sin(kx - \omega t) \tag{12.1.4}$$

where A is the amplitude, k is the wave number, x is the displacement on the x-axis.

$$k = \frac{2\pi}{\lambda} \tag{12.1.5}$$

where λ is the wavelength. Angular frequency described as:

$$\omega = 2\pi\nu = \frac{2\pi}{T} \tag{12.1.6}$$

where ν is frequency and period (T) is the amount of time for the wave to travel one wavelength.

Interference

An important property of waves is the ability to combine with other waves. There are two type of interference: constructive and destructive. Constructive interference occurs when two or more waves are in phase and and their displacements add to produce a higher amplitude. On the contrary, destructive interference occurs when two or more waves are out of phase and their displacements negate each other to produce lower amplitude.

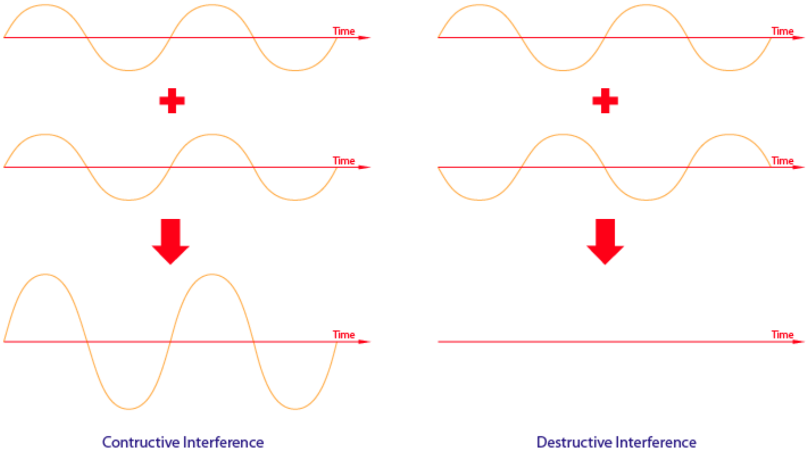

Figure 9 & 10: Constructive and Destructive Interference

Interference can be demonstrated effectively through the double slit experiment. This experiment consists of a light source pointing toward a plate with one slit and a second plate with two slits. As the light travels through the slits, we notice bands of alternating intensity on the wall behind the second plate. The banding in the middle is the most intense because the two waves are perfectly in phase at that point and thus constructively interfere. The dark bands are caused by out of phase waves which result in destructive interference. This is why you observe nodes on figure 4. In a similar way, if electrons are used instead of light, electrons will be represented both as waves and particles.

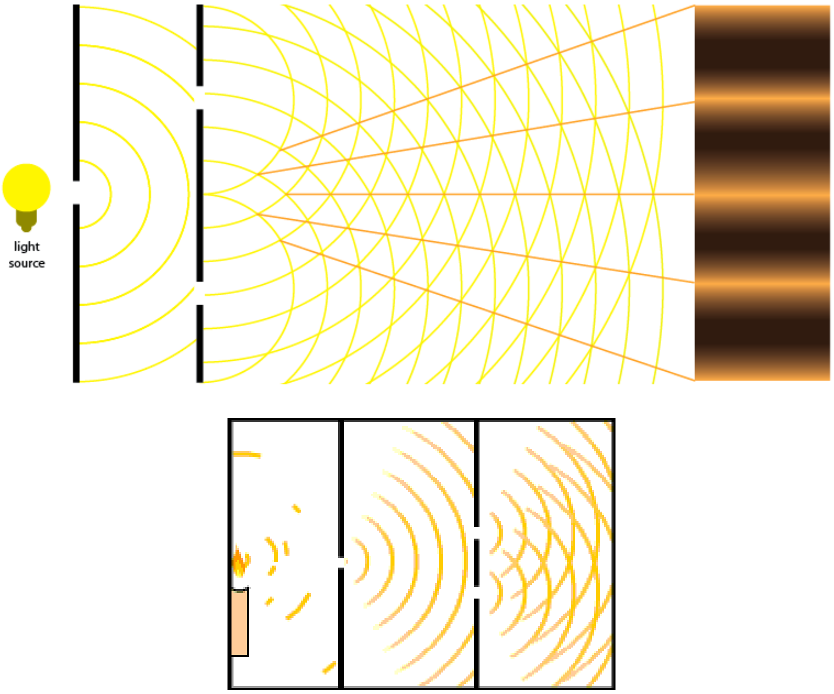

Fig. 11 & 12: Double-Slit Interference Experiment

Wave-Particle Duality

Electromagnetic radiation can either acts as a wave or a particle, a photon. As a wave, it is represented by velocity, wavelength, and frequency. Light is an EM wave since the speed of EM waves is the same as the speed of light. As a particle, EM is represented as a photon, which transports energy. When a photon is absorbed, the electron can be moved up or down an energy level. When it moves up, it absorbs energy, when it moves down, energy is released. Thus, since each atom has its own distinct set of energy levels, each element emits and absorbs different frequencies. Photons with higher energies produce shorter wavelengths and photons with lower energies produce longer wavelengths.

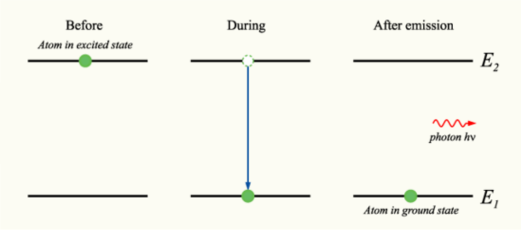

Fig. 13: Photon Before and After Emission

Ionizing and Non-Ionizing Radiation

Electromagnetic Radiation is also categorized into two groups based, ionizing and non-ionizing, on the severity of the radiation. Ionizing radiation holds a great amount of energy to remove electrons and cause the matter to become ionized. Thus, higher frequency waves such as the X-rays and gamma-rays have ionizing radiation. However, lower frequency waves such as radio waves, do not have ionizing radiation and are grouped as non-ionizing.

Electromagnetic Radiation and Temperature

Electromagnetic radiation released is related to the temperature of the body. Stephan-Boltzmann Law says that if this body is a black body, one which perfectly absorbs and emits radiation, the radiation released is equal to the temperature raised to the fourth power. Therefore, as temperature increases, the amount of radiation released increases greatly. Objects that release radiation very well also absorb radiation at certain wavelengths very well. This is explained by the Kirchhoff's Law. Wavelengths are also related to temperature. As the temperature increases, the wavelength of maximum emission decreases.

Problems

1. What is the wavelength of a wave with a frequency of 4.28 Hz?
2. What is the frequency of a wave with a wavelength of 200 cm?
3. What is the frequency of a wave with a wavelength of 500 pm?
4. What is the wavelength of a wave with a frequency of 2.998×10^5 Hz?
5. A radio transmits a frequency of 100 Hz. What is the wavelength of this wave?

Answers:

1. 700m
2. 1.5×10^8 Hz
3. 4.0×10^{17} Hz
4. 100m
5. 2.998×10^6 m

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12.2: The Nature of Matter

In 1923, Louis de Broglie, a French physicist, proposed a hypothesis to explain the theory of the atomic structure.By using a series of substitution de Broglie hypothesizes particles to hold properties of waves. Within a few years, de Broglie's hypothesis was tested by scientists shooting electrons and rays of lights through slits. What scientists discovered was the electron stream acted the same was as light proving de Broglie correct.

Contributors and Attributions

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12.3: The Atomic Spectrum of Hydrogen

A hydrogen discharge tube is a slim tube containing hydrogen gas at low pressure with an electrode at each end. If a high voltage (5000 volts) is applied, the tube lights up with a bright pink glow. If the light is passed through a prism or diffraction grating, it is split into its various colors. This is a small part of the hydrogen emission spectrum. Most of the spectrum is invisible to the eye because it is either in the infrared or the ultraviolet region of the electromagnetic spectrum.

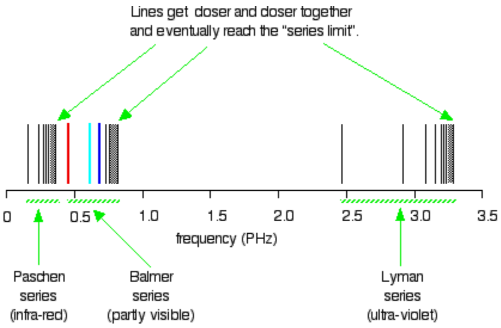
The photograph shows part of a hydrogen discharge tube on the left, and the three most apparent lines in the visible part of the spectrum on the right. (Ignore the "smearing," particularly to the left of the red line. This is caused by flaws in the way the photograph was taken. See note below.)

This photograph is by courtesy of Dr Rod Nave of the Department of Physics and Astronomy at Georgia State University, Atlanta.

Extending hydrogen's emission spectrum into the UV and IR

The hydrogen spectrum is complex, comprising more than the three lines visible to the naked eye. It is possible to detect patterns of lines in both the ultraviolet and infrared regions of the spectrum as well. These fall into a number of "series" of lines named after the person who discovered them. The diagram below shows three of these series, but there are others in the infrared to the left of the Paschen series shown in the diagram.

The diagram is quite complicated. Consider first at the Lyman series on the right of the diagram; this is the broadest series, and the easiest to decipher.



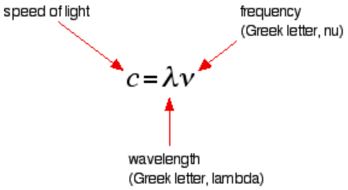
The frequency scale is marked in PHz—petaHertz. Peta means "10^{15} times". The value 3 PHz is equal to 3×10^{15} Hz. The quantity "hertz" indicates "cycles per second".

The Lyman series is a series of lines in the ultraviolet region. The lines grow closer and closer together as the frequency increases. Eventually, they are so close together that it becomes impossible to see them as anything other than a continuous spectrum. This is suggested by the shaded part on the right end of the series. At one particular point, known as the series limit, the series ends.

In Balmer series or the Paschen series, the pattern is the same, but the series are more compact. In the Balmer series, notice the position of the three visible lines from the photograph further up the page.

Frequency and Wavelength

The hydrogen spectrum is often drawn using wavelengths of light rather than frequencies. Unfortunately, because of the mathematical relationship between the frequency of light and its wavelength, two completely different views of the spectrum are obtained when it is plotted against frequency or against wavelength. The mathematical relationship between frequency and wavelength is the following:



Rearranging this gives equations for either wavelength or frequency:

$$\lambda = \frac{c}{\nu} \tag{12.3.1}$$

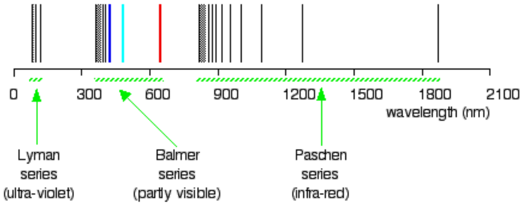
or

$$\nu = \frac{c}{\lambda} \tag{12.3.2}$$

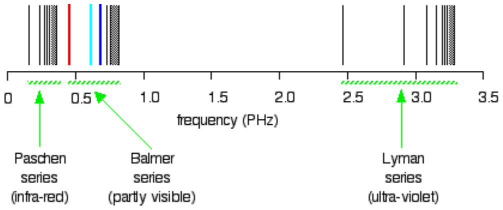
There is an inverse relationship between the two variables—a high frequency means a low wavelength and vice versa.

Drawing the hydrogen spectrum in terms of wavelength

This is what the spectrum looks like plotted in terms of wavelength instead of frequency:



Compare this to the same spectrum in terms of frequency:



When juxtaposed, the two plots form a confusing picture. The remainder of the article employs the spectrum plotted against frequency, because in this spectrum it is much easier visualize what is occurring in the atom.

The Balmer and Rydberg Equations

In an amazing demonstration of mathematical insight, in 1885 Balmer came up with a simple formula for predicting the wavelength of any of the lines in what we now know as the Balmer series. Three years later, Rydberg generalized this so that it was possible to determine the wavelengths of any of the lines in the hydrogen emission spectrum. Rydberg's equation is as follows:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{12.3.3}$$

where

- R_H is the *Rydberg* constant.
- n_1 and n_2 are integers (whole numbers). n_2 is always greater than n_1. In other words, if n_1 is, say, 2 then n_2 can be any whole number between 3 and infinity.

The various combinations of numbers that can be substituted into this formula allow the calculation the wavelength of any of the lines in the hydrogen emission spectrum; there is close agreement between the wavelengths generated by this formula and those observed in a real spectrum.

A modified version of the Rydberg equation can be used to calculate the frequency of each of the lines:

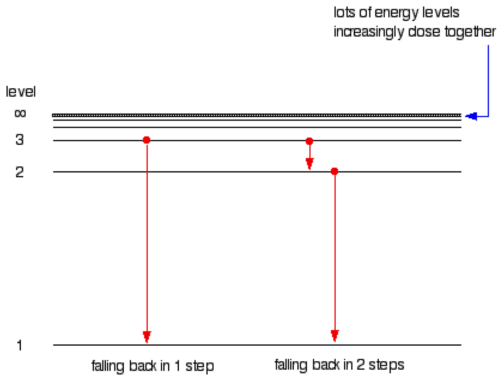
$$\begin{aligned} \nu &= \frac{c}{\lambda} \\ &= c \times \frac{1}{\lambda} \\ \text{If } \frac{1}{\lambda} &= R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \\ \nu &= c.R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \end{aligned}$$

The origin of the hydrogen emission spectrum

The lines in the hydrogen emission spectrum form regular patterns and can be represented by a (relatively) simple equation. Each line can be calculated from a combination of simple whole numbers. Why does hydrogen emit light when excited by a high voltage and what is the significance of those whole numbers?

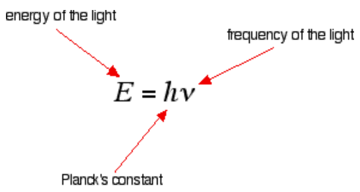
When unexcited, hydrogen's electron is in the first energy level—the level closest to the nucleus. But if energy is supplied to the atom, the electron is excited into a higher energy level, or even removed from the atom altogether. The high voltage in a discharge tube provides that energy. Hydrogen molecules are first broken up into hydrogen atoms (hence the atomic hydrogen emission spectrum) and electrons are then promoted into higher energy levels.

Suppose a particular electron is excited into the third energy level. It would tend to lose energy again by falling back down to a lower level. It can do this in two different ways. It could fall all the way back down to the first level again, or it could fall back to the second level and then, in a second jump, down to the first level.



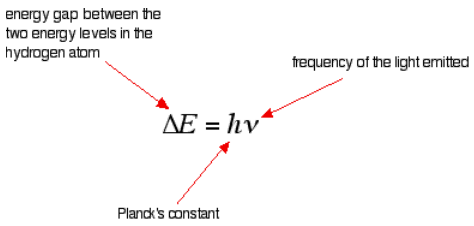
Assigning particular electron jumps to individual lines in the spectrum

If an electron falls from the 3-level to the 2-level, it must lose an amount of energy exactly equal to the energy difference between those two levels. That energy which the electron loses is emitted as light (which "light" includes UV and IR as well as visible radiation). Each frequency of light is associated with a particular energy by the equation:



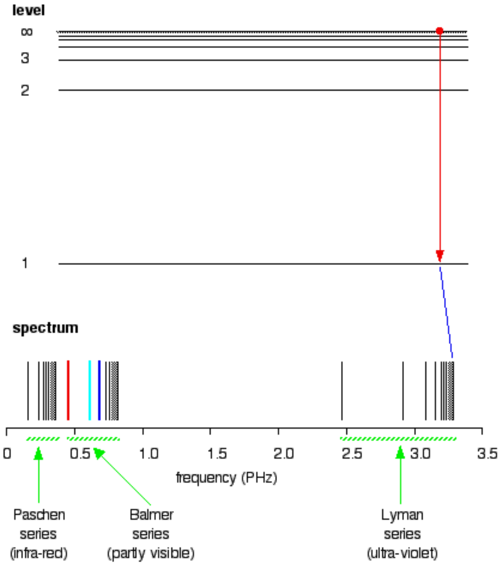
The higher the frequency, the higher the energy of the light. If an electron falls from the 3-level to the 2-level, red light is seen. This is the origin of the red line in the hydrogen spectrum. From the frequency of the red light, its energy can be calculated. That energy must be exactly the same as the energy gap between the 3-level and the 2-level in the hydrogen atom.

The last equation can therefore be rewritten as a measure of the energy gap between two electron levels:

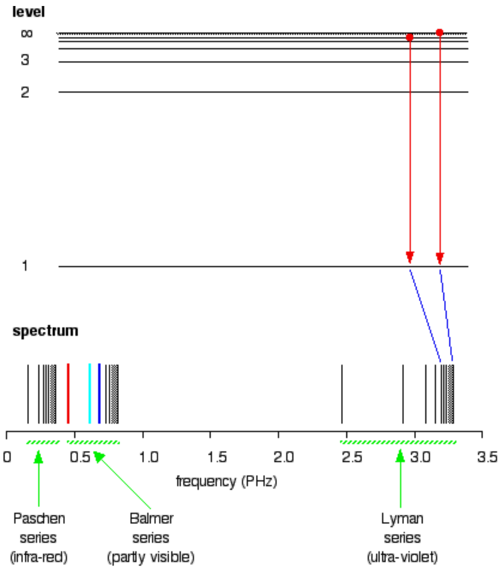


The greatest possible fall in energy will therefore produce the highest frequency line in the spectrum. The greatest fall will be from the infinity level to the 1-level. (The significance of the infinity level will be made clear later.)

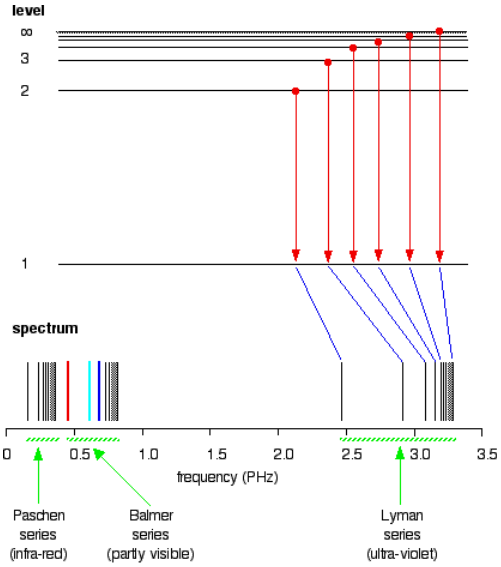
The next few diagrams are in two parts, with the energy levels at the top and the spectrum at the bottom.



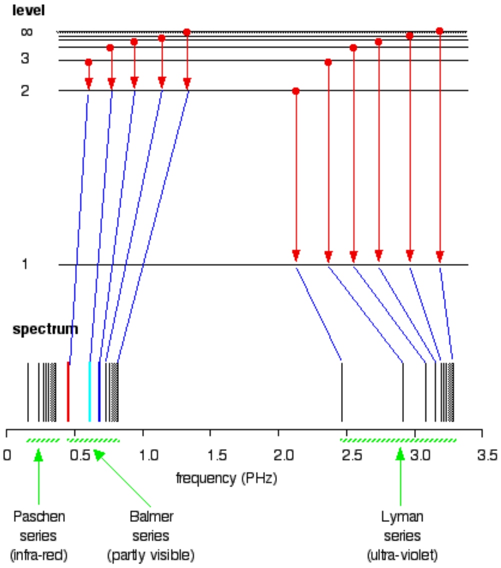
If an electron falls from the 6-level, the difference is slightly less than before, and so the frequency is slightly lower (because of the scale of the diagram, it is impossible to depict the levels beyond 7).



All other possible jumps to the first level make up the whole Lyman series. The spacings between the lines in the spectrum reflect the changes in spacings between the energy levels.



If the same is done for the 2-level, the Balmer series is shown. These energy gaps are all much smaller than in the Lyman series, and so the frequencies produced are also much lower.



The Paschen series is made up of the transitions to the 3-level, but they are omitted to avoid cluttering the diagram.

The significance of the numbers in the Rydberg equation

In the Rydberg equation, n_1 and n_2 represent the energy levels at either end of the jump that produces a particular line in the spectrum.

- In the Lyman series, $n_1 = 1$, because electrons transition to the 1-level to produce lines in the Lyman series.
- In the Balmer series, $n_1 = 2$, because electrons fall to the 2-level.

n_2 is the level being jumped from. In the case before, in which a red line is produced by electrons falling from the 3-level to the 2-level, n_2 is equal to 3.

The significance of the infinity level

The infinity level represents the highest possible energy an electron can have as a part of a hydrogen atom. If the electron exceeds that energy, it is no longer a part of the atom. The infinity level represents the point at which ionization of the atom occurs to form a positively charged ion.

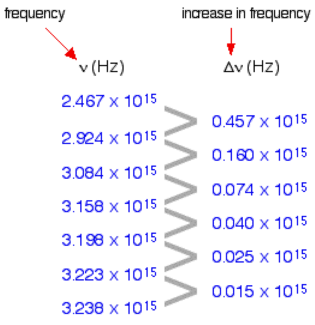
Using the spectrum to find the ionization energy of hydrogen

When there is no additional energy supplied to it, hydrogen atom's electron is found at the 1-level. This is known as its ground state. If enough energy is supplied to move the electron up to the infinity level, the atom is ionized. The ionization energy per electron is therefore a measure of the difference in energy between the 1-level and the infinity level. In above diagrams, that particular energy jump produces the series limit of the Lyman series.

The frequency of the Lyman series limit can be used to calculate the energy required to promote the electron in one atom from the 1-level to the point of ionization. This energy can then be used to calculate the ionization energy per mole of atoms. A problem with this approach is that the frequency of a series limit is quite difficult to find accurately from a spectrum because the lines are so close together in that region that the spectrum looks continuous.

Finding the frequency of the series limit graphically

The following is a list of the frequencies of the seven most widely spaced lines in the Lyman series, together with the increase in frequency between successive lines.

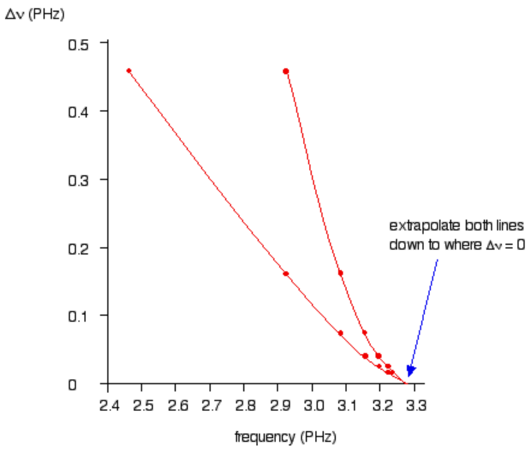


ν (Hz)	Δν (Hz)
2.467×10^{15}	
	0.457×10^{15}
2.924×10^{15}	
	0.160×10^{15}
3.084×10^{15}	
	0.074×10^{15}
3.158×10^{15}	
	0.040×10^{15}
3.198×10^{15}	
	0.025×10^{15}
3.223×10^{15}	
	0.015×10^{15}
3.238×10^{15}	

As the lines become closer together, the increase in frequency is lessened. At the series limit, the gap between the lines is zero. Consequently, if the increase in frequency is plotted against the actual frequency, the curve can be extrapolated to the point at which the increase becomes zero, the frequency of the series limit.

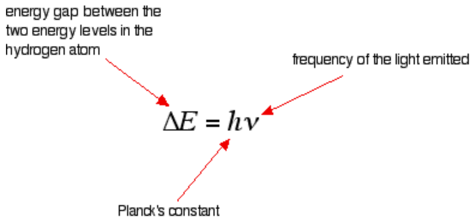
In fact, two graphs can be plotted from the data in the table above. The frequency difference is related to two frequencies. For example, the figure of 0.457 is found by subtracting 2.467 from 2.924. Which of the two values should be plotted against 0.457 does not matter, as long as consistency is maintained—the difference must always be plotted against either the higher or the lower figure. At the limit, the two frequency numbers are the same.

As illustrated in the graph below, plotting both of the possible curves on the same graph makes it easier to decide exactly how to extrapolate the curves. Because these are curves, they are much more difficult to extrapolate than straight lines.



Both lines indicate a series limit at about 3.28 x 10^{15} Hz.

With this information, it is possible calculate the energy needed to remove a single electron from a hydrogen atom. Recall the equation above:



The energy gap between the ground state and the point at which the electron leaves the atom can be determined by substituting the frequency and looking up the value of Planck's constant from a data book.

$$\begin{aligned} \Delta E &= h\nu \quad (12.3.4) \\ &= (6.626 \times 10^{-34})(3.28 \times 10^{15}) \quad (12.3.5) \\ &= 2.173 \times 10^{-18}\ J \quad (12.3.6) \end{aligned}$$

This is the ionization energy for a single atom. To find the normally quoted ionization energy, this value is multiplied by the number of atoms in a mole of hydrogen atoms (the Avogadro constant) and then dividing by 1000 to convert joules to kilojoules.

$$\begin{aligned} Ionization\ energy &= (2.173 \times 10^{-18})(6.022 \times 10^{23})(\frac{1}{1000}) \quad (12.3.7) \\ &= 1310\ kJ\ mol^{-1} \quad (12.3.8) \end{aligned}$$

This compares well with the normally quoted value for hydrogen's ionization energy of 1312 kJ mol^{-1}.

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12.4: The Bohr Model

Learning Objectives

- Introduce the fundamentals behind the Bohr Atom and demonstrate it can predict the Rydberg's equation for the atomic spectrum of hydrogen

Rutherford's Failed Planetary Atom

Ernest Rutherford had proposed a model of atoms based on the α-particle scattering experiments of Hans Geiger and Ernest Marsden. In these experiments helium nuclei (α-particles) were shot at thin gold metal foils. Most of the particles were not scattered; they passed unchanged through the thin metal foil. Some of the few that were scattered were scattered in the backward direction; i.e. they recoiled. This backward scattering requires that the foil contain heavy particles. When an α-particle hits one of these heavy particles it simply recoils backward, just like a ball thrown at a brick wall. Since most of the α-particles don't get scattered, the heavy particles (the nuclei of the atoms) must occupy only a very small region of the total space of the atom. Most of the space must be empty or occupied by very low-mass particles. These low-mass particles are the electrons that surround the nucleus.

There are some basic problems with the Rutherford model. The Coulomb force that exists between oppositely charge particles means that a positive nucleus and negative electrons should attract each other, and the atom should collapse. To prevent the collapse, the electron was postulated to be orbiting the positive nucleus. The Coulomb force (discussed below) is used to change the direction of the velocity, just as a string pulls a ball in a circular orbit around your head or the gravitational force holds the moon in orbit around the Earth. The origin for this hypothesis that suggests this perspective is plausible is the similarity of gravity and Coulombic interactions. The expression for the force of gravity between two masses (Newton's Law of gravity) is

$$F_{gravity} \propto \frac{m_1 m_2}{r^2} \tag{12.4.1}$$

with m_1 and m_2 representing the **mass** of object 1 and 2, respectively and r representing the distance between the objects centers

The expression for the Coulomb force between two charged species is

$$F_{Coulomb} \propto \frac{Q_1 Q_2}{r^2} \tag{12.4.2}$$

with Q_1 and Q_2 representing the **charge** of object 1 and 2, respectively and r representing the distance between the objects centers.

However, this analogy has a problem too. An electron going around in a circle is constantly being accelerated because its velocity vector is changing. A charged particle that is being accelerated emits radiation. This property is essentially how a radio transmitter works. A power supply drives electrons up and down a wire and thus transmits energy (electromagnetic radiation) that your radio receiver picks up. The radio then plays the music for you that is encoded in the waveform of the radiated energy.

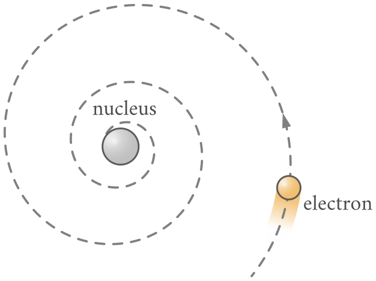


Figure 1.8.1 : The classical death spiral of an electron around a nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

If the orbiting electron is generating radiation, it is losing energy. If an orbiting particle loses energy, the radius of the orbit decreases. To conserve angular momentum, the frequency of the orbiting electron increases. The frequency increases continuously as the electron collapses toward the nucleus. Since the frequency of the rotating electron and the frequency of the radiation that is emitted are the same, both change continuously to produce a continuous spectrum and not the observed discrete lines. Furthermore, if one calculates how long it takes for this collapse to occur, one finds that it takes about 10^{-11} seconds. This means that nothing in the world based on the structure of atoms could exist for longer than about 10^{-11} seconds. Clearly something is terribly wrong with this classical picture, which means that something was missing at that time from the known laws of physics.

Conservative Forces can be explained with Potentials

A conservative force is dependent only on the position of the object. If a force is conservative, it is possible to assign a numerical value for the potential at any point. When an object moves from one location to another, the force changes the potential energy of the object by an amount that does not depend on the path taken. The potential can be constructed as simple derivatives for 1-D forces:

$$F = -\frac{dV}{dx}$$

or as gradients in 3-D forces

$$F = -\nabla V$$

where ∇ is the vector of partial derivatives

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

The most familiar conservative forces are gravity and Coulombic forces.

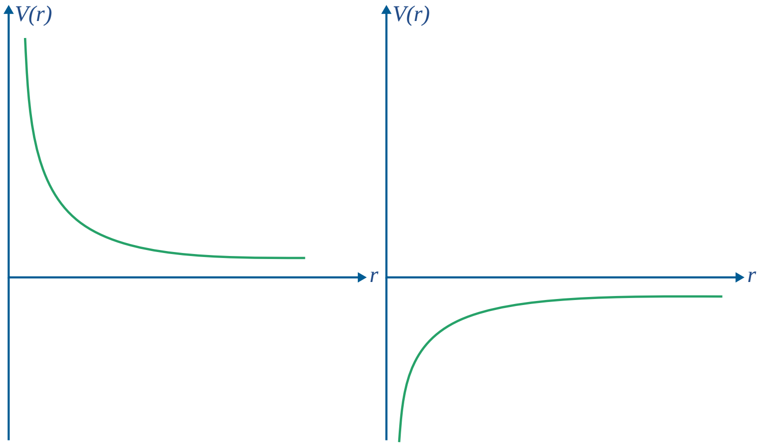
The Coulomb force law (Equation 12.4.2) comes from the corresponding Coulomb potential (sometimes call electrostatic potential)

$$V(r) = \frac{kQ_1Q_2}{r} \tag{12.4.3}$$

and it can be easily verified that the Coulombic force from this interaction ($F(r)$) is

$$F(r) = -\frac{dV}{dr} \tag{12.4.4}$$

As r is varied, the energy will change, so that we have an example of a potential energy curve $V(r)$ (Figure $12.4.2; left$). If Q_1 and Q_2 are the same sign, then the curve which is a purely **repulsive potential**, i.e., the energy increases monotonically as the charges are brought together and decreases monotonically as they are separated. From this, it is easy to see that like charges (charges of the same sign) repel each other.



Repulsive Coulomb Potential *Attractive Coulomb Potential*

Figure 1.8.2 : Potential energy curve for the Coulomb interactions between two charges of same sign (left) and opposite signs (right). (CC BY-NC; Ümit Kaya via LibreTexts)

If the charges are of opposite sign, then the curve appears roughly Figure $12.4.2; right$ and this is a purely **attractive potential**. Thus, the energy decreases as the charges are brought together, implying that opposite charges attract

The Bohr Model

It is observed that line spectra discussed in the previous sections show that hydrogen atoms absorb and emit light at only discrete wavelengths. This observation is connected to the discrete nature of the allowed energies of a quantum mechanical system. Quantum mechanics postulates that, in contrast to classical mechanics, the energy of a system can only take on certain discrete values. This leaves us with the question: How do we determine what these allowed discrete energy values are? After all, it seems that Planck's formula for the allowed energies came out of nowhere.

The model we will describe here, due to Niels Bohr in 1913, is an early attempt to predict the allowed energies for single-electron atoms such as H, He^+, Li^{2+}, Be^{3+}, etc. Although Bohr's reasoning relies on classical concepts and hence, is not a correct explanation, the reasoning is interesting, and so we examine this model for its historical significance.

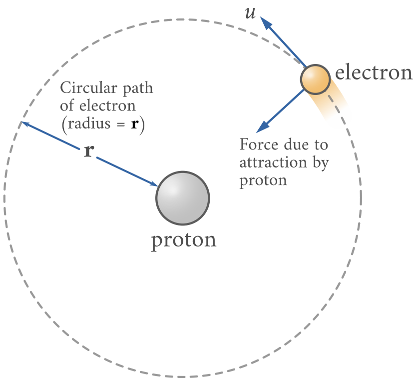


Figure 1.8.3 : Bohr atom with an electron revolving around a fixed nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

Consider a nucleus with charge $+Ze$ and one electron orbiting the nucleus. In this analysis, we will use another representation of the constant k in Coulomb's law (Equation 12.4.3), which is more commonly represented in the form:

$$k = \frac{1}{4\pi\epsilon_0} \tag{12.4.5}$$

where ϵ_0 is known as the **permittivity of free space** with the numerical value $\epsilon_0 = 8.8541878 \times 10^{-12}\, C^2 J^{-1} m^{-1}$.

The total energy of the electron (the nucleus is assumed to be fixed in space at the origin) is the sum of kinetic and potential energies:

$$E_{total} = \underbrace{\frac{p^2}{2m_e}}_{\text{kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r}}_{\text{potential energy}}$$

The force on the electron is

$$\vec{F} = -\frac{Ze^2}{4\pi\epsilon_0 r^3} r$$

and its magnitude is

$$F = |\vec{F}| = \frac{Ze^2}{4\pi\epsilon_0 r^3}|r| = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

since $\vec{F} = m_e\vec{a}$, the magnitude, it follows that $|\vec{F}| = m_e|\vec{a}|$. If we assume that the orbit is circular, then the acceleration is *purely centripetal*, so

$$|a| = \frac{v^2}{r}$$

where v is the velocity of the electron. Equating force $|F|$ to $m_e|a|$, we obtain

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = m_e \frac{v^2}{r}$$

or

$$\frac{Ze^2}{4\pi\epsilon_0} = m_e v^2 r$$

or

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = (m_e v r)^2 \tag{12.4.6}$$

The reason for writing the equation this way is that the quantity $m_e vr$ is the classical orbital angular momentum of the electron. Bohr was familiar with Maxwell's theory of classical electromagnetism and knew that in a classical theory, the orbiting electron should radiate energy away and eventually collapse into the nucleus (Figure 1.8.1). He circumvented this problem by following Planck's idea underlying blackbody radiation and positing that the orbital angular momentum $m_e vr$ of the electron could only take on specific values

$$m_e v r = n\hbar \tag{12.4.7}$$

with $n = 1, 2, 3, \ldots$.

> *Note that the electron must be in motion, so $n = 0$ is not allowed.*

Substituting Equation 12.4.7 into the Equation 12.4.6, we find

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = n^2(\hbar)^2 \tag{12.4.8}$$

Equation 12.4.8 implies that orbits could only have certain allowed radii

$$r_n = \frac{4\pi\epsilon_0 \hbar^2}{Ze^2 m_e} n^2 \tag{12.4.9}$$

$$= \frac{a_0}{Z} n^2 \tag{12.4.10}$$

with $n = 1, 2, 3, \ldots$. The collection of constants has been defined to be a_0

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e}$$

a quantity that is known as the **Bohr radius**.

We can also calculate the allowed momenta since $m_e vr = n\hbar$, and $p = m_e v$. Thus,

$$\begin{aligned} p_n r_n &= n\hbar \\ p_n &= \frac{n\hbar}{r_n} \\ &= \frac{\hbar Z}{a_0 n} \\ &= \frac{Ze^2 m_e}{4\pi\epsilon_0 \hbar n} \end{aligned}$$

From p_n and r_n, we can calculate the allowed energies from

$$E_n = \frac{p_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r_n}$$

Substituting in the expressions for p_n and r_n and simplifying gives

$$E_n = -\frac{Z^2 e^4 m_e}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} = -\frac{e^4 m_e}{8\epsilon_0^2 h^2}\frac{Z^2}{n^2} \tag{12.4.11}$$

We can redefine a new energy scale by defining **the Rydberg** as

$$1\ Ry = \frac{e^4 m_e}{8\epsilon_0^2 h^2} = 2.18 \times 10^{-18}\ J.$$

and this simplifies the allowed energies predicted by the Bohr model (Equation 12.4.11) as

$$E_n = -(2.18\times 10^{-18})\frac{Z^2}{n^2}\ J = -\frac{Z^2}{n^2}\ R_y \tag{12.4.12}$$

Hence, the energy of the electron in an atom also is quantized. Equation 12.4.12 gives the energies of the electronic states of the hydrogen atom. It is very useful in analyzing spectra to represent these energies graphically in an energy-level diagram. An energy-level diagram has energy plotted on the vertical axis with a horizontal line drawn to locate each energy level (Figure 1.8.4).

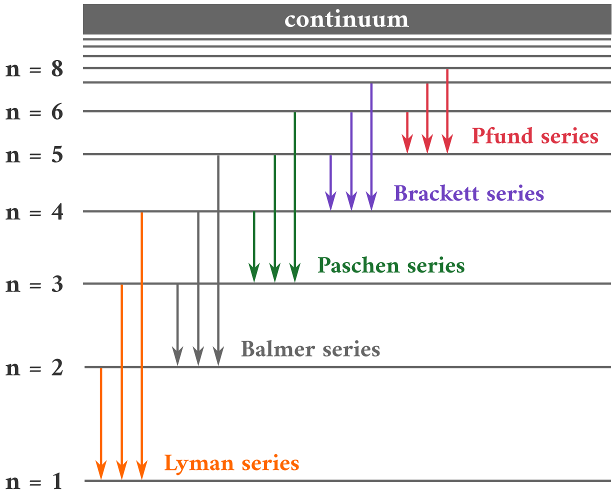


Figure 1.8.4 : Energy levels predicted by the Bohr model of hydrogen ($Z = 1$). (CC BY-NC; Ümit Kaya via LibreTexts)

These turn out to be the correct energy levels, apart from small corrections that cannot be accounted for in this pseudo-classical treatment. Despite the fact that the energies are essentially correct, the Bohr model masks the true quantum nature of the electron, which only emerges from a fully quantum mechanical analysis.

Exercise 1.8.1

Calculate a value for the Bohr radius using Equation 12.4.8 to check that this equation is consistent with the value 52.9 pm. What would the radius be for $n = 1$ in the Li^{2+} ion?

Answer

Starting from Equation 12.4.8 and solving for r:

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = n^2\hbar^2$$

$$r = \frac{4n^2\hbar^2\pi\epsilon_0}{Ze^2 m_e}$$

with

- e is the fundamental charge: $e = 1.60217662 \times 10^{-19} C^2$

- m_e is the mass of an electron: $m_e = 9.10938356 \times 10^{-31} kg$
- ϵ_o is the permittivity of free space: $\epsilon_o = 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$
- $\hbar$ is the reduced planks constant: $\hbar = 1.0546 \times 10^{-34} m^2 kg/s$

For the ground-state of the hydrogen atom: $Z = 1$ and $n = 1$.

$$\begin{aligned} r &= \frac{4\hbar^2\pi\epsilon_0}{e^2 m_e} \\ &= \frac{4(1.0546 \times 10^{-34} m^2 kg/s)^2 \times \pi \times 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}}{(1.60217662 \times 10^{-19} C)^2 (9.10938356 \times 10^{-31} kg)} \\ &= 5.29 \times 10^{-11} m = 52.9\, pm \end{aligned}$$

For the ground-state of the lithium +2 ion: $Z = 3$ and $n = 1$

$$\begin{aligned} r &= \frac{4\hbar^2\pi\epsilon_0}{3e^2 m_e} \\ &= \frac{4(1.0546 \times 10^{-34} m^2 kg/s)^2 \times \pi \times 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}}{3(1.60217662 \times 10^{-19} C)^2 (9.10938356 \times 10^{-31} kg)} \\ &= 1.76 \times 10^{-11} m = 17.6\, pm \end{aligned}$$

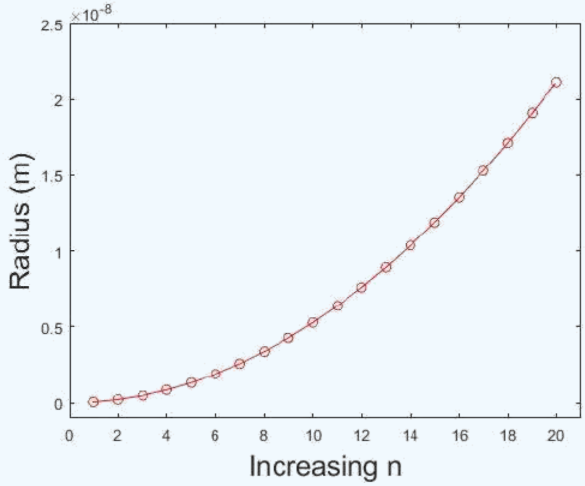
As expected, the Li^{2+} has a smaller radius than the H atoms because of the increased nuclear charge.

? Exercise 1.8.2 : Rydberg states

How do the radii of the hydrogen orbits vary with n? Prepare a graph showing r as a function of n. States of hydrogen atoms with $n = 200$ have been prepared (called Rydberg states). What is the diameter of the atoms in these states?

Answer

This is a straightforward application of Equation of 12.4.10. The hydrogen atom has only certain allowable radii and these radii can be predicted from the equation that relates them with each n. Note that the electron must be in motion so $n = 0$ is not allowed.



This plot shows the relationship of radius as a function of n. Note that at $n = 1$ the radius is not zero. (CC BY-NC; Ümit Kaya via LibreTexts)

$4\pi\epsilon_0 = 1.113 \times 10^{-10} \text{C}^2 \text{J}^{-1} \text{m}^{-1}$ and $\hbar = 1.054 \times 10^{-34} \text{Js}$, also knowing

$$\begin{aligned} e &= 1.602 \times 10^{-19} \text{C with} \\ m_e &= 9.109 \times 10^{-31} \text{kg} \end{aligned}$$

and Z is the nuclear charge, we use this equation directly. A simplification can be made by taking advantage of the fact that

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e}$$

resulting in

$$r_n = \frac{a_0}{Z} n^2$$

where $a_0 = 5.292 \times 10^{-11} \mathrm{m}$ which is the Bohr Radius.

Suppose we want to find the radius where $n = 200$. $n^2 = 40000$ so plugging in directly we have

$$\begin{aligned} r_n &= \frac{(5.292 \times 10^{-11})}{(1)}(40000) \\ &= 2.117 \times 10^{-6} m \end{aligned}$$

for the radius of a hydrogen atom with an electron excited to the $\mathrm{n} = 200$ state. The diameter is then $4.234 \times 10^{-6} \mathrm{m}$.

The Wave Argument for Quantization

The above discussion is based off of a classical picture of an orbiting electron with the quantization from the angular momentum (Equation 12.4.7) requirement lifted from Planck's quantization arguments. Hence, only allows certain trajectories are stable (with differing radii). However, as discussed previously, the electron will have a wavelike property also with a de Broglie wavelength λ

$$\lambda = \frac{h}{p}$$

Hence, a larger momentum p implies a shorter wavelength. That means as n increases (Equation 12.4.12), the wavelength must also increase; this is a common feature in quantum mechanics and will be often observed. In the Bohr atom, the circular symmetry and the wave property of the electron requires that the electron waves have an integer number of wavelengths (Figure $12.4.1A$). If not, then the waves will overlap imperfectly and cancel out (i.e., the electron will cease to exist) as demonstrated in Figure $12.4.1B$.

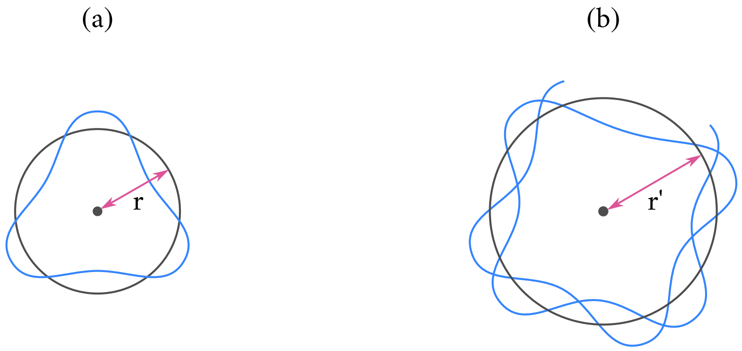


Figure 1.8.5 : Waves on a string have a wavelength related to the length of the string, allowing them to interfere constructively. (A) If we imagine the string bent into a closed circle, we get a rough idea of how electrons in circular orbits can interfere constructively. (B) If the wavelength does not fit into the circumference, the electron interferes destructively; it cannot exist in such an orbit. (CC BY-NC; Ümit Kaya via LibreTexts)

A more detailed discussion of the effect of electron waves in atoms will be discuss in the following chapters.

Derivation of the Rydberg Equation from Bohr Model

Given a prediction of the allowed energies of a system, how could we go about verifying them? The general experimental technique known as *spectroscopy* permits us to probe the various differences between the allowed energies. Thus, if the prediction of the actual energies, themselves, is correct, we should also be able to predict these differences. Let us assume that we are able to place the electron in Bohr's hydrogen atom into an energy state E_n for $n > 1$, i.e. one of its so-called *excited states*. The electron will rapidly return to its lowest energy state, known as the *ground state* and, in doing so, emit light. The energy carried away by the light is determined by the condition that the total energy is conserved (Figure 1.8.6).

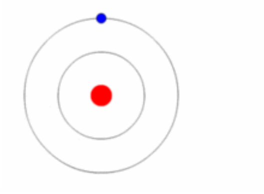


Figure 1.8.6 : A simple illustration of Bohr's model of the atom, with an electron making quantum leaps. (CC BY-SA 3.0 unported; Kurzon via Wikipedia)

Thus, if n_i is the integer that characterizes the initial (excited) state of the electron, and n_f is the final state (here we imagine that $n_f = 1$, but is applicable in cases that $n_f < n_i$, i.e., emission)

$$E_{nf} = E_{ni} - h\nu$$

or

$$\nu = \frac{E_{ni} - E_{nf}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \tag{12.4.13}$$

We can now identify the Rydberg constant R_H with the ratio of constants on the right hand side of Equation 12.4.13

$$R_H = \frac{m_e e^4}{8\epsilon_0^2 h^3}$$

Evaluating R_H from the fundamental constants in this formula gives a value within 0.5% of that obtained experimentally from the hydrogen atom spectrum.

Thus, by observing the emitted light, we can determine the energy difference between the initial and final energy levels, which results in the emission spectra discussed in Sections 1.4 and 1.5. Different values of n_f determine which emission spectrum is observed, and the examples shown in the figure are named after the individuals who first observed them. The figure below shows some of the transitions possible for different n_f and n_i values discussed previously.

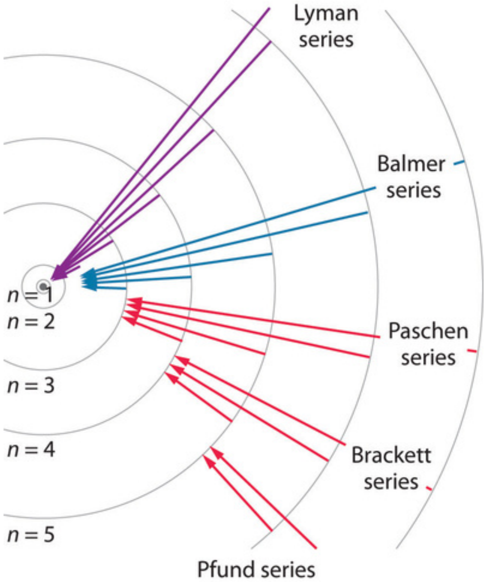


Figure 1.8.7 : Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. Orbits are not drawn to scale. (CC BY-NC-SA 3.0; anonymous)

If the atom absorbs light it ends up in an excited state as a result of the absorption. The absorption is only possible for light of certain frequencies, and again, conservation of energy determines what these frequencies are. If light is absorbed, then the final energy E_{nf} will be related to the initial energy E_{ni} with $n_f > n_i$ by

$$E_{nf} = E_{ni} + h\nu$$

or

$$\nu = \frac{E_{nf} - E_{ni}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

Exercise 1.8.3

a. Calculate the energy of a photon that is produced when an electron in a hydrogen atom goes from an orbit with $n = 4$ to an orbit with $n = 1$.
b. What happens to the energy of the photon as the initial value of n approaches infinity?

Answer

a:

$$\begin{aligned} E_{\mathrm{nf}} &= E_{ni} - h\nu \\ E_{photon} = h\nu &= E_{nf} - E_{ni} \\ &= \frac{Z^2 e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\ &= \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{1^2} - \frac{1}{4^2}\right) \\ &= 2.18 \times 10^{-18}\left(1 - \frac{1}{16}\right) \\ &= 2.04 \times 10^{-18} J \end{aligned}$$

b:

As $n_i \rightarrow \infty$

$$\begin{aligned} E_{photon} &= \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\ \frac{1}{n_i^2} &\rightarrow 0 \\ E_{photon} &\rightarrow \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2}\right) \end{aligned}$$

Bohr’s proposal explained the hydrogen atom spectrum, the origin of the Rydberg formula, and the value of the Rydberg constant. Specifically it demonstrated that the integers in the Rydberg formula are a manifestation of quantization. The energy, the angular momentum, and the radius of the orbiting electron all are quantized. This quantization also parallels the concept of stable orbits in the Bohr model. Only certain values of E, M, and r are possible, and therefore the electron cannot collapse onto the nucleus by continuously radiating energy because it can only have certain energies, and it cannot be in certain regions of space. The electron can only jump from one orbit (quantum state) to another. The quantization means that the orbits are stable, and the electron cannot spiral into the nucleus in spite of the attractive Coulomb force.

Although Bohr’s ideas successfully explained the hydrogen spectrum, they failed when applied to the spectra of other atoms. In addition a profound question remained. Why is angular momentum quantized in units of $\hbar$? As we shall see, de Broglie had an answer to this question, and this answer led Schrödinger to a general postulate that produces the quantization of angular momentum as a consequence. This quantization is not quite as simple as proposed by Bohr, and we will see that it is not possible to determine the distance of the electron from the nucleus as precisely as Bohr thought. In fact, since the position of the electron in the hydrogen atom is not at all as well defined as a classical orbit (such as the moon orbiting the earth) it is called an orbital. An electron orbital represents or describes the position of the electron around the nucleus in terms of a mathematical function called a wavefunction that yields the **probability** of positions of the electron.

Contributors and Attributions

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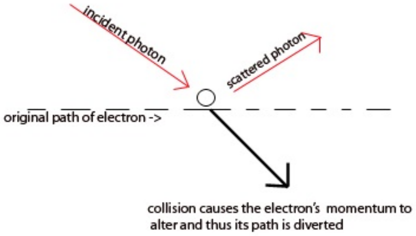
12.5: The Quantum Mechanical Model of the Atom

In classical physics, studying the behavior of a physical system is often a simple task due to the fact that several physical qualities can be measured simultaneously. However, this possibility is absent in the quantum world. In 1927 the German physicist Werner Heisenberg described such limitations as the Heisenberg Uncertainty Principle, or simply the Uncertainty Principle, stating that it is not possible to measure both the momentum and position of a particle simultaneously.

The Nature of Measurement

In order to understand the conceptual background of the Heisenberg Uncertainty Principle it is important to understand how physical values are measured. In almost any measurement that is made, light is reflected off the object that is being measured and processed. The shorter the wavelength of light used, or the higher its frequency and energy, the more accurate the results. For example, when attempting to measure the speed of a tennis ball as it is dropped off of a ledge, photons(measurement of light) are shot off the tennis ball, reflected, and then processed by certain equipment. Because the tennis ball is so large compared to the photons, it is unaffected by the efforts of the observer to measure its physical quantities. However, if a photon is shot at an electron, the minuscule size of the electron and its unique wave-particle duality introduces consequences that can be ignored when taking measurements of macroscopic objects.

Heisenberg himself encountered such limitations as he attempted to measure the position of an electron with a microscope. As noted, the accuracy of any measurement is limited by the wavelength of light illuminating the electron. Therefore, in principle, one can determine the position as accurately as one wishes by using light of very high frequency, or short wave-lengths. However, the collision between such high energy photons of light with the extremely small electron causes the momentum of the electron to be disturbed.



Thus, increasing the energy of the light (and increasing the accuracy of the electron's position measurement), increases such a deviation in momentum. Conversely, if a photon has low energy the collision does not disturb the electron, yet the position cannot be accurately determined. Heisenberg concluded in his famous 1927 paper on the topic,

> "At the instant of time when the position is determined, that is, at the instant when the photon is scattered by the electron, the electron undergoes a discontinuous change in momentum. This change is the greater the smaller the wavelength of the light employed, i.e., the more exact the determination of the position. At the instant at which the position of the electron is known, its momentum therefore can be known only up to magnitudes which correspond to that discontinuous change; thus, the more precisely the position is determined, the less precisely the momentum is known..." (Heisenberg, 1927, p. 174-5).

Heisenberg realized that since both light and particle energy are quantized, or can only exist in discrete energy units, there are limits as to how small, or insignificant, such an uncertainty can be. As proved later in this text, that bound ends up being expressed by Planck's Constant, $h = 6.626*10^{-34}$ J*s.

It is important to mention that The Heisenberg Principle should not be confused with the observer effect. The observer effect is generally accepted to mean that the act of observing a system will influence that which is being observed. While this is important in understanding the Heisenberg Uncertainty Principle, the two are not interchangeable. The error in such thinking can be explained using the wave-particle duality of electromagnetic waves, an idea first proposed by Louis de Broglie. Wave-particle duality asserts that any energy exhibits both particle- and wave-like behavior. As a consequence, in quantum mechanics, a particle cannot have both a definite position and momentum. Thus, the limitations described by Heisenberg are a natural occurrence and have nothing to do with any limitations of the observational system.

Heisenberg’s Uncertainty Principle

It is mathematically possible to express the uncertainty that, Heisenberg concluded, always exists if one attempts to measure the momentum and position of particles.First, we must define the variable “x” as the position of the particle, and define “p” as the momentum of the particle. The momentum of a photon of light is known to simply be its frequency, expressed by the ratio h/λ, where h represents Planck’s constant and λ represents the wavelength of the photon. The position of a photon of light is simply its wavelength, \lambda\).. In order to represent finite change in quantities, the Greek uppercase letter delta, or Δ, is placed in front of the quantity. Therefore,

$$\Delta p = \frac{h}{\lambda} \tag{12.5.1}$$

$$\Delta x = \lambda \tag{12.5.2}$$

By substituting Δx for λ in the first equation, we derive

$$\Delta p = \frac{h}{\Delta x} \tag{12.5.3}$$

or,

$$\Delta p \Delta x = h \tag{12.5.4}$$

Note, we can derive the same formula by assuming the particle of interest is behaving as a particle, and not as a wave. Simply let Δp=mu, and Δx=h/mu (from De Broglie’s expression for the wavelength of a particle). Substituting in Δp for mu in the second equation leads to the very same equation derived above-ΔpΔx=h. This equation was refined by Heisenberg and his colleague Niels Bohr, and was eventually rewritten as

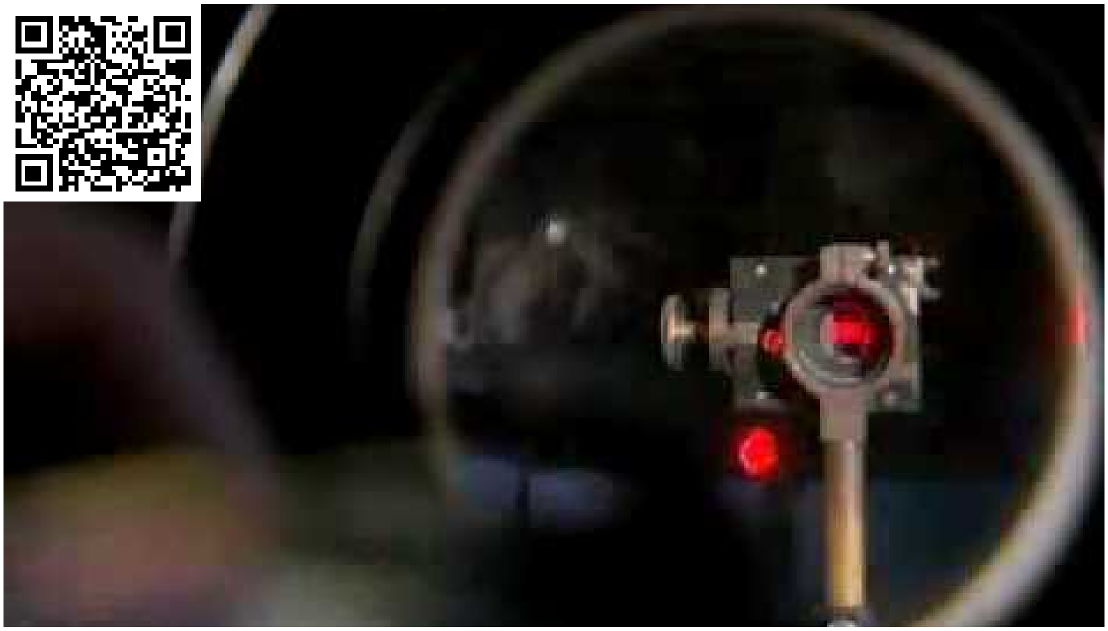
$$\Delta p \Delta x \geq \frac{h}{4\pi} \tag{12.5.5}$$

What this equation reveals is that the more accurately a particle’s position is known, or the smaller Δx is, the less accurately the momentum of the particle Δp is known. Mathematically, this occurs because the smaller Δx becomes, the larger Δp must become in order to satisfy the inequality. However, the more accurately momentum is known the less accurately position is known.

Understanding the Uncertainty Principle through Wave Packets and the Slit Experiment

It is hard for most people to accept the uncertainty principle, because in classical physics the velocity and position of an object can be calculated with certainty and accuracy. However, in quantum mechanics, the wave-particle duality of electrons does not allow us to accurately calculate both the momentum and position because the wave is not in one exact location but is spread out over space. A "wave packet" can be used to demonstrate how either the momentum or position of a particle can be precisely calculated, but not both of them simultaneously. An accumulation of waves of varying wavelengths can be combined to create an average wavelength through an interference pattern: this average wavelength is called the "wave packet". The more waves that are combined in the "wave packet", the more precise the position of the particle becomes and the more uncertain the momentum becomes because more wavelengths of varying momenta are added. Conversely, if we want a more precise momentum, we would add less wavelengths to the "wave packet" and then the position would become more uncertain. Therefore, there is no way to find both the position and momentum of a particle simultaneously.

Several scientists have debated the Uncertainty Principle, including Einstein. Einstein created a slit experiment to try and disprove the Uncertainty Principle. He had light passing through a slit, which causes an uncertainty of momentum because the light behaves like a particle and a wave as it passes through the slit. Therefore, the momentum is unknown, but the initial position of the particle is known. Here is a video that demonstrates particles of light passing through a slit and as the slit becomes smaller, the final possible array of directions of the particles becomes wider. As the position of the particle becomes more precise when the slit is narrowed, the direction, or therefore the momentum, of the particle becomes less known as seen by a wider horizontal distribution of the light.



The Importance of the Heisenberg Uncertainty Principle

Heisenberg's Uncertainty Principle not only helped shape the new school of thought known today as quantum mechanics, but it also helped discredit older theories. Most importantly, the Heisenberg Uncertainty Principle made it obvious that there was a fundamental error in the Bohr model of the atom. Since the position and momentum of a particle cannot be known simultaneously, Bohr's theory that the electron traveled in a circular path of a fixed radius orbiting the nucleus was obsolete. Furthermore, Heisenberg's uncertainty principle, when combined with other revolutionary theories in quantum mechanics, helped shape wave mechanics and the current scientific understanding of the atom.

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Outside Links

- http://en.Wikipedia.org/wiki/Uncertainty_principle
- http://plato.stanford.edu/entries/qt-uncertainty/
- http://farside.ph.utexas.edu/teachin...es/node26.html
- www.marts100.com/hup.htm
- http://en.wikibooks.org/wiki/Quantum...inty_Principle
- www.youtube.com/watch?v=KT7xJ0tjB4A

Problems

1. What aspect of the Bohr model of the atom does the Heisenberg Uncertainty Principle discredit?
2. What is the difference between the Heisenberg Uncertainty Principle and the Observer Effect?
3. A Hydrogen atom has a radius of 0.05nm with a position accuracy of 1.0%. What is the uncertainty in determining the velocity?
4. What is the uncertainty in the speed of a beam of electrons whose position is known with an uncertainty of 10 nm?
5. Using the Uncertainty Principle, find the radius of an atom (in nm) that has an electron with a position accuracy of 3.0% and a known velocity of $2 \times 10^9\ m/s$.

Answers:

1.) The Heisenberg Uncertainty Principle discredits the aspect of the Bohr atom model that an electron is constrained to a one-dimensional orbit of a fixed radius around the nucleus.

2.) The Observer Effect means the act of observing a system will influence what is being observed, whereas the Heisenberg Uncertainty Principle has nothing to do with the observer or equipment used during observation. It simply states that a particle behaves both as a wave and a particle and therefore cannot have both a definite momentum and position.

3.) Uncertainty principle: $\Delta x \Delta p \geq h/4\Pi$

Can be written (x)(m)(v)(%)=h/4Π

(position)(mass of electron)(velocity)(percent accuracy)=(Plank's Constant)/4Π

$$(.05*10^{-9}\text{ m})(9.11*10^{-31}\text{ kg})(v)(.01)=(6.626*10^{-34}\text{ J*s})/4\Pi$$

$$v=1*10^{8}\text{ m/s}$$

4.) Uncertainty principle: $\Delta x \Delta p \geq h/4\Pi$

$$(10*10^{-9}\text{ m})(\Delta p)\geq(6.626*10^{-34}\text{ J*s})/4\Pi$$

$$\Delta p\geq 5*10^{-26}\text{ (kg*m)/s}$$

5.) Uncertainty principle: $\Delta x \Delta p \geq h/4\Pi$

Can be written (x)(m)(v)(%)=h/4Π

(position)(mass of electron)(velocity)(percent accuracy)=h/4Π

$$(\text{radius})(9.11*10^{-31}\text{ kg})(2*10^{9})(.03)=(6.626*10^{-34}\text{ J*s})/4\Pi$$

$$r=9*10^{-12}\text{ m}$$

$$r=9*10^{-3}\text{ nm}$$

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12.6: Particle in a Box

A total of four quantum numbers are used to describe completely the movement and trajectories of each electron within an atom. The combination of all quantum numbers of all electrons in an atom is described by a wave function that complies with the Schrödinger equation. Each electron in an atom has a unique set of quantum numbers; according to the Pauli Exclusion Principle, no two electrons can share the same combination of four quantum numbers. Quantum numbers are important because they can be used to determine the electron configuration of an atom and the probable location of the atom's electrons. Quantum numbers are also used to understand other characteristics of atoms, such as ionization energy and the atomic radius.

In atoms, there are a total of four quantum numbers: the principal quantum number (n), the orbital angular momentum quantum number (l), the magnetic quantum number (m_l), and the electron spin quantum number (m_s). The principal quantum number, n, describes the energy of an electron and the most probable distance of the electron from the nucleus. In other words, it refers to the size of the orbital and the energy level an electron is placed in. The number of subshells, or l, describes the shape of the orbital. It can also be used to determine the number of angular nodes. The magnetic quantum number, m_l, describes the energy levels in a subshell, and m_s refers to the spin on the electron, which can either be up or down.

The Principal Quantum Number (n)

The principal quantum number, n, designates the principal electron shell. Because n describes the most probable distance of the electrons from the nucleus, the larger the number n is, the farther the electron is from the nucleus, the larger the size of the orbital, and the larger the atom is. n can be any positive integer starting at 1, as $n = 1$ designates the first principal shell (the innermost shell). The first principal shell is also called the ground state, or lowest energy state. This explains why n can not be 0 or any negative integer, because there exists no atoms with zero or a negative amount of energy levels/principal shells. When an electron is in an excited state or it gains energy, it may jump to the second principle shell, where $n = 2$. This is called absorption because the electron is "absorbing" photons, or energy. Known as emission, electrons can also "emit" energy as they jump to lower principle shells, where n decreases by whole numbers. As the energy of the electron increases, so does the principal quantum number, e.g., n = 3 indicates the third principal shell, n = 4 indicates the fourth principal shell, and so on.

$$n = 1, 2, 3, 4 \dots \tag{12.6.1}$$

✓ Example 12.6.1

If n = 7, what is the principal electron shell?

✓ Example 12.6.2

If an electron jumped from energy level n = 5 to energy level n = 3, did absorption or emission of a photon occur?

Answer

Emission, because energy is lost by release of a photon.

The Orbital Angular Momentum Quantum Number (l)

The orbital angular momentum quantum number l determines the shape of an orbital, and therefore the angular distribution. The number of angular nodes is equal to the value of the angular momentum quantum number l. (For more information about angular nodes, see Electronic Orbitals.) Each value of l indicates a specific s, p, d, f subshell (each unique in shape.) The value of l is dependent on the principal quantum number n. Unlike n, the value of l can be zero. It can also be a positive integer, but it cannot be larger than one less than the principal quantum number ($n - 1$):

$$l = 0, 1, 2, 3, 4 \dots, (n - 1) \tag{12.6.2}$$

✓ Example 12.6.3

If $n = 7$, what are the possible values of l?

Answer

Since l can be zero or a positive integer less than ($n-1$), it can have a value of 0, 1, 2, 3, 4, 5 or 6.

✓ Example 12.6.4

If $l=4$, how many angular nodes does the atom have?

Answer

The number of angular nodes is equal to the value of l, so the number of nodes is also 4.

The Magnetic Quantum Number (m_l)

The magnetic quantum number m_l determines the number of orbitals and their orientation within a subshell. Consequently, its value depends on the orbital angular momentum quantum number l. Given a certain l, m_l is an interval ranging from $-l$ to $+l$, so it can be zero, a negative integer, or a positive integer.

$$m_l = -l, (-l+1), (-l+2), \ldots, -2, -1, 0, 1, 2, \ldots (l–2), (l–1), +l \tag{12.6.3}$$

✓ Example 12.6.5

Example: If $n=3$, and $l=2$, then what are the possible values of m_l?

Answer

Since m_l must range from $-l$ to $+l$, then m_l can be: -2, -1, 0, 1, or 2.

The Electron Spin Quantum Number (m_s)

Unlike n, l, and m_l, the electron spin quantum number m_s does not depend on another quantum number. It designates the direction of the electron spin and may have a spin of +1/2, represented by↑, or –1/2, represented by ↓. This means that when m_s is positive the electron has an upward spin, which can be referred to as "spin up." When it is negative, the electron has a downward spin, so it is "spin down." The significance of the electron spin quantum number is its determination of an atom's ability to generate a magnetic field or not. (Electron Spin.)

$$m_s = \pm \frac{1}{2} \tag{12.6.4}$$

✓ Example 12.6.5

List the possible combinations of all four quantum numbers when $n=2$, $l=1$, and $m_l=0$.

Answer

The fourth quantum number is independent of the first three, allowing the first three quantum numbers of two electrons to be the same. Since the spin can be +1/2 or =1/2, there are two combinations:

- $n=2, l=1, m_l=0, m_s=+1/2$
- $n=2, l=1, m_l=0, m_s=-1/2$

✓ Example 12.6.6

Can an electron with $m_s=1/2$ have a downward spin?

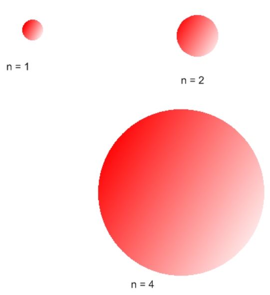
Answer

No, if the value of m_s is positive, the electron is "spin up."

A Closer Look at Shells, Subshells, and Orbitals

Principal Shells

The value of the principal quantum number n is the level of the principal electronic shell (principal level). All orbitals that have the same n value are in the same principal level. For example, all orbitals on the second principal level have a principal quantum number of n=2. When the value of n is higher, the number of principal electronic shells is greater. This causes a greater distance between the farthest electron and the nucleus. As a result, the size of the atom and its atomic radius increases.



Because the atomic radius increases, the electrons are farther from the nucleus. Thus it is easier for the atom to expel an electron because the nucleus does not have as strong a pull on it, and the ionization energy decreases.

✓ Example 12.6.7

Which orbital has a higher ionization energy, one with $n=3$ or $n=2$?

Answer

The orbital with n=2, because the closer the electron is to the nucleus or the smaller the atomic radius, the more energy it takes to expel an electron.

Subshells

The number of values of the orbital angular number l can also be used to identify the number of subshells in a principal electron shell:

- When n = 1, l= 0 (l takes on one value and thus there can only be one subshell)
- When n = 2, l= 0, 1 (l takes on two values and thus there are two possible subshells)
- When n = 3, l= 0, 1, 2 (l takes on three values and thus there are three possible subshells)

After looking at the examples above, we see that the value of n is equal to the number of subshells in a principal electronic shell:

- Principal shell with n = 1 has one subshell
- Principal shell with n = 2 has two subshells
- Principal shell with n = 3 has three subshells

To identify what type of possible subshells n has, these subshells have been assigned letter names. The value of l determines the name of the subshell:

Name of Subshell	Value of l
s subshell	0
p subshell	1
d subshell	2
f subshell	3

Therefore:

- Principal shell with n = 1 has one s subshell (l = 0)
- Principal shell with n = 2 has one s subshell and one p subshell (l = 0, 1)
- Principal shell with n = 3 has one s subshell, one p subshell, and one d subshell (l = 0, 1, 2)

We can designate a principal quantum number, n, and a certain subshell by combining the value of n and the name of the subshell (which can be found using l). For example, 3p refers to the third principal quantum number (n=3) and the p subshell (l=1).

✓ Example 12.6.8

What is the name of the orbital with quantum numbers n=4 and l=1?

Answer

Knowing that the principal quantum number n is 4 and using the table above, we can conclude that it is 4p.

✓ Example 12.6.9

What is the name of the oribital(s) with quantum number n=3?

Answer

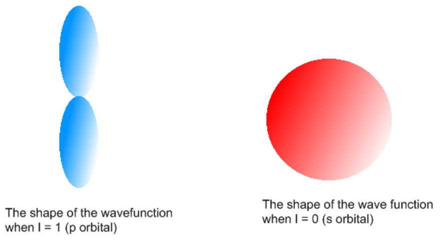
3s, 3p, and 3d. Because n=3, the possible values of l = 0, 1, 2, which indicates the shapes of each subshell.

Orbitals

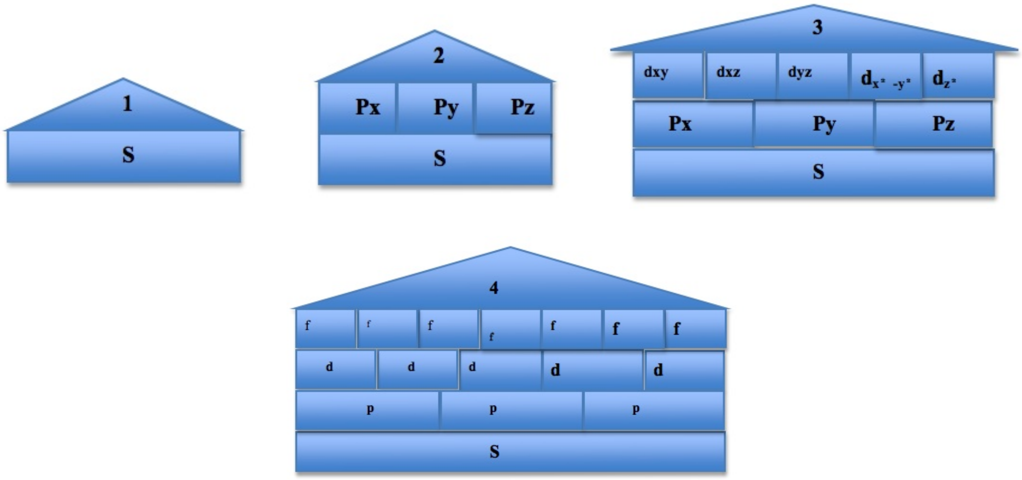
The number of orbitals in a subshell is equivalent to the number of values the magnetic quantum number ml takes on. A helpful equation to determine the number of orbitals in a subshell is 2l +1. This equation will not give you the value of ml, but the number of possible values that ml can take on in a particular orbital. For example, if l=1 and ml can have values -1, 0, or +1, the value of 2l+1 will be three and there will be three different orbitals. The names of the orbitals are named after the subshells they are found in:

	s orbitals	**p orbitals**	**d orbitals**	**f orbitals**
l	0	1	2	3
m_l	0	-1, 0, +1	-2, -1, 0, +1, +2	-3, -2, -1, 0, +1, +2, +3
Number of orbitals in designated subshell	1	3	5	7

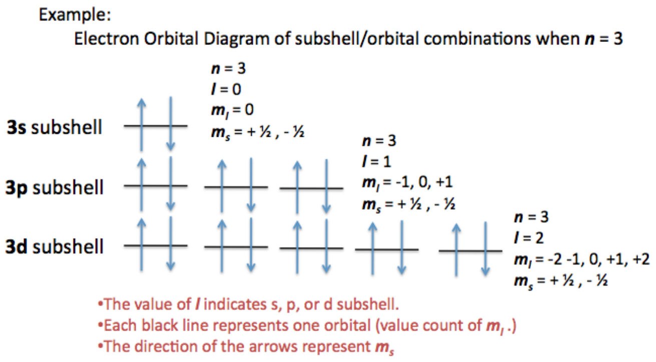
In the figure below, we see examples of two orbitals: the p orbital (blue) and the s orbital (red). The red s orbital is a 1s orbital. To picture a 2s orbital, imagine a layer similar to a cross section of a jawbreaker around the circle. The layers are depicting the atoms angular nodes. To picture a 3s orbital, imagine another layer around the circle, and so on and so on. The p orbital is similar to the shape of a dumbbell, with its orientation within a subshell depending on m_l. The shape and orientation of an orbital depends on l and m_l.



To visualize and organize the first three quantum numbers, we can think of them as constituents of a house. In the following image, the roof represents the principal quantum number n, each level represents a subshell l, and each room represents the different orbitals ml in each subshell. The s orbital, because the value of ml can only be 0, can only exist in one plane. The p orbital, however, has three possible values of ml and so it has three possible orientations of the orbitals, shown by Px, Py, and Pz. The pattern continues, with the d orbital containing 5 possible orbital orientations, and f has 7:



Another helpful visual in looking at the possible orbitals and subshells with a set of quantum numbers would be the electron orbital diagram. (For more electron orbital diagrams, see Electron Configurations.) The characteristics of each quantum number are depicted in different areas of this diagram.



Restrictions

- Pauli Exclusion Principle: In 1926, Wolfgang Pauli discovered that a set of quantum numbers is specific to a certain electron. That is, no two electrons can have the same values for n, l, ml, and ms. Although the first three quantum numbers identify a specific orbital and may have the same values, the fourth is significant and must have opposite spins.
- Hund's Rule: Orbitals may have identical energy levels when they are of the same principal shell. These orbitals are called degenerate, or "equal energy." According to Hund's Rule, electrons fill orbitals one at a time. This means that when drawing electron configurations using the model with the arrows, you must fill each shell with one electron each before starting to pair them up. Remember that the charge of an electron is negative and electrons repel each other. Electrons will try to create distance between it and other electrons by staying unpaired. This further explains why the spins of electrons in an orbital are opposite (i.e. +1/2 and -1/2).
- Heisenberg Uncertainty Principle: According to the Heisenberg Uncertainty Principle, we cannot precisely measure the momentum and position of an electron at the same time. As the momentum of the electron is more and more certain, the position of the electron becomes less certain, and vice versa. This helps explain integral quantum numbers and why n=2.5 cannot exist as a principal quantum number. There must be an integral number of wavelengths (n) in order for an electron to maintain a standing wave. If there were to be partial waves, the whole and partial waves would cancel each other out and the particle would not move. If the particle was at rest, then its position and momentum would be certain. Because this is not so, n

must have an integral value. It is not that the principal quantum number can only be measured in integral numbers, it is because the crest of one wave will overlap with the trough of another, and the wave will cancel out.

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Problems

1. Suppose that all you know about a certain electron is that its principal quantum number is 3. What are the possible values for the other four quantum numbers?
2. Is it possible to have an electron with these quantum numbers: $n=2$, $l=1$, $m_l=3$, $m_s=1/2$? Why or why not?
3. Is it possible to have two electrons with the same n, l, and m_l?
4. How many subshells are in principal quantum level $n=3$?
5. What type of orbital is designated by quantum numbers $n=4$, $l=3$, and $m_l=0$?

Solutions

1.
   - When $n=3, l=0, m_l=0$, and $m_s=+1/2$ or $-1/2$
   - $l=1, m_l=-1, 0, or +1$, and $m_s=+1/2$ or $-1/2$
   - $l=2, m_l=-2, -1, 0, 1, \text{ or } +2$, and $m_s=+1/2$ or $-1/2$
2. No, it is not possible. $m_l=3$ is not in the range of $-l$ to $+l$. The value should be be either -1, 0, or +1.
3. Yes, it is possible to have two electrons with the same n, l, and m_l. The spin of one electron must be +1/2 while the spin of the other electron must be -1/2.
4. There are three subshells in principal quantum level $n=3$.
5. Since $l=3$ refers to the f subshell, the type of orbital represented is 4f (combination of the principal quantum number n and the name of the subshell).

Contributors and Attributions

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12.9: Orbital Shapes and Energies

An atom is composed of a nucleus containing neutrons and protons with electrons dispersed throughout the remaining space. Electrons, however, are not simply floating within the atom; instead, they are fixed within electronic orbitals. Electronic orbitals are regions within the atom in which electrons have the highest probability of being found.

Quantum Numbers describing Electronic Orbitals

There are multiple orbitals within an atom. Each has its own specific energy level and properties. Because each orbital is different, they are assigned specific quantum numbers: 1s, 2s, 2p 3s, 3p,4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p. The numbers, (n=1,2,3, etc.) are called *principal quantum numbers* and can only be positive numbers. The letters (*s,p,d,f*) represent the *orbital angular momentum quantum number* (ℓ) and the orbital angular momentum quantum number may be 0 or a positive number, but can never be greater than n-1. Each letter is paired with a specific ℓ value:

s: subshell = 0
p: subshell = 1
d: subshell = 2
f: subshell = 3

An orbital is also described by its *magnetic quantum number* (m_ℓ). The magnetic quantum number can range from $-\ell$ to $+\ell$. This number indicates how many orbitals there are and thus how many electrons can reside in each atom.

Orbitals that have the same or identical energy levels are referred to as **degenerate.** An example is the 2p orbital: $2p_x$ has the same energy level as $2p_y$. This concept becomes more important when dealing with molecular orbitals. The **Pauli exclusion principle** states that no two electrons can have the same exact orbital configuration; in other words, the same quantum numbers. However, the electron can exist in spin up ($m_s = +1/2$) or with spin down ($m_s = -1/2$) configurations. This means that the s orbital can contain up to two electrons, the p orbital can contain up to six electrons, the d orbital can contain up to 10 electrons, and the f orbital can contain up to 14 electrons.

Table 1: Breakdown and Properties of Subshells

s subshell	p subshell	d subshell	f subshell
$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$
$m_\ell = 0$	m_ℓ= -1, 0, +1	m_ℓ= -2, -1, 0, +1, +2	m_ℓ= -3, -2, -1, 0, +1, +2, +3
One s orbital	Three p orbitals	Five d orbitals	Seven f orbitals
2 s orbital electrons	6 p orbital electrons	10 d orbital electrons	14 f orbital electrons

Visualizing Electron Orbitals

As discussed in the previous section, the magnetic quantum number (m_l) can range from –l to +l. The number of possible values is the number of lobes (orbitals) there are in the s, p, d, and f subshells. As shown in Table 1, the s subshell has one lobe, the p subshell has three lobes, the d subshell has five lobes, and the f subshell has seven lobes. Each of these lobes is labeled differently and is named depending on which plane the lobe is resting in. If the lobe lies along the x plane, then it is labeled with an x, as in $2p_x$. If the lobe lies along the xy plane, then it is labeled with a xy such as d_{xy}. Electrons are found within the lobes. The plane (or planes) that the orbitals do not fill are called nodes. These are regions in which there is a 0 probability density of finding electrons. For example, in the d_{yx} orbital, there are nodes on planes xz and yz. This can be seen in Figure $12.9.1$.

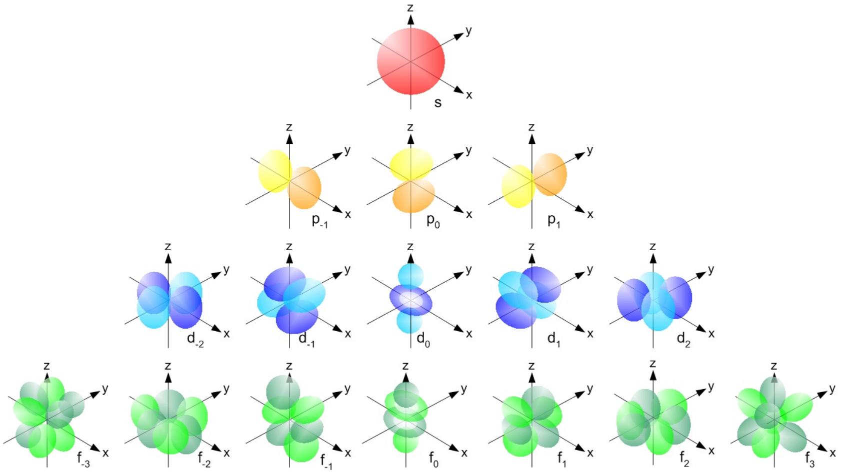

Figure 12.9.1: The 1s orbital (red), the 2p orbitals (yellow), the 3d orbitals (blue) and the 4f orbitals (green) are contrasted.

Radial and Angular Nodes

There are two types of nodes, angular and radial nodes. **Angular nodes** are typically flat plane (at fixed angles), like those in the diagram above. The ℓ quantum number determines the number of angular nodes in an orbital. **Radial nodes** are spheres (at fixed radius) that occurs as the principal quantum number increases. The total nodes of an orbital is the sum of angular and radial nodes and is given in terms of the n and l quantum number by the following equation:

$$N = n - l - 1 \tag{12.9.1}$$

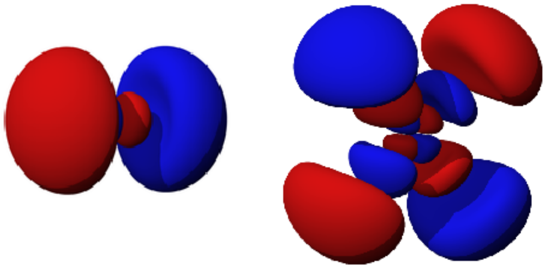

Figure 12.9.2: Two orbitals. (left) The $3p_x$ orbital has one radial node and one angular node. (right) The $5d_{xz}$ orbital has two radial nodes and two angular nodes. Images used with permission from Wikipedia

For example, determine the nodes in the $3p_z$ orbital, given that n = 3 and ℓ = 1 (because it is a p orbital). The total number of nodes present in this orbital is equal to n-1. In this case, 3-1=2, so there are 2 total nodes. The quantum number ℓ determines the number of angular nodes; there is 1 angular node, specifically on the xy plane because this is a p_z orbital. Because there is one node left, there must be one radial node. To sum up, the $3p_z$ orbital has 2 nodes: 1 angular node and 1 radial node. This is demonstrated in Figure 2.

Another example is the $5d_{xy}$ orbital. There are four nodes total (5-1=4) and there are two angular nodes (d orbital has a quantum number ℓ=2) on the xz and zy planes. This means there there must be two radial nodes. The number of radial and angular nodes can only be calculated if the principal quantum number, type of orbital (s,p,d,f), and the plane that the orbital is resting on (x,y,z, xy, etc.) are known.

Electron Configuration within an Orbital

We can think of an atom like a hotel. The nucleus is the lobby where the protons and neutrons are, and in the floors above, we find the rooms (orbitals) with the electrons. The principal quantum number is the floor number, the subshell type lets us know what type of room it is (s being a closet, p being a single room, d having two adjoining rooms, and f being a suit with three rooms) , the magnetic quantum number lets us know how many beds there are in the room, and two electrons can sleep in one bed (this is because each has a different spin; -1/2 and 1/2). For example, on the first floor we have the s orbital. The s orbital is a closet and has one bed in it so the first floor can hold a total of two electrons. The second floor has the room styles s and p. The s is a closet with one bed as we know and the p room is a single with three beds in it so the second floor can hold a total of 8 electrons.

Each orbital, as previously mentioned, has its own energy level associated to it. The lowest energy level electron orbitals are filled first and if there are more electrons after the lowest energy level is filled, they move to the next orbital. The order of the electron orbital energy levels, starting from least to greatest, is as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p.

Since electrons all have the same charge, they stay as far away as possible because of repulsion. So, if there are open orbitals in the same energy level, the electrons will fill each orbital singly before filling the orbital with two electrons. For example, the 2p shell has three p orbitals. If there are more electrons after the 1s, and 2s orbitals have been filled, each p orbital will be filled with one electron first before two electrons try to reside in the same p orbital. This is known as **Hund's rule**.

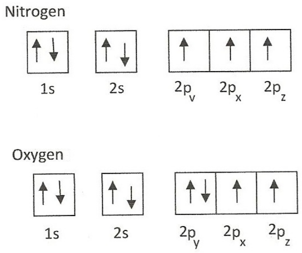

Figure 12.9.3: Electron configuration of nitrogen and oxygen atoms

The way electrons move from one orbital to the next is very similar to walking up a flight of stairs. When walking up stairs, you place one foot on the first stair and then another foot on the second stair. At any point in time, you can either stand with both feet on the first stair, or on the second stair but it is impossible to stand in between the two stairs. This is the way electrons move from one electron orbital to the next. Electrons can either jump to a higher energy level by absorbing, or gaining energy, or drop to a lower energy level by emitting, or losing energy. However, electrons will never be found in between two orbitals.

Problems

1. Which orbital would the electrons fill first? The 2s or 2p orbital?
2. How many d orbitals are there in the d subshell?
3. How many electrons can the p orbital hold?
4. Determine the number of angular and radial nodes of a 4f orbital.
5. What is the shape of an orbital with 4 radial nodes and 1 angular node in the xy plane?

Solutions

1. The 2s orbital would be filled before the 2p orbital because orbitals that are lower in energy are filled first. The 2s orbital is lower in energy than the 2p orbital.
2. There are 5 d orbitals in the d subshell.
3. A p orbital can hold 6 electrons.
4. Based off of the given information, n=4 and ℓ=3. Thus, there are 3 angular nodes present. The total number of nodes in this orbital is: 4-1=3, which means there are no radial nodes present.

5. 1 angular node means ℓ=1 which tells us that we have a p subshell, specifically the p_z orbital because the angular node is on the xy plane. The total number of nodes in this orbital is: 4 radial nodes +1 angular node=5 nodes. To find n, solve the equation: nodes=n-1; in this case, 5=n-1, so n=6. This gives us a: $6p_z$ orbital

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12.10: Electron Spin and the Pauli Principle

Electron Spin or Spin Quantum Number is the fourth quantum number for electrons in atoms and molecules. Denoted as m_s, the electron spin is constituted by either upward ($m_s = +1/2$) or downward ($m_s = -1/2$) arrows.

Introduction

In 1920, Otto Stern and Walter Gerlach designed an experiment, which unintentionally led to the discovery that electrons have their own individual, continuous spin even as they move along their orbital of an atom. Today, this electron spin is indicated by the fourth quantum number, also known as the **Electron Spin Quantum Number** and denoted by m_s. In 1925, Samuel Goudsmit and George Uhlenbeck made the claim that features of the hydrogen spectrum that were unexamined might by explained by assuming electrons act as if it has a spin. This spin can be denoted by an arrow pointing up, which is +1/2, or an arrow pointing down, which is -1/2.

The experiment mentioned above by Otto Stern and Walter Gerlach was done with silver which was put in an oven and vaporized. The result was that silver atoms formed a beam that passed through a magnetic field in which it split in two.

An explanation of this is that an electron has a magnetic field due to its spin. When electrons that have opposite spins are put together, there is no net magnetic field because the positive and negative spins cancel each other out. The silver atom used in the experiment has a total of 47 electrons, 23 of one spin type, and 24 of the opposite. Because electrons of the same spin cancel each other out, the one unpaired electron in the atom will determine the spin. There is a high likelihood for either spin due to the large number of electrons, so when it went through the magnetic field it split into two beams.

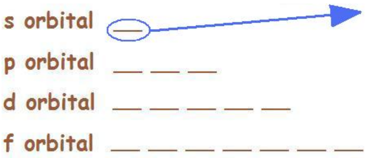
Brief Explanation of Quantum Numbers

Note: In this module, capital "L" will be used instead of small case "l" for angular momentum quantum number.

A total of four quantum numbers were developed to better understand the movement and pathway of electrons in its designated orbital within an atom.

1. Principal quantum number (*n*): energy level *n* = 1, 2, 3, 4, ...
2. Orbital Angular Momentum Quantum Number (*L*): shape (of orbital) *L* = 0, 1, 2, 3, ...*n*-1
3. Magnetic Quantum Number (m_L): orientation m_L = interval of (-*L*, +*L*)
4. **Electron Spin Quantum Number** (m_s): independent of other three quantum numbers because m_s *is always = –½ or +½*

(For more information about the three quantum numbers above, see Quantum Number.)



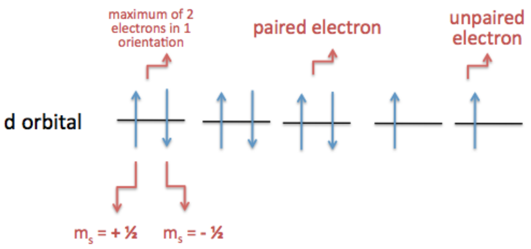
The lines represent how many orientations each orbital has, (e.g. the s-orbital has one orientation, a p-orbital has three orientations, etc.) and each line can hold up to two electrons, represented by up and down arrows. An electron with an up arrow means it has an electron spin of $+\frac{1}{2}$, and an electron with a down arrow means it has an electron spin of $-\frac{1}{2}$.

Electron Spin

Significance: determines if an atom will or will not generate a magnetic field (For more information, scroll down to *Magnetic Spin, Magnetism, and Magnetic Field Lines*). Although the electron spin is limited to +½ or –½, certain rules apply when assigning electrons of different spins to fill a subshell (orientations of an orbital) . For more information, scroll down to *Assigning Spin Direction*.

Magnetic Spin, Magnetism, and Magnetic Field Lines

Example :



This is **paramagnetic** because there exists one or more unpaired electrons.

An atom with **unpaired** electrons are termed as **paramagnetic**

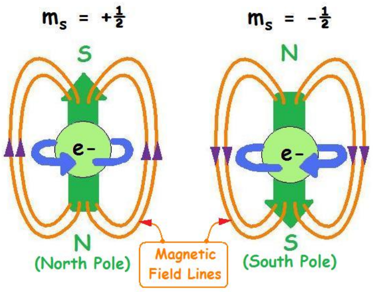
- results in a **net** magnetic field because electrons within the orbital are not stabilized or balanced enough
- atoms are attracted to magnets

An atom with **paired** electrons are termed as **diamagnetic**

- results in **no** magnetic field because electrons are uniform and stabilized within the orbital
- atoms are not attracted to magnets

Applying concepts of magnetism with liquid nitrogen and liquid oxygen:

The magnetic spin of an electron follows in the direction of the magnetic field lines as shown below.



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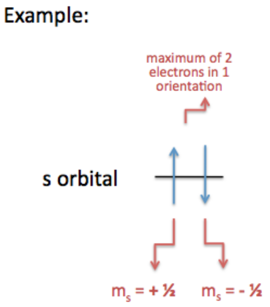
Assigning Spin Direction

An effective visual on how to assign spin directions can be represented by the orbital diagram (shown previously and below.) Restrictions apply when assigning spin directions to electrons, so the following Pauli Exclusion Principle and Hund's Rule help explain this. The direction of the electron spin **magnetic quantum number, m_s**, can only be determined its interaction with a magnetic field. Electrons whose spin is parallel to an external magnetic field (spin up with +$\frac{1}{2}$ spin) have a lower energy than those whose magnetic spin is anti-parallel (spin down with -$\frac{1}{2}$ spin) to the external magnetic and fill first.

When one is filling an orbital, such as the p orbital, you must fill all orbitals possible with spin up electrons before assigning the opposite spin. For example, when filling the fluorine, which will have a total of two electrons in the s orbital and a total of five electrons in the p orbital, one will start with the s orbital which will contain two electrons. So, the first electron one assigns will be spin up and the next spin down. Moving on to the three p orbitals that one will start by assigning a spin up electron in each of the three orbitals. That takes up three of the five electrons, so with the remaining two electrons, one returns to the first and second p orbital and assigns the spin down electron. This means there will be one unpaired electron in fluorine so it will be paramagnetic.

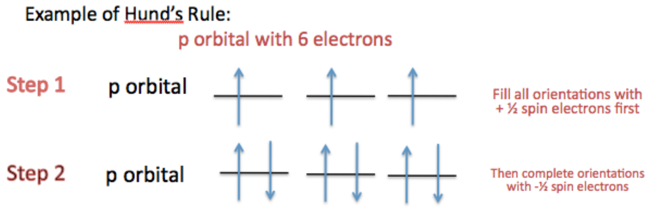
Pauli Exclusion Principle

The Pauli exclusion principle declares that there can only be a maximum of two electrons for every one orientation, and the two electrons must be opposite in spin direction; meaning one electron has $m_s = +\frac{1}{2}$ and the other electron has $m_s = -\frac{1}{2}$.



Hund's Rule

Hund's Rule declares that the electrons in the orbital are filled up first by electrons whose spins are parallel to each other. Once all the orbitals are filled with unpaired +$\frac{1}{2}$ spins, the orbitals are then filled with -$\frac{1}{2}$ spin. (**See examples below, labeled electronic configuration.)**



(For more information on Pauli Exclusion Principle and Hund's Rules, see Electronic Configuration.)

Identifying Spin Direction

1. Determine the number of electrons the atom has.
2. Draw the electron configuration for the atom. See Electronic Configurations for more information.
3. Distribute the electrons, using up and down arrows to represent the electron spin direction.

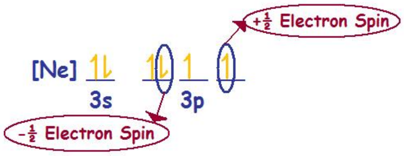
✓ Example 1: Sulfur

Sulfur - S (16 electrons)

Electronic Configuration:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ **OR** [Ne] $3s^2\ 3p^4$

As shown in the following image, this is a demonstration of a -$\frac{1}{2}$ and a +$\frac{1}{2}$ Electron Spin.



Principal Quantum Number & (s, p, d, f) Orbitals

When given a principal quantum number, n, with either the s, p, d or f-orbital, identify all the possibilities of L, m_L and m_s.

Example 2

Given 5f, identify all the possibilities of the four quantum numbers.

Solution

In this problem, the principal quantum number is n = 5 (the subshell number placed in front of the orbital, the f-orbital in this case). Since we are looking at the f-obital, therefore L = 3. (Look under "Subshells" in the module Quantum Numbers for more information) Knowing L = 3, we can interpret that $m_L = 0, \pm 1, \pm 2, \pm 3$ since m_L = -L,...,-1, 0, 1,...+L. As for m_s, since it isn't specified in the problem as to whether it is $-\frac{1}{2}$ or $+\frac{1}{2}$, therefore for this problem, it could be both; meaning that the electron spin quantum number is $\pm\frac{1}{2}$.

Example 3

Given 6s and m_L= +1, identify all the possibilities of the four quantum numbers.

Solution

The principal quantum number is n = 6. Looking at the s-orbital, we know that L = 0. Knowing that m_L = -L,...,-1, 0, 1,...+L, therefore m_L = +1 is **not possible** since in this problem, the interval of m_L can only equal to 0 according to the angular momentum quantum number, L.

Example 4

Given 4d and $m_s = +\frac{1}{2}$, identify all the possibilities of the four quantum numbers.

Solution

The principal quantum number is n = 4. Given that it is a d-orbital, we know that L = 2. Therefore, $m_L = 0, \pm 1, \pm 2$ since m_L = -L,...,-1, 0, 1,...+L. For m_s, this problem specifically said $m_s = +\frac{1}{2}$; meaning that the electron spin quantum number is $+\frac{1}{2}$.

Electron Spin: Where to begin?

First, draw a table labeled n, L, $m_L$and m_s, as shown below:

n	L	m_L	m_s

Then, depending on what the question is asking for, fill in the boxes accordingly. Finally, determine the number of electrons for the given quantum number, n, with regards to L, m_L and m_s.

Example 5

How many electrons can have n = 5 and L = 1? <u>6</u>

n	L	m_L	m_s
5	1	-1	$-\frac{1}{2}, +\frac{1}{2}$
		0	$-\frac{1}{2}, +\frac{1}{2}$

		+1	$-\frac{1}{2}$, $+\frac{1}{2}$

This problem includes both $-\frac{1}{2}$, $+\frac{1}{2}$, therefore the answer is **6** electrons based on the three possible values of m_L.

Example 6

How many electrons can have n = 5 and $m_s = -\frac{1}{2}$? 9

n	L	m_L	m_s
5	4	± 4	$-\frac{1}{2}$
	3	± 3	$-\frac{1}{2}$
	2	± 2	$-\frac{1}{2}$
	1	± 1	$-\frac{1}{2}$
	0	0	$-\frac{1}{2}$

This problem only wants the Spin Quantum Number to be $-\frac{1}{2}$, the answer is **9** electrons based on the 9 different values of m_L .

Example 7

How many electrons can have n = 3, L = 2 and m_L = 3? zero

Solution

n	L	m_L	m_s
3	2	NOT POSSIBLE	

Since **m_L = -L...-1, 0, +1...+L** (See Electronic Orbitals for more information), m_L is not possible because L = 2, so it is impossible for m_L to be equal to 3. So, there is **zero** electrons.

Example 8

How many electrons can have n = 3, m_L = +2 and $m_s = +\frac{1}{2}$? 1

Solution

n	L	m_L	m_s
3	2	+2	$+\frac{1}{2}$

This problem only wants the Spin Quantum Number to be $+\frac{1}{2}$, the answer is **1** electron based on the value of m_L and m_s.

References

1. Petrucci, Ralph. Harwood, William. Herring, Geoffrey. Madura, Jeffery. *General Chemistry: Principles and Modern Applications, 9th Edition.* Pearson Education, Inc. New Jersey, 2007.
2. Li, Gengyun. *What is the Electron Spin?* Spin Publishing, 2003.
3. Motz, Lloyd and Weaver, Jefferson H. *The Unfolding Universe: A Stellar Journey.* Perseus, 1989.

Practice Problems

1. Identify the spin direction (e.g. $m_s = -\frac{1}{2}$ or $+\frac{1}{2}$ or $\pm\frac{1}{2}$) of the outermost electron in a Sodium (Na) atom.
2. Identify the spin direction of the outermost electron in a Chlorine (Cl) atom.
3. Identify the spin direction of the outermost electron in a Calcium (Ca) atom.
4. Given 5p and $m_s = +\frac{1}{2}$, identify all the possibilities of the four quantum numbers.

5. Given 6f, identify all the possibilities of the four quantum numbers.
6. How many electrons can have n = 4 and L = 1?
7. How many electrons can have n = 4, L = 1, m_L = -2 and m_s = $+\frac{1}{2}$?
8. How many electrons can have n = 5, L = 3, m_L = ± 2 and m_s = $+\frac{1}{2}$?
9. How many electrons can have n = 5, L = 4, m_L = +3 and m_s = $-\frac{1}{2}$?
10. How many electrons can have n = 4, L = 2, m_L = ±1 and m_s = $-\frac{1}{2}$?
11. How many electrons can have n = 3, L = 3, m_L = +2?

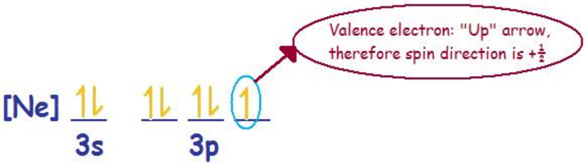
Solutions: Check your work!

Problem (1): Sodium (Na) --> Electronic Configuration [Ne] $3s^1$

Spin direction for the valence electron or $m_s = +\frac{1}{2}$

Sodium (Na) with a neutral charge of zero is paramagnetic, meaning that the electronic configuration for Na consists of one or more unpaired electrons.

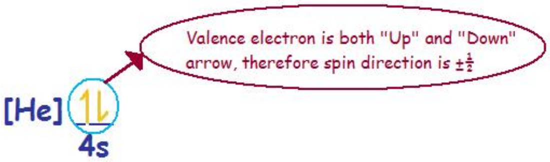
Problem (2): Chlorine (Cl) --> Electronic Configuration [Ne] $3s^2$ $3p^5$



Spin direction for the valence electron or $m_s = +\frac{1}{2}$

Chlorine (Cl) with a neutral charge of zero is paramagnetic.

Problem (3): Calcium (Ca) --> Electronic Configuration [He] $4s^2$



Spin direction for the valence electron or $m_s = \pm\frac{1}{2}$

Whereas for Calcium (Ca) with a neutral charge of zero, it is diamagnetic; meaning that ALL the electrons are paired as shown in the image above.

Problem (4): Given 5p and $m_s = -\frac{1}{2}$, identify all the possibilities of the four quantum numbers.

The principal quantum number is n = 5. Given that it is a p-orbital, we know that L = 1. And based on L, m_L = 0, ± 1 since m_L = -L,...,-1, 0, 1,...+L. As for m_s, this problem specifically says $m_s = -\frac{1}{2}$, meaning that the spin direction is $-\frac{1}{2}$, pointing downwards ("down" spin).

Problem (5): Given 6f, identify all the possibilities of the four quantum numbers.

The principal quantum number is n = 6. Given that it is a f-orbital, we know that L = 3. Based on L, m_L = 0, ± 1, ± 2, ± 3 since m_L = -L,...,-1, 0, 1,...+L. As for m_s, since it isn't specified in the problem as to whether it is $-\frac{1}{2}$ or $+\frac{1}{2}$, therefore for this problem, it could be both; meaning that the electron spin quantum number is $\pm\frac{1}{2}$.

Problem (6): How many electrons can have n = 4 and L = 1? 6

n	L	m_L	m_s
4	1	± 1	$-\frac{1}{2}, +\frac{1}{2}$
		0	

This problem includes both $-\frac{1}{2}$, $+\frac{1}{2}$, therefore the answer is **6** electrons based on the m_L.

Problem (7): How many electrons can have n = 4, L = 1, m_L = -2 and $m_s = +\frac{1}{2}$? zero

n	L	m_L	m_s
4	1	NOT POSSIBLE	$+\frac{1}{2}$

Since **m_L = -L...-1, 0, +1...+L**, m_L is not possible because L = 1, so it is impossible for m_L to be equal to 2 when m_L MUST be with the interval of -L and +L. So, there is **zero** electron.

Problem (8): How many electrons can have n = 5, L = 3, $m_L = \pm 2$ and $m_s = +\frac{1}{2}$? 2

n	L	m_L	m_s
5	3	± 2	$+\frac{1}{2}$
		± 1	
		0	

This problem only wants the Spin Quantum Number to be $+\frac{1}{2}$ and $m_L = \pm 2$, therefore **2** electrons can have n = 5, L = 3, $m_L = \pm 2$ and $m_s = +\frac{1}{2}$.

Problem (9): How many electrons can have n = 5, L = 4 and m_L = +3? 2

n	L	m_L	m_s
5	4	-3, +3	$-\frac{1}{2}, +\frac{1}{2}$
		± 2	
		± 1	
		0	

This problem includes both $-\frac{1}{2}$ and $+\frac{1}{2}$ and given that m_L = +3, therefore the answer is **2** electrons.

Problem (10): How many electrons can have n = 4, L = 2 and $m_L = \pm 1$? 4

n	L	m_L	m_s
4	2	± 1	$-\frac{1}{2}, +\frac{1}{2}$
		0	

This problem includes both $-\frac{1}{2}$ and $+\frac{1}{2}$ and given that $m_L = \pm 1$, therefore the answer is **4** electrons.

Problem (11): How many electrons can have n = 3, L = 3, m_L = +2 and $m_s = -\frac{1}{2}$? zero

n	L	m_L	m_s
3	3 (NOT POSSIBLE)	± 2	$-\frac{1}{2}$
		± 1	
		0	

Since **L = n - 1,** there is **<u>zero</u>** electron, not possible because in this problem, n = L = 3.

Contributors and Attributions

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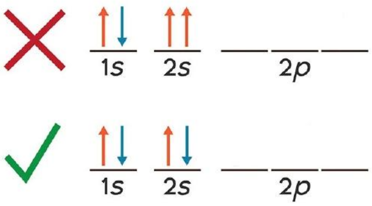
The **Pauli Exclusion Principle** states that, in an atom or molecule, no two electrons can have the **same** four electronic quantum numbers. As an orbital can contain a maximum of only two electrons, the two electrons must have opposing spins. This means if one electron is assigned as a spin up (+1/2) electron, the other electron must be spin-down (-1/2) electron.

Electrons in the same orbital have the same first three quantum numbers, e.g., $n = 1, l = 0, m_l = 0$ for the 1*s* subshell. Only two electrons can have these numbers, so that their spin moments must be either $m_s = -1/2$ or $m_s = +1/2$. If the 1*s* orbital contains only one electron, we have one m_s value and the electron configuration is written as $1s^1$ (corresponding to hydrogen). If it is fully occupied, we have two m_s values, and the electron configuration is $1s^2$ (corresponding to helium). Visually these two cases can be represented as



As you can see, the 1*s* and 2s subshells for beryllium atoms can hold only two electrons and when filled, the electrons must have opposite spins. Otherwise they will have the same four quantum numbers, in violation of the Pauli Exclusion Principle.

The Aufbau section discussed how electrons fill the lowest energy orbitals first, and then move up to higher energy orbitals only after the lower energy orbitals are full. However, there is a problem with this rule. Certainly, 1s orbitals should be filled before 2s orbitals, because the 1s orbitals have a lower value of n, and thus a lower energy. What about filling the three different 2p orbitals? In what order should they be filled? The answer to this question involves Hund's rule.

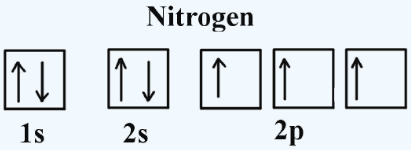
Hund's rule states that:

1. Every orbital in a sublevel is singly occupied before any orbital is doubly occupied.
2. All of the electrons in singly occupied orbitals have the same spin (to maximize total spin).

When assigning electrons to orbitals, an electron first seeks to fill all the orbitals with similar energy (also referred to as degenerate orbitals) before pairing with another electron in a half-filled orbital. Atoms at ground states tend to have as many unpaired electrons as possible. In visualizing this process, consider how electrons exhibit the same behavior as the same poles on a magnet would if they came into contact; as the negatively charged electrons fill orbitals, they first try to get as far as possible from each other before having to pair up.

✓ Example 12.10.1: Nitrogen Atoms

Consider the correct electron configuration of the nitrogen (Z = 7) atom: $1s^2\ 2s^2\ 2p^3$

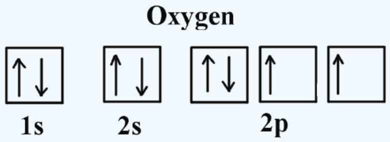


The p orbitals are half-filled; there are three electrons and three p orbitals. This is because the three electrons in the 2p subshell will fill all the empty orbitals first before pairing with electrons in them.

Keep in mind that elemental nitrogen is found in nature typically as molecular nitrogen, N_2, which requires molecular orbitals instead of atomic orbitals as demonstrated above.

✓ Example 12.10.2: Oxygen Atoms

Next, consider oxygen (Z = 8) atom, the element after nitrogen in the same period; its electron configuration is: $1s^2\ 2s^2\ 2p^4$



Oxygen has one more electron than nitrogen; as the orbitals are all half-filled, the new electron must pair up. Keep in mind that elemental oxygen is found in nature typically as molecular oxygen, O_2, which has molecular orbitals instead of atomic orbitals as demonstrated above.

Hund's Rule Explained

According to the first rule, electrons always enter an empty orbital before they pair up. Electrons are negatively charged and, as a result, they repel each other. Electrons tend to minimize repulsion by occupying their own orbitals, rather than sharing an orbital with another electron. Furthermore, quantum-mechanical calculations have shown that the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus. Electron shielding is further discussed in the next section.

For the second rule, unpaired electrons in singly occupied orbitals have the same spins. Technically speaking, the first electron in a sublevel could be either "spin-up" or "spin-down." Once the spin of the first electron in a sublevel is chosen, however, the spins of all of the other electrons in that sublevel depend on that first spin. To avoid confusion, scientists typically draw the first electron, and any other unpaired electron, in an orbital as "spin-up."

✓ Example 12.10.3: Carbon and Oxygen

Consider the electron configuration for carbon atoms: $1s^22s^22p^2$: The two 2s electrons will occupy the same orbital, whereas the two 2p electrons will be in different orbital (and aligned the same direction) in accordance with Hund's rule.

Consider also the electron configuration of oxygen. Oxygen has 8 electrons. The electron configuration can be written as $1s^22s^22p^4$. To draw the orbital diagram, begin with the following observations: the first two electrons will pair up in the 1s orbital; the next two electrons will pair up in the 2s orbital. That leaves 4 electrons, which must be placed in the 2p orbitals. According to Hund’s rule, all orbitals will be singly occupied before any is doubly occupied. Therefore, two p orbital get one electron and one will have two electrons. Hund's rule also stipulates that all of the unpaired electrons must have the same spin. In keeping with convention, the unpaired electrons are drawn as "spin-up", which gives (Figure 1).

Purpose of Electron Configurations

When atoms come into contact with one another, it is the outermost electrons of these atoms, or valence shell, that will interact first. An atom is least stable (and therefore most reactive) when its valence shell is not full. The valence electrons are largely responsible for an element's chemical behavior. Elements that have the same number of valence electrons often have similar chemical properties.

Electron configurations can also predict stability. An atom is most stable (and therefore unreactive) when all its orbitals are full. The most stable configurations are the ones that have full energy levels. These configurations occur in the noble gases. The noble gases are very stable elements that do not react easily with any other elements. Electron configurations can assist in making predictions about the ways in which certain elements will react, and the chemical compounds or molecules that different elements will form.

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12.11: Polyelectronic Atoms

Electrons with more than one atom, such as Helium (He), and Nitrogen (N), are referred to as multi-electron atoms. Hydrogen is the only atom in the periodic table that has one electron in the orbitals under ground state. We will learn how additional electrons behave and affect a certain atom.

Introduction

Let's review some basic concepts. First, electrons repel against each other. Particles with the same charge repel each other, while oppositely charged particles attract each other. For example, a proton, which is positively charged, is attracted to electrons, which are negatively charged. However, if we put two electrons together or two protons together, they will repel one another. Since neutrons lack a charge, they will neither repel nor attract protons or electrons.

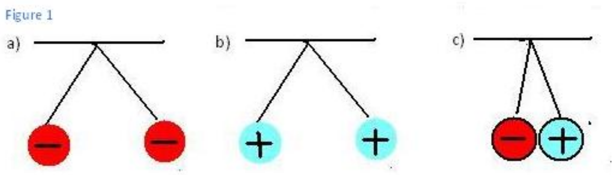

Figure 1: a) The two electrons are placed together and repel each other because of the same charge. b) The two protons are repelling each other for the same reason. c) When oppositely charged particles, an electron and a proton, are placed together, they attract each other.

Protons and neutrons are located in an atom's nucleus. Electrons float around the atom in energy levels. Energy levels consist of orbitals and sub-orbitals. The lower the energy level the electron is located at, the closer it is to nucleus. As we go down and to the right of the periodic table, the number of electrons that an element has increases. Since there are more electrons, the atom experiences greater repulsion and electrons will tend to stay as far away from each other as possible. Our main focus is what effects take place when more electrons surround the nucleus. To better understand the following concepts it is a good idea to first review quantum mechanics.

Shielding (Screening)

With more protons in the nucleus, the attractive force for electrons to the nucleus is stronger. Thus, the orbital energy becomes more negative (less energy). Orbital energy also depends on the type of l orbital an electron is located in. The lower the number of l, the closer it is to the nucleus. For example, $l=0$ is the s orbital. S orbitals are closer to the nucleus than the p orbitals ($l=1$) that are closer to the nucleus than the d orbitals ($l=2$) that are closer to the f orbitals ($l=3$).

More electrons create the shielding or screening effect. **Shielding** or **screening** means the electrons closer to the nucleus block the outer valence electrons from getting close to the nucleus. See figure 2. Imagine being in a crowded auditorium in a concert. The enthusiastic fans are going to surround the auditorium, trying to get as close to the celebrity on the stage as possible. They are going to prevent people in the back from seeing the celebrity or even the stage. This is the shielding or screening effect. The stage is the nucleus and the celebrity is the protons. The fans are the electrons. Electrons closest to the nucleus will try to be as close to the nucleus as possible. The outer/valence electrons that are farther away from the nucleus will be shielded by the inner electrons. Therefore, the inner electrons prevent the outer electrons from forming a strong attraction to the nucleus. The degree to which the electrons are being screened by inner electrons can be shown by $ns<np<nd<nf$ where n is the energy level. The inner electrons will be attracted to the nucleus much more than the outer electrons. Thus, the attractive forces of the valence electrons to the nucleus are reduced due to the shielding effects. That is why it is easier to remove valence electrons than the inner electrons. It also reduces the nuclear charge of an atom.

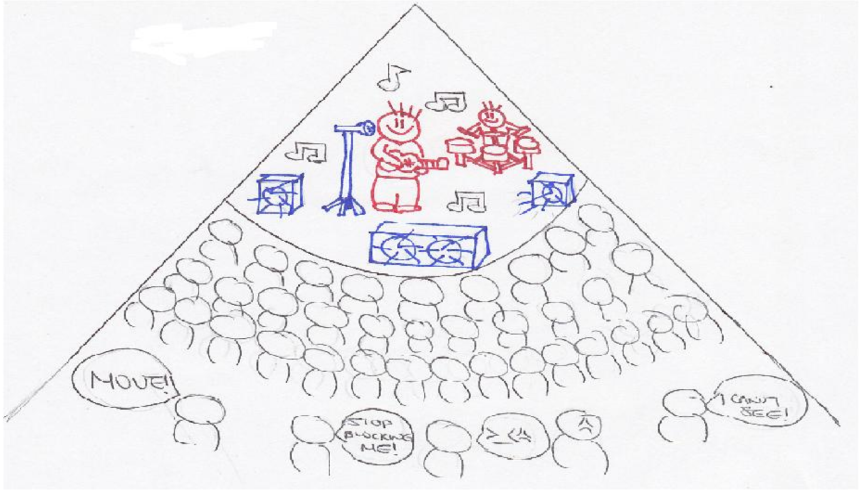

Figure 2.1

Penetration

Penetration is the ability of an electron to get close to the nucleus. The penetration of ns > np > nd > nf. Thus, the closer the electron is to the nucleus, the higher the penetration. Electrons with higher penetration will shield outer electrons from the nucleus more effectively. The s orbital is closer to the nucleus than the p orbital. Thus, electrons in the s orbital have a higher penetration than electrons in the p orbital. That is why the s orbital electrons shield the electrons from the p orbitals. Electrons with higher penetration are closer to the nucleus than electrons with lower penetration. Electrons with lower penetration are being shielded from the nucleus more.

Radial Probability Distribution

Radial probability distribution is a type of probability to find where an electron is mostly likely going to be in an atom. The higher the penetration, the higher probability of finding an electron near the nucleus. As shown by the graphs, electrons of the s orbital are found closer to the nucleus than the p orbital electrons. Likewise, the lower the energy level an electron is located at, the higher chance it has of being found near the nucleus. The smaller the energy level (n) and the orbital angular momentum quantum number (l) of an electron is, the more likely it will be near the nucleus. As electrons get to higher and higher energy levels, the harder it is to locate it because the radius of the sphere is greater. Thus, the probability of locating an electron will be more difficult. Radial probability distribution can be found by multiplying $4\pi r^2$, the area of a sphere with a radius of r and $R^2(r)$.

Radial Probability Distribution = $4\pi r^2 \times R^2(r)$

By using the radial probability distribution equation, we can get a better understanding about an electron's behavior, as shown on Figures 3.1-3.3.

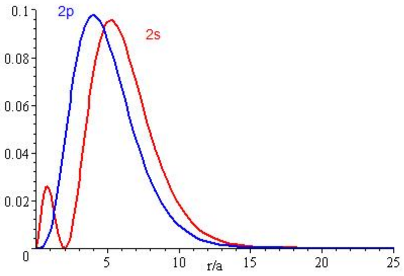

Figure 3.3

Figures 3.1, 3.2, and 3.3 show that the lower the energy level, the higher the probability of finding the electron close to the nucleus. Also, the lower momentum quantum number gets, the closer it is to the nucleus.

Contributors and Attributions

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12.12: The History of the Periodic Table

The periodic law was developed independently by Dmitri Mendeleev and Lothar Meyer in 1869. Mendeleev created the first periodic table and was shortly followed by Meyer. They both arranged the elements by their mass and proposed that certain properties periodically reoccur. Meyer formed his periodic law based on the atomic volume or molar volume, which is the atomic mass divided by the density in solid form. Mendeleev's table is noteworthy because it exhibits mostly accurate values for atomic mass and it also contains blank spaces for unknown elements.

Introduction

In 1804 physicist John Dalton advanced the atomic theory of matter, helping scientists determine the mass of the known elements. Around the same time, two chemists Sir Humphry Davy and Michael Faraday developed electrochemistry which aided in the discovery of new elements. By 1829, chemist Johann Wolfgang Doberiner observed that certain elements with similar properties occur in group of three such as; chlorine, bromine, iodine; calcium, strontium, and barium; sulfur, selenium, tellurium; iron, cobalt, manganese. However, at the time of this discovery too few elements had been discovered and there was confusion between molecular weight and atomic weights; therefore, chemists never really understood the significance of Doberiner's triad.

In 1859 two physicists Robert Willhem Bunsen and Gustav Robert Kirchoff discovered spectroscopy which allowed for discovery of many new elements. This gave scientists the tools to reveal the relationships between elements. Thus in 1864, chemist John A. R Newland arranged the elements in increasing of atomic weights. Explaining that a given set of properties reoccurs every eight place, he named it the law of Octaves.

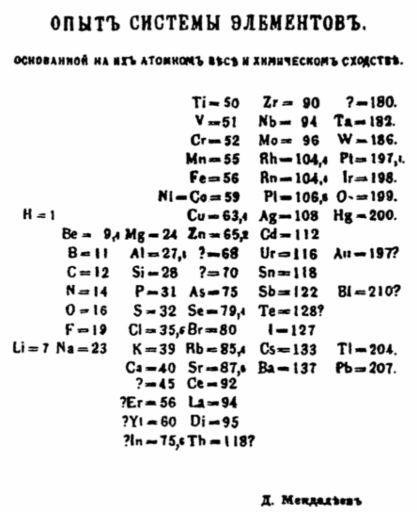
The Periodic Law

In 1869, **Dmitri Mendeleev** and **Lothar Meyer** individually came up with their own periodic law "when the elements are arranged in order of increasing atomic mass, certain sets of properties recur periodically." Meyer based his laws on the atomic volume (the atomic mass of an element divided by the density of its solid form), this property is called **Molar volume**.

$$\text{Atomic (molar) volume } (\text{cm}^3/\text{mol}) = \frac{\text{molar mass } (\text{g/ mol})}{\rho\ (\text{cm}^3/\text{g})}$$

Mendeleev's Periodic Table

Mendeleev's periodic table is an arrangement of the elements that group similar elements together. He left blank spaces for the undiscovered elements (atomic masses, element: 44, scandium; 68, gallium; 72, germanium; & 100, technetium) so that certain elements can be grouped together. However, Mendeleev had not predicted the noble gases, so no spots were left for them.



ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4.
			Fe=56	Rn=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

Д. Менделѣевъ

Figure 1: Mendeleev's original periodic table[4]

In Mendeleev's table, elements with similar characteristics fall in vertical columns, called groups. Molar volume *increases* from top to bottom of a group[3]

✓ Example

The alkali metals (Mendeleev's group I) have high molar volumes and they also have low melting points which decrease in the order:

Li (174 ^oC) > Na (97.8 ^oC) > K (63.7 ^oC) > Rb (38.9 ^oC) > Cs (28.5 ^oC)

Atomic Number as the Basis for the Periodic Law

Assuming there were errors in atomic masses, Mendeleev placed certain elements not in order of increasing atomic mass so that they could fit into the proper groups (similar elements have similar properties) of his periodic table. An example of this was with argon (atomic mass 39.9), which was put in front of potassium (atomic mass 39.1). Elements were placed into groups that expressed similar chemical behavior.

In 1913 Henry G.J. Moseley did researched the X-Ray spectra of the elements and suggested that the energies of electron orbitals depend on the nuclear charge and the nuclear charges of atoms in the target, which is also known as anode, dictate the frequencies of emitted X-Rays. Moseley was able to tie the X-Ray frequencies to numbers equal to the nuclear charges, therefore showing the placement of the elements in Mendeleev's periodic table. The equation he used:

$$\nu = A(Z-b)^2$$

with

- ν: X-Ray frequency
- Z: Atomic Number
- A and b: constants

> With Moseley's contribution the Periodic Law can be restated:
>
> Similar properties recur periodically when elements are arranged according to increasing atomic number."

Atomic numbers, not weights, determine the factor of chemical properties. As mentioned before, argon weights more than potassium (39.9 vs. 39.1, respectively), yet argon is in front of potassium. Thus, we can see that elements are arranged based on their atomic number. The periodic law is found to help determine many patterns of many different properties of elements; melting and boiling points, densities, electrical conductivity, reactivity, acidic, basic, valance, polarity, and solubility.

The table below shows that elements increase from left to right accordingly to their atomic number. The vertical columns have similar properties within their group for example Lithium is similar to sodium, beryllium is similar to magnesium, and so on.

Group	1	2	13	14	15	16	17	18
Element	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Atomic Number	3	4	5	6	7	8	9	10
Atomic Mass	6.94	9.01	10.81	12.01	14.01	15.99	18.99	20.18
Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
Atomic Number	11	12	13	14	15	16	17	18
Atomic Mass	22.99	24.31	26.98	20.09	30.97	32.07	35.45	39.95

Elements in Group 1 (periodic table) have similar chemical properties and are called alkali metals. Elements in Group 2 have similar chemical properties, they are called the alkaline earth metals.

Short form periodic table

The short form periodic table is a table where elements are arranged in 7 rows, periods, with increasing atomic numbers from left to right. There are 18 vertical columns known as groups. This table is based on Mendeleev's periodic table and the periodic law.

Long form Periodic Table

In the long form, each period correlates to the building up of electronic shell; the first two groups (1-2) (s-block) and the last 6 groups (13-18) (p-block) make up the main-group elements and the groups (3-12) in between the s and p blocks are called the transition metals. Group 18 elements are called noble gases, and group 17 are called halogens. The f-block elements, called inner transition metals, which are at the bottom of the periodic table (periods 8 and 9); the 15 elements after barium (atomic number 56) are called lanthanides and the 14 elements after radium (atomic number 88) are called actinides.

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Problems

1) The periodic law states that

a. similar properties recur periodically when elements are arranged according to increasing atomic number
b. similar properties recur periodically when elements are arranged according to increasing atomic weight
c. similar properties are everywhere on the periodic table
d. elements in the same period have same characteristics

2) **Which element is most similar to Sodium**

a. Potassium
b. Aluminum
c. Oxygen
d. Calcium

3) According to the periodic law, would argon be in front of potassium or after? Explain why.

4) Which element is most similar to Calcium?

a. Carbon
b. Oxygen
c. Strontium
d. Iodine

5) Who were the two chemists that came up with the periodic law?

a. John Dalton and Michael Faraday
b. Dmitri Mendeleev and Lothar Meyer
c. Michael Faraday and Lothar Meyer
d. John Dalton and Dmitri Mendeleev

Answers

1. A
2. A

3. Argon would in front of potassium because the periodic law states that the periodic table increases from left to right based on atomic number not atomic weights
4. C
5. B

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12.13: The Aufbau Principles and the Periodic Table

Aufbau comes from the German word "Aufbauen" which means "to build". In essence when writing electron configurations we are building up electron orbitals as we proceed from atom to atom. As we write the electron configuration for an atom, we will fill the orbitals in order of increasing atomic number. The Aufbau principle originates from the Pauli's exclusion principle which says that no two *fermions* (e.g., electrons) in an atom can have the same set of quantum numbers, hence they have to "pile up" or "build up" into higher energy levels. How the electrons build up is a topic of electron configurations.

✓ Example 12.13.1

If we follow the pattern across a period from B (Z=5) to Ne (Z=10) the number of electrons increase and the subshells are filled. Here we are focusing on the p subshell in which as we move towards Ne, the p subshell becomes filled.

- B (Z=5) configuration: $1s^2$ $2s^2$ $2p^1$
- C (Z=6) configuration: $1s^2$ $2s^2$ $2p^2$
- N (Z=7) configuration: $1s^2$ $2s^2$ $2p^3$
- O (Z=8) configuration: $1s^2$ $2s^2$ $2p^4$
- F (Z=9) configuration: $1s^2$ $2s^2$ $2p^5$
- Ne (Z=10) configuration: $1s^2$ $2s^2$ $2p^6$

Electron configuration can be described as how electrons are assembled within the orbitals shells and subshells of an atom. It is important to understand what an electron is in order to fully understand the electron configuration. An electron is a sub atomic particle that is associated with a negative charge. Electrons are found outside of the nucleus, as opposed to neutrons (particles with neutral charge,) and protons (particles with positive charge.) Furthermore, electrons are associated with energy, more specifically quantum energy, and exemplify wave-like and particle-like characteristics. The word configuration simply means the arrangement of something. Therefore electron configuration in straightforward language means the arrangement of electrons.

Introduction

In general when filling up the electron diagram, it is customary to fill the lowest energies first and work your way up to the higher energies. Principles and rules such as the Pauli exclusion principle, Hund's rule, and the Aufbau process are used to determine how to properly configure electrons. The Pauli exclusion rule basically says that at most, 2 electrons are allowed to be in the same orbital. Hund's rule explains that each orbital in the subshell must be occupied with one single electron first before two electrons can be in the same orbital. Lastly, the Aufbau process describes the process of adding electron configuration to each individualized element in the periodic table. Fully understanding the principles relating to electron configuration will promote a better understanding of how to design them and give us a better understanding of each element in the periodic table. How the periodic table was formed has an intimate correlation with electron configuration. After studying the relationship between electron configuration and the period table, it was pointed out by Niels Bohr that electron configurations are similar for elements within the same group in the periodic table. Groups occupy the vertical rows as opposed to a period which is the horizontal rows in the table of elements.

S, P, D, and F Blocks

- It is easy to see how similar electron configurations are in a group when written out. (Allow "n" to be the principal quantum number.) Lets first take a look at group 1 atoms. Group 1 atoms are the alkali metals. Let n=1. Notice the similar configuration within all the group 1 elements.

Group	Element	Configuration
1	H	$1s^1$
1	Li	$[He]2s^1$
1	Na	$[Ne]3s^1$
1	K	$[Ar]4s^1$
1	Rb	$[Kr]5s^1$

1	Cs	[Xe]6s^{1}
1	Fr	[Rn]7s^{1}

Now consider group 16 elements. These elements also will also have similar electron configurations to each another because they are in the same group; these elements have 6 valence electrons.

Group	Element	Configuration
16	O	[He]2s^{2}2p^{4}
16	S	[Ne]3s^{2}3p^{4}
16	Se	[Ar]3d^{10}4s^{2} 4p^{4}
16	Te	[Kr]4d^{10}5s^{2} 5p^{4}
16	Po	[Xe]4f^{14} 5d^{10}6s^{2} 6p^{4}

Outside links

- 1. Question, True or False: Elements in the same period have similar electron configurations.

  Answer: False. Elements in the same GROUP have similar electron configurations.

  2. Question: What element has the electron configuration [Ar] 4s^{2} 3d^{10} 4p^{5}?

  Answer: Bromine

  3. Question: What element has the electron configuration [Xe] 4f^{14} 5d^{10} 6s^{2} 6p$^{3?}$

  Answer: Bismuth

  4. Question: Demonstrate how elements in a group share similar characteristics by filling in the electron configurations for the Group 18 elements:

Group	Element	Configuration
18	He	
18	Ne	
18	Ar	
18	Kr	
18	Xe	
18	Rn	

  Answer: 1s^{2}, [He]2s^{2}2p^{6}, [Ne]3s^{2}3p^{6}, [Ar]3d^{10}4s^{2}4p^{6}, [Kr]4d^{10}5s^{2}5p^{6}, [Xe]4f^{14}5d^{10}6s^{2}6p^{6}

  5. Question: How many valence electrons are there in Iodine?

  Answer: Iodine, z=53, group 17. This means there are seven valence electrons.

  6. Question: What is the highest number of electrons a 4p subshell can hold?

  Answer: 6! Each 3 p orbital can hold 2 electrons so if they are all filled, the answer is 6. You get this by multiplying the three orbitals by 2 electrons per orbital, so 3 multiplied by 2 equals 6.

  Make up some practice problems for the future readers.

Contributors and Attributions

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12.15: Periodic Trends in Atomic Properties

The elements in the periodic table are arranged in order of increasing atomic number. All of these elements display several other trends and we can use the periodic law and table formation to predict their chemical, physical, and atomic properties. Understanding these trends is done by analyzing the elements electron configuration; all elements prefer an octet formation and will gain or lose electrons to form that stable configuration.

Atomic Radius

We can never determine the atomic radius of an atom because there is never a zero probability of finding an electron, and thus never a distinct boundary to the atom. All that we can measure is the distance between two nuclei (internuclear distance). A covalent radius is one-half the distance between the nuclei of two identical atoms. An ionic radius is one-half the distance between the nuclei of two ions in an ionic bond. The distance must be apportioned for the smaller cation and larger anion. A metallic radius is one-half the distance between the nuclei of two adjacent atoms in a crystalline structure. The noble gases are left out of the trends in atomic radii because there is great debate over the experimental values of their atomic radii. The SI units for measuring atomic radii are the nanometer (nm) and the picometer (pm). $1\,nm = 1 \times 10^{-9}\,m$ and $1\,pm = 1 \times 10^{-12}\,m$.

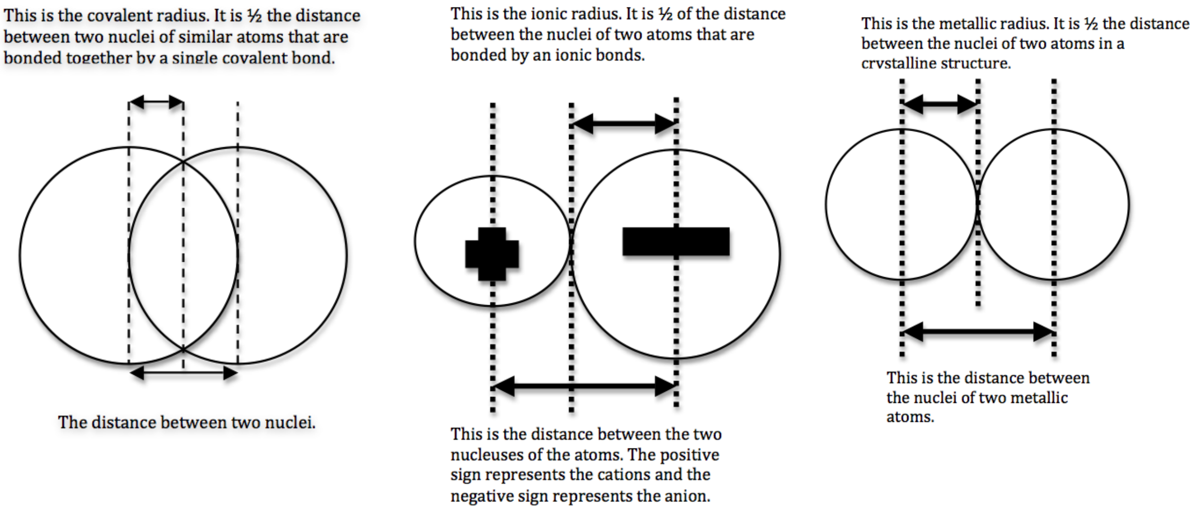
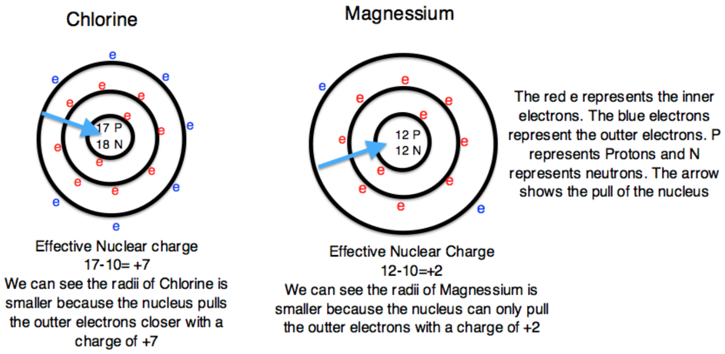


Figure 12.15.1: (left) Covalent Radii, (middle) Ionic Radii, (right) Metallic Radii. Provided courtesy of Jessica Thornton (UCD)

To explain this trend, the concept of screening and penetration must be understood. Penetration is commonly known as the distance that an electron is from the nucleus. Screening is defined as the concept of the inner electrons blocking the outer electrons from the nuclear charge. Within this concept we assume that there is no screening between the outer electrons and that the inner electrons shield the outer electrons from the total positive charge of the nucleus. In order to comprehend the extent of screening and penetration within an atom, scientists came up with the **effective nuclear charge,** Z_{eff}. The equation for calculating the effective nuclear charge is shown below.

$$Z_{eff} = Z - S$$

In the equation S represents the number of inner electrons that screen the outer electrons. Students can easily find S by using the atomic number of the noble gas that is one period above the element. For example, the S we would use for Chlorine would be 10 (the atomic number of Neon). Z is the total number of electrons in the atom. Since we know that a neutral atom has an identical number of protons and electrons, we can use the atomic number to define Z. For example, Chlorine would have a Z value of 17 (the atomic number of Chlorine). Continuing to use Chlorine as an example, the 10 inner electrons (S) would screen out the positive charge of ten protons. Therefore there would be and effective nuclear charge of 17-10 or +7. The effective nuclear charge shows that the nucleus is pulling the outer electrons with a +7 charge and therefore the outer electrons are pulled closer to the nucleus and the atomic radii is smaller. In summary, the greater the nuclear charge, the greater pull the nucleus has on the outer electrons and the smaller the atomic radii. In contrast, the smaller nuclear charge, the lesser pull the nucleus has on the outer electrons, and the larger atomic radii. Additionally, as the atomic number increases, the effective nuclear charge also increases. Figure 3 depicts the effect that the effective nuclear charge has on atomic radii.



The red e represents the inner electrons. The blue electrons represent the outter electrons. P represents Protons and N represents neutrons. The arrow shows the pull of the nucleus

Effective Nuclear charge
17-10= +7
We can see the radii of Chlorine is smaller because the nucleus pulls the outter electrons closer with a charge of +7

Effective Nuclear Charge
12-10=+2
We can see the radii of Magnessium is smaller because the nucleus can only pull the outter electrons with a charge of +2

Figure 12.15.2: Courtesy of Jessica Thornton (UCD)

Now we are ready to describe the atomic radius trend in the periodic table. The atomic number increases moving left to right across a period and subsequently so does the effective nuclear charge. Therefore, moving left to right across a period the nucleus has a greater pull on the outer electrons and the atomic radii decreases. Moving down a group in the periodic table, the number of filled electron shells increases. In a group, the valence electrons keep the same effective nuclear charge, but now the orbitals are farther from the nucleus. Therefore, the nucleus has less of a pull on the outer electrons and the atomic radii are larger.

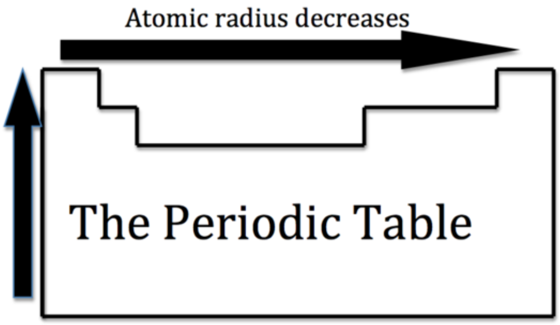
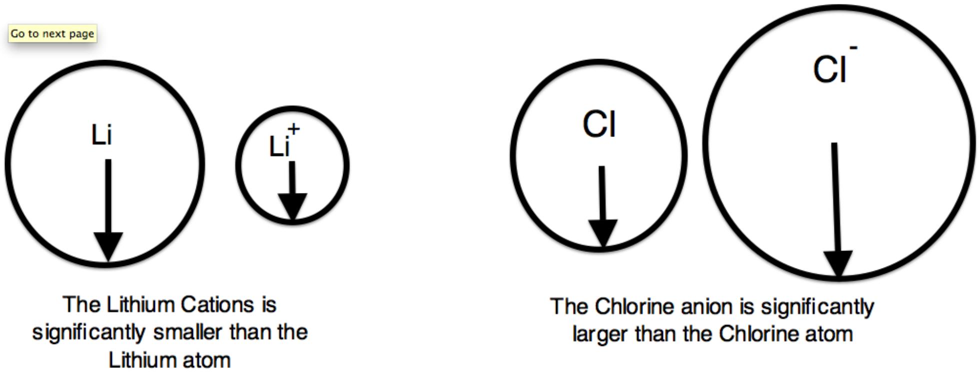


Figure 12.15.3: Courtesy of Jessica Thornton (UCD)

We can now use these concept to explain the atomic radius differences of cations and anions. A cation is an atom that has lost one of its outer electrons. Cations have a smaller radius than the atom that they were formed from. With the loss of an electron, the positive nuclear charge out powers the negative charge that the electrons exert. Therefore, the positive nucleus pulls the electrons tighter and the radius is smaller. An anion is an atom that has gained an outer electron. Anions have a greater radius than the atom that they were formed from. The gain of an electron does not alter the nuclear charge, but the addition of an electron causes a decrease in the effective nuclear charge. Therefore, the electrons are held more loosely and the atomic radius is increased.



The Lithium Cations is significantly smaller than the Lithium atom

The Chlorine anion is significantly larger than the Chlorine atom

Figure 12.15.4: Courtesy of Jessica Thornton (UCD)

Ionization Energy (ionization potential)

Expelling an electron from an atom requires enough energy to overcome the magnetic pull of the positive charge of the nucleus. Therefore, ionization energy (I.E. or I) is the energy required to completely remove an electron from a gaseous atom or ion. The Ionization Energy is always positive.

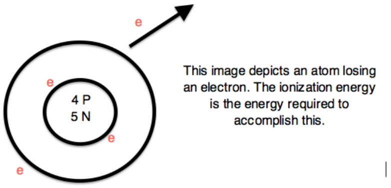


Figure 12.15.5: Courtesy of Jessica Thornton (UCD)

The energy required to remove one valence electron is the first ionization energy, the second ionization energy is the energy required to remove a second valence electron, and so on.

- 1st ionization energy

$$\mathrm{Na(g)} \longrightarrow \mathrm{Na^{+}(g)} + \mathrm{e^{-}(g)}$$

- 2nd ionization energy

$$\mathrm{Na^{+}(g)} \longrightarrow \mathrm{Na^{2+}(g)} + \mathrm{e^{-}}$$

Ionization energies increase relative to high effective charge. The highest ionization energies are the noble gases because they all have high effective charge due to their octet formation and require a high amount of energy to destroy that stable configuration. The highest amount of energy required occurs with the elements in the upper right hand corner. Additionally, elements in the left corner have a low ionization energy because losing an electron allows them to have the noble gas configuration. Therefore, it requires less energy to remove one of their valence electrons

Table 1: Ionization Energies of certain elements (1st IE, 2nd IE, etc)

Element	1st	2nd	3rd	4th	5th	6th	7th
Na	496	4562					
Mg	738	1451	7733				
Al	577	1817	2745	11580			
Si	786	1577	3232	4356	16090		
P	1060	1903	2912	4957	6274	21270	
S	999.6	2251	3361	4564	7013	8496	27110
Cl	1256	2297	3822	5158	6542	9362	11020
Ar	1520	2666	3931	5771	7238	8781	12000

These are the ionization energies for the period three elements. Notice how Na after in the second I.E, Mg in the third I.E., Al in the fourth I.E., and so on, all have a huge increase in energy compared to the proceeding one. This occurs because the proceeding configuration was in a stable octet formation; therefore it requires a much larger amount of energy to ionize.

Ionization Energies increase going left to right across a period and increase going up a group. As you go up a group, the ionization energy increases, because there are less electron shielding the outer electrons from the pull of the nucleus. Therefore, it requires more energy to out power the nucleus and remove an electron. As we move across the periodic table from left to right, the ionization energy increases , due to the effective nuclear charge increasing. This is because the larger the effective nuclear charge, the stronger the nucleus is holding onto the electron and the more energy it takes to release an electron.

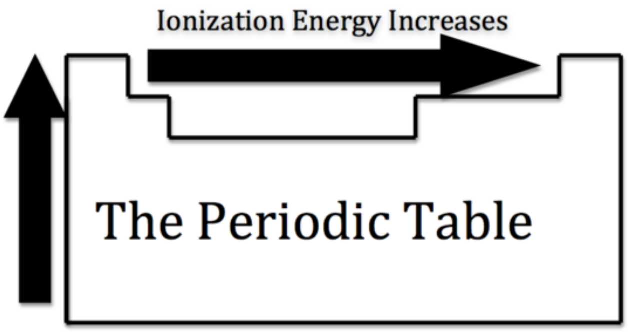


Figure 12.15.6: Courtesy of Jessica Thornton (UCD)

The ionization energy is only a general rule. There are some instances when this trend does not prove to be correct. These can typically be explained by their electron configuration. For example, Magnesium has a higher ionization energy than Aluminum. Magnesium has an electron configuration of [Ne]3s2. Magnesium has a high ionization energy because it has a filled 3s orbital and it requires a higher amount of energy to take an electron from the filled orbital.

Electron Affinity

Electron affinity (E.A.) is the energy change that occurs when an electron is added to a gaseous atom. Electron affinity can further be defined as the enthalpy change that results from the addition of an electron to a gaseous atom. It can be either positive or negative value. The greater the negative value, the more stable the anion is.

- (Exothermic) The electron affinity is positive

$$\mathrm{X(g)} + \mathrm{e}^- \longrightarrow \mathrm{X}^- + \mathrm{Energy}$$

- (Endothermic) The electron affinity is negative

$$\mathrm{X(g)} + \mathrm{e}^- + \mathrm{Energy} \longrightarrow \mathrm{X}^-$$

It is more difficult to come up with trends that describe the electron affinity. Generally, the elements on the right side of the periodic table will have large negative electron affinity. The electron affinities will become less negative as you go from the top to the bottom of the periodic table. However, Nitrogen, Oxygen, and Fluorine do not follow this trend. The noble gas electron configuration will be close to zero because they will not easily gain electrons.

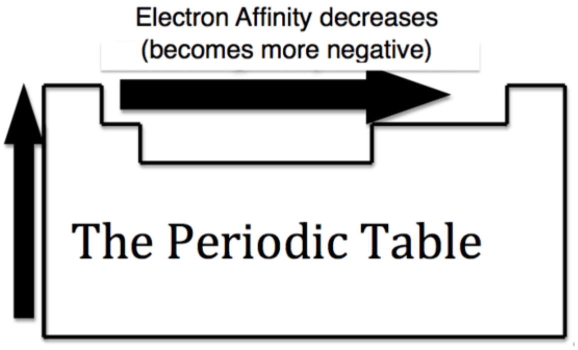


Figure 12.15.7: Courtesy of Jessica Thornton (UCD)

Electronegativity

Electronegativity is the measurement of an atom to compete for electrons in a bond. The higher the electronegativity, the greater its ability to gain electrons in a bond. Electronegativity will be important when we later determine polar and nonpolar molecules. Electronegativity is related with ionization energy and electron affinity. Electrons with low ionization energies have low electronegativities because their nuclei do not exert a strong attractive force on electrons. Elements with high ionization energies have high electronegativities due to the strong pull exerted by the positive nucleus on the negative electrons. Therefore the electronegativity increases from bottom to top and from left to right.

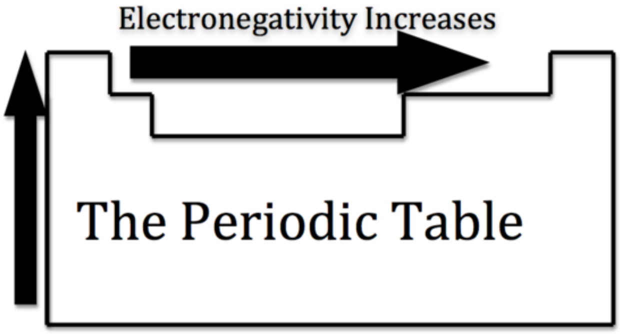


Figure 12.15.8: Courtesy of Jesscia Thornton (UCD)

Metallic Character

The metallic character is used to define the chemical properties that metallic elements present. Generally, metals tend to lose electrons to form cations. Nonmetals tend to gain electrons to form anions. They also have a high oxidation potential therefore they are easily oxidized and are strong reducing agents. Metals also form basic oxides; the more basic the oxide, the higher the metallic character.

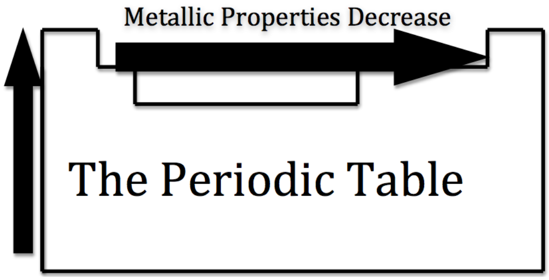


Figure 12.15.9: Courtesy of Jessica Thornton (UCD)

As you move across the table from left to right, the metallic character decreases, because the elements easily accept electrons to fill their valance shells. Therefore, these elements take on the nonmetallic character of forming anions. As you move up the table, the metallic character decreases, due to the greater pull that the nucleus has on the outer electrons. This greater pull makes it harder for the atoms to lose electrons and form cations.

Other Trends

Melting Points: Trends in melting points and molecular mass of binary carbon-halogen compounds and hydrogen halides are due to intermolecular forces. Melting destroys the arrangement of atoms in a solid, therefore the amount of heat necessary for melting to occur depends on the strength of attraction between the atoms. This strength of attraction increases as the number of electrons increase. Increase in electrons increases bonding.

Example: Melting point of HF should be approximately -145 °C based off melting points of HCl, HBr, and HI, but the observed value is -83.6°C.

Heat and electricity conductibility vary regularly across a period. Melting points may increase gradually or reach a peak within a group then reverse direction.

Example: Third period elements Na, Mg, and Al are good conductors of heat and electricity while Si is only a fair conductor and the nonmetals P, S, Cl and Ar are poor conductors.

Redox Potentials

Oxidation Potential

Oxidation is a reaction that results in the loss of an electron. Oxidation potential follows the same trends as the ionization energy. That is because the smaller the ionization energy, the easier it is to remove an electron. (e.g)

$$K_{(s)} \rightarrow K^{+} + e^{-}$$

Reduction Potential

Reduction is a reaction that results in the gaining of an electron. Reduction potentials follow the same trend as the electron affinity. That is because the larger, negative electron affinity, the easier it is to give an electron. Example of Reduction:

$$F_{(s)} + e^- \rightarrow F^-$$

Uses in knowing the Periodic Properties of Elements

1. Predicting greater or smaller atomic size and radial distribution in neutral atoms and ions
2. Measuring and comparing ionization energies
3. Comparing electron affinities and electronegativities
    - Predicting redox potential
    - Comparing metallic character with other elements; its ability to form cations
    - Predicting what reaction may or may not occur due to the trends
    - Determining greater cell potential (sum of oxidation and reduction potential) between reactions
    - Completing chemical reactions according to trends

Summary of Periodic Trends

The Periodic Table of Elements categorizes like elements together. Dmitri Mendeleev, a Russian scientist, was the first to create a widely accepted arrangement of the elements in 1869. Mendeleev believed that when the elements are arranged in order of increasing atomic mass, certain sets of properties recur periodically. Although most modern periodic tables are arranged in eighteen groups (columns) of elements, Mendeleev's original periodic table had the elements organized into eight groups and twelve periods (rows).

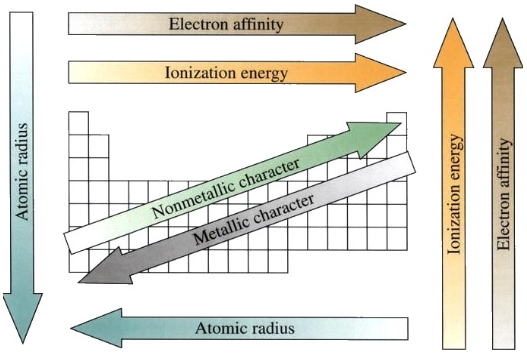


Figure 12.15.10: Courtesy of Wikipedia for releasing this image into the public domain

On the periodic table, elements that have similar properties are in the same groups (vertical). From left to right, the atomic number (z) of the elements increases from one period to the next (horizontal). The groups are numbered at the top of each column and the periods on the left next to each row. The main group elements are groups 1,2 and 13 through 18. These groups contain the most naturally abundant elements, and are the most important for life. The elements shaded in light pink in the table above are known as transition metals. The two rows of elements starting at z=58, are sometimes called inner transition metals and have that have been extracted and placed at the bottom of the table, because they would make the table too wide if kept continuous. The 14 elements following lanthanum (z=57) are called lanthanides, and the 14 following actinium (z=89) are called actinides.

Elements in the periodic table can be placed into two broad categories, metals and nonmetals. Most metals are good conductors of heat and electricity, are malleable and ductile, and are moderate to high melting points. In general, nonmetals are nonconductors of heat and electricity, are nonmalleable solids, and many are gases at room temperature. Just as shown in the table above, metals and nonmetals on the periodic table are often separated by a stairstep diagonal line, and several elements near this line are often called metalloids (Si, Ge, As, Sb, Te, and At). Metalloids are elements that look like metals and in some ways behave like metals but also have some nonmetallic properties. The group to the farthest right of the table, shaded orange, is known as the noble gases. Noble gases are treated as a special group of nonmetals.

Alkali Metals/Alkali Earth Metals

The Alkali metals are comprised of group 1 of the periodic table and consist of Lithium, Sodium, Rubidium, Cesium, and Francium. These metals are highly reactive and form ionic compounds (when a nonmetal and a metal come together) as well as many other compounds. Alkali metals all have a charge of +1 and have the largest atom sizes than any of the other elements on each of their respective periods.

Alkali Earth Metals are located in group 2 and consist of Beryllium, Magnesium, Calcium, Strontium, Barium, and Radium. Unlike the Alkali metals, the earth metals have a smaller atom size and are not as reactive. These metals may also form ionic and other compounds and have a charge of +2.

Transition Metals

The transition metals range from groups IIIB to XIIB on the periodic table. These metals form positively charged ions, are very hard, and have very high melting and boiling points. Transition metals are also good conductors of electricity and are malleable.

Lanthanides and Actinides

> Lanthanides (shown in row ** in chart above) and Actinides (shown in row * in chart above), form the block of two rows that are placed at the bottom of the periodic table for space issues. These are also considered to be transition metals. Lanthanides are form the top row of this block and are very soft metals with high boiling and melting points. Actinides form the bottom row and are radioactive. They also form compounds with most nonmetals. To find out why these elements have their own section, check out the electron configurations page.

Metalloids

As mentioned in the introduction, metalloids are located along the staircase separating the metals from the nonmetals on the periodic table. Boron, silicon, germanium, arsenic, antimony, and tellurium all have metal and nonmetal properties. For example, Silicon has a metallic luster but is brittle and is an inefficient conductor of electricity like a nonmetal. As the metalloids have a combination of both metallic and nonmetal characteristics, they are intermediate conductors of electricity or "semiconductors".

Halogens

Halogens are comprised of the five nonmetal elements Flourine, Chlorine, Bromine, Iodine, and Astatine. They are located on group 17 of the periodic table and have a charge of -1. The term "halogen" means "salt-former" and compounds that contain one of the halogens are salts. The physical properties of halogens vary significantly as they can exist as solids, liquids, and gases at room temperature. However in general, halogens are very reactive, especially with the alkali metals and earth metals of groups 1 and 2 with which they form ionic compounds.

Noble Gases

The noble gases consist of group 18 (sometimes reffered to as group O) of the periodic table of elements. The noble gases have very low boiling and melting points and are all gases at room temperature. They are also very nonreactive as they already have a full valence shell with 8 electrons. Therefore, the noble gases have little tendency to lose or gain electrons.

Useful Relationships from the Periodic Table

The periodic table of elements is useful in determining the charges on simple monoatomic ions. For main-group elements, those categorized in groups 1, 2, and 13-18, form ions they lose the same number of electrons as the corresponding group number to which they fall under. For example, K atoms (group 1) lose one electron to become K^+ and Mg atoms (group 2) lose two electrons to form Mg^{2+}. The other main-group elements found in group 13 and higher form more than one possible ion.

The elements in groups 3-12 are called transition elements, or transition metals. Similar to the main-group elements described above, the transition metals form positive ions but due to their capability of forming more than two or more ions of differing charge, a relation between the group number and the charge is non-existent.

? Exercise 12.15.1

Arrange these elements according to decreasing atomic size: Na, C, Sr, Cu, Fr

Answer

Fr, Sr, Cu, Na, C

Exercise 12.15.1

Arrange these elements according to increasing negative E. A.: Ba, F, Si, Ca, O

Answer

Ba, Ca, Si, O, F

Exercise 12.15.1

Arrange these elements according to increasing metallic character: Li, S, Ag, Cs, Ge

Answer

Li, S, Ge, Ag, Cs

Exercise 12.15.1

Which reaction do you expect to have the greater cell potential?

a. \ce{2Na(s) + Cl2(g)→ 2NaCl(s) or 2Cs(s) +Cl2(g) → 2RbCl(s)
b. $2\,\mathrm{Na(s)} + \mathrm{Cl_2(g)} \rightarrow 2\,\mathrm{NaCl(s) or Be(s)} + \mathrm{Cl_2(g)} \rightarrow \mathrm{BeCl_2(s)}$

Answer

Second equation

First equation

Exercise 12.15.1

Which equation do you expect to occur?

1. \(\ce{I2(s) + 2Br (aq) → Br2(l) + 2I(aq)}\)
2. $\mathrm{Cl_2(g)} + 2\,\mathrm{I(aq)} \rightarrow \mathrm{I_2(s)} + 2\,\mathrm{Cl(aq)}$

Answer

5. A) Yes

B) No

Problems

*Highlight Answer:_____ to view answers.

1. An element that is an example of a metalloid is (a) S; (b) Zn; (c) Ge; (d) Re; (e) none of these

Answer:

2. In the periodic table, the vertical (up and down) columns are called (a) periods; (b) transitions; (c) families/groups; (d) metalloids; (e) none of these.

Answer:

3. Why are noble gases inert (nonreactive)?

Answer:

4. What are compounds that contain a halogen called?

Answer:

5. Lanthanides and Actinides are: (a) alkali earth metals; (b) transition metals; (c) metalloids; (d) alkali metals; (e) none of these

Answer:

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SECTION OVERVIEW

12.16: The Properties of a Group: The Alkali Metals

Alkali metals are the chemical elements found in Group 1 of the periodic table. The alkali metals include: lithium, sodium, potassium, rubidium, cesium, and francium. Although often listed in Group 1 due to its electronic configuration, hydrogen is not technically an alkali metal since it rarely exhibits similar behavior. The word "alkali" received its name from the Arabic word "al qali," meaning "from ashes", which since these elements react with water to form hydroxide ions, creating **alkaline solutions** (pH>7).

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CHAPTER OVERVIEW

8: Aqueous Solution Equilibria

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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8.1: Solutions of Acids or Bases Containing a Common Ion

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common-ion effect is used to describe the effect on an equilibrium when one or more species in the reaction is shared with another reaction. This results in a shifitng of the equilibrium properties.

Introduction

The solubility products K_{sp}'s are equilibrium constants in hetergeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[\mathrm{Na^+}] + [\mathrm{K^+}] = [\mathrm{Cl^-}]$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion.

Common Ions

When NaCl and KCl are dissolved in the same solution, the $\mathrm{Cl^-}$ ions are *common* to both salts. In a system containing NaCl and KCl, the $\mathrm{Cl^-}$ ions are common ions.

$$\mathrm{NaCl} \rightleftharpoons \mathrm{Na^+} + \mathrm{Cl^-}$$

$$\mathrm{KCl} \rightleftharpoons \mathrm{K^+} + \mathrm{Cl^-}$$

$$\mathrm{CaCl_2} \rightleftharpoons \mathrm{Ca^{2+}} + 2\,\mathrm{Cl^-}$$

$$\mathrm{AlCl_3} \rightleftharpoons \mathrm{Al^{3+}} + 3\,\mathrm{Cl^-}$$

$$\mathrm{AgCl} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Cl^-}$$

For example, when AgCl is dissolved into a solution already containing NaCl (actually $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions), the $\mathrm{Cl^-}$ ions come from the ionization of both AgCl and NaCl. Thus, $[\mathrm{Cl^-}]$ differs from $[\mathrm{Ag^+}]$. The following examples show how the concentration of the common ion is calculated.

Example 8.1.1

What are $[\mathrm{Na^+}]$, $[\mathrm{Cl^-}]$, $[\mathrm{Ca^{2+}}]$, and $[\mathrm{H^+}]$ in a solution containing 0.10 M each of NaCl, $\mathrm{CaCl_2}$, and HCl?

Solution

Due to the conservation of ions, we have

$$[\mathrm{Na^+}]=[\mathrm{Ca^{2+}}]=[\mathrm{H^+}]=0.10\,\mathrm{M}.$$

but

$$\begin{aligned}[\mathrm{Cl^-}] &= 0.10\;(\text{due to NaCl})\\ &+0.20\;(\text{due to CaCl}_2)\\ &+0.10\;(\text{due to HCl})\\ &=0.40\,\mathrm{M}\end{aligned}$$

? Exercise 8.1.1

John poured 10.0 mL of 0.10 M NaCl, 10.0 mL of 0.10 M KOH, and 5.0 mL of 0.20 M HCl solutions together and then he made the total volume to be 100.0 mL. What is $[\mathrm{Cl^-}]$ in the final solution?

$$[\mathrm{Cl^-}] = \dfrac{0.1\ \mathrm{M} \times 10\ \mathrm{mL} + 0.2\ \mathrm{M} \times 5.0\ \mathrm{mL}}{100.0\ \mathrm{mL}} = 0.020\ \mathrm{M}$$

Le Chatelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

✓ Example 8.1.2

Consider the lead(II) ion concentration in this *saturated* solution of $\mathrm{PbCl_2}$. The balanced reaction is

$$\mathrm{PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)} \tag{8.1.1}$$

Defining s as the concentration of dissolved lead(II) chloride, then:

$$[Pb^{2+}] = s$$

$$[Cl^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (2s)^2 \\ 1.7 \times 10^{-5} &= 4s^3 \\ s^3 &= \frac{1.7 \times 10^{-5}}{4} \\ &= 4.25 \times 10^{-6} \\ s &= \sqrt[3]{4.25 \times 10^{-6}} \\ &= 1.62 \times 10^{-2}\ mol\ dm^{-3} \end{aligned}$$

The concentration of lead(II) ions in the solution is 1.62 x 10^{-2} M. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression in Equation 8.1.1. What happens to that equilibrium if extra chloride ions are added? According to *Le* Chatelier, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

A Simple Example

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[\mathrm{Pb^{2+}}] = s$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution.

In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[\mathrm{Cl}^{-}] = 0.100\ M$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^{-}]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.00100 \end{aligned}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3}\ \mathrm{M} \end{aligned}$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[\mathrm{Pb}^{2\,+}] = 0.0162\ M$$

Solution in 0.100 M NaCl solution:

$$[\mathrm{Pb}^{2\,+}] = 0.0017\ M$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.

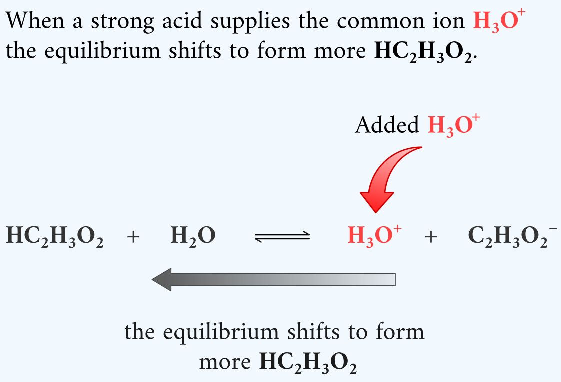
> Adding a common ion to a system at equilibrium affects the equilibrium composition, but **not** the ionization constant.

Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

✓ Example $8.1.3A$

The common ion effect of H_3O^+ on the ionization of acetic acid

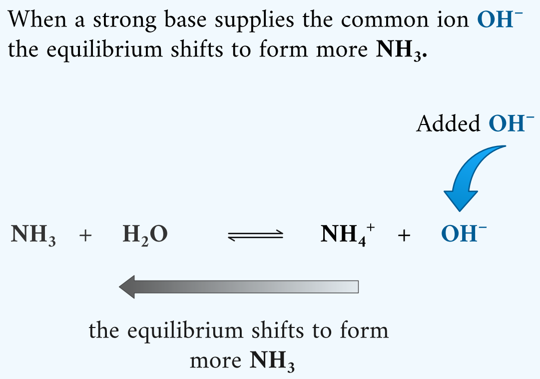


The common ion effect can be conceptualized as an applied Le Chatelier effect. Adding products will shift the equilibrium to more favor the reactants. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium.

Example $8.1.3B$

Consider the common ion effect of OH^- on the ionization of ammonia



The common ion effect can be conceptualized as an applied Le Chatelier effect. Adding products will shift the equilibrium to more favor the reactants. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with Le Chatelier's Principle), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K.

Common Ion Effect on Solubility

Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes the equilibrium to shift left, toward the reactants, causing precipitation.

Example $8.1.4$

Consider the reaction:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$$

What happens to the solubility of $PbCl_2(s)$ when 0.1 M $NaCl$ is added?

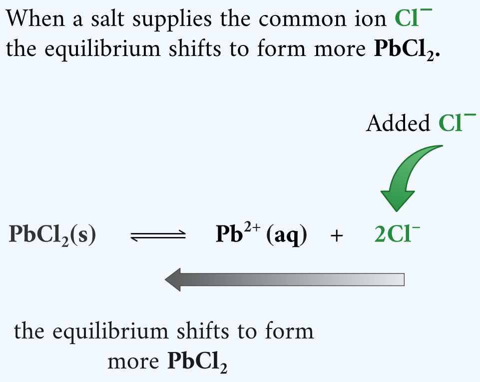
Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: Cl^-

Notice: $Q_{sp} > K_{sp}$ The addition of $NaCl$ has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of $PbCl_2(s)$ is equivalent to the concentration of Pb^{2+} produced because they are in a 1:1 ratio.



The common ion effect can be conceptualized as an applied Le Chatelier effect. Adding products will shift the equilibrium to more favor the reactants. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Because K_{sp} for the reaction is 1.7×10^{-5}, the overall reaction would be

$$(s)(2s)^2 = 1.7 \times 10^{-5}.$$

Solving the equation for s gives $s = 1.62 \times 10^{-2}$ M. The coefficient on $\mathrm{Cl^-}$ is 2, so it is assumed that twice as much $\mathrm{Cl^-}$ is produced as $\mathrm{Pb^{2+}}$, hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl$^-$ added would be 0.1 M because $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ are in a 1:1 ratio in the ionic salt, NaCl. Therefore, the overall molarity of $\mathrm{Cl^-}$ would be $2s + 0.1$, with $2s$ referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$\begin{aligned} Q_{sp} &= [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2 \\ &= 1.8 \times 10^{-5} \\ &= (s)(2s + 0.1)^2 \\ s &= [Pb^{2+}] \\ &= 1.8 \times 10^{-3} M \\ 2s &= [\mathrm{Cl^-}] \\ &\approx 0.1 M \end{aligned}$$

Notice that the molarity of $\mathrm{Pb^{2+}}$ is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[\mathrm{Cl^-}]$ is approximately 0.1 M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for $\mathrm{PbCl_2(s)}$ is greater than the equilibrium constant because of the added $\mathrm{Cl^-}$. This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

References

1. Harwood, William S., F. G. Herring, Jeffry D. Madura, and Ralph H. Petrucci. General Chemistry Principles and Modern Applications. 9th ed. New Jersey: Prentice Hall, 2007.

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- **Common Ion Effect** by Chung (Peter) Chieh, Emmellin Tung, Jim Clark, Mahtab Danai is licensed CC BY 4.0.

8.2: Buffered Solutions

When it comes to buffer solution one of the most common equation is the Henderson-Hasselbalch approximation. An important point that must be made about this equation is it's useful only if stoichiometric or initial concentration can be substituted into the equation for equilibrium concentrations.

Origin of the Henderson-Hasselbalch Equation

Where the Henderson-Hasselbalch approximation comes from

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \tag{8.2.1}$$

where,

- A^- is the conjugate base
- HA is the weak acid

We know that K_a is equal to the products over the reactants and, by definition, H_2O is essentially a pure liquid that we consider to be equal to one.

$$K_a = [H_3O^+][A^-] \tag{8.2.2}$$

Take the $-\log$ of both sides:

$$-\log\ K_a = -\log([H_3O^+][A^-]) \tag{8.2.3}$$

$$-\log\ K_a = -\log[H_3O^+]\ -\log[A^-] \tag{8.2.4}$$

Using the following two relationships:

$$-\log[K_a] = pK_a \tag{8.2.5}$$

$$-\log[H_3O^+] = pH \tag{8.2.6}$$

We can simplify the above equation:

$$pK_a = pH - \log[A^-] \tag{8.2.7}$$

If we add $\log[A^-]$ to both sides, we get the **Henderson-Hasselbalch approximation:**

$$pH = pK_a + \log[A^-] \tag{8.2.8}$$

This approximation is only **valid** when:

1. The conjugate base / acid falls between the values of 0.1 and 10
2. The molarity of the buffers exceeds the value of the K_a by a factor of at least 100

✓ Example 8.2.1

Suppose we needed to make a buffer solution with a pH of 2.11. In the first case, we would try and find a weak acid with a pK_a value of 2.11. However, at the same time the molarities of the acid and the its salt must be equal to one another. This will cause the two molarities to cancel; leaving the $\log[A^-]$ equal to $\log(1)$ which is zero.

$$pH = pK_a + \log[A^-] = 2.11 + \log(1) = 2.11$$

This is a very unlikely scenario, however, and you won't often find yourself with Case #1

✓ Example 8.2.2

What mass of $NaC_7H_5O_2$ must be dissolved in 0.200 L of 0.30 M $HC_7H_5O_2$ to produce a solution with pH = 4.78? (Assume solution volume is constant at 0.200L)

Solution

$$HC_7H_5O_2 + H_20 \rightleftharpoons H_3O^+ + C_7H_5O_2$$

$$K_a = 6.3 \times 10^{-5}$$

$$K_a = \frac{[H_3O^+][C_7H_5O_2]}{[HC_7H_5O_2]} = 6.3 \times 10^{-5}$$

$$[H_3O^+] = 10^{-pH} = 10^{-4.78} = 16.6 \times 10^{-6}\ M\ [HC_7H_5O_2] = 0.30\ M\ [C_7H_5O_2] =$$

$$[C_7H_5O_2^-] = K_a \times \frac{[HC_7H_5O_2]}{[H_3O^+]}$$

$$1.14\ M = 6.3 \times 10^{-5} \times \frac{0.30}{16.6 \times 10^{-6}}$$

Mass = 0.200 L x 1.14 mol $C_7H_5O_2^-$ / 1L x 1mol $NaC_7H_5O_2$ / 1 mol $C_7H_5O_2^-$ x 144 g $NaC_7H_5O_2$ / 1 mol $NaC_7H_5O_2$ = 32.832 g $NaC_7H_5O_2$

References

1. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey 2007.

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8.3: Exact Treatment of Buffered Solutions

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SECTION OVERVIEW

8.4: Buffer Capacity

A buffer is a solution that can resist pH change upon the addition of an acidic or basic components. It is able to neutralize small amounts of added acid or base, thus maintaining the pH of the solution relatively stable. This is important for processes and/or reactions which require specific and stable pH ranges. Buffer solutions have a working pH range and capacity which dictate how much acid/base can be neutralized before pH changes, and the amount by which it will change.

8.5: Titrations and pH Curves

K_a is an **acid dissociation constant**, also known as the **acid ionization constant**. It describes the likelihood of the compounds and the ions to break apart from each other. As we already know, strong acids completely dissociate, whereas weak acids only partially dissociate. A big K_a value will indicate that you are dealing with a very strong acid and that it will completely dissociate into ions. A small K_a will indicate that you are working with a weak acid and that it will only partially dissociate into ions.

General Guide to Solving Problems involving K_a

Generally, the problem usually gives an initial acid concentration and a K_a value. From there you are expected to know:

1. How to write the K_a formula
2. Set up in an ICE table based on the given information
3. Solve for the concentration value, x.
4. Use x to find the equilibrium concentration.
5. Use the concentration to find pH.

How to write the K_a formula

The general formula of an acid dissociating into ions is

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{8.5.1}$$

with

- HA is the acid,
- A^- is the conjugate base and
- H_3O^+ is the the hydronium ion

By definition, the K_a formula is written as the products of the reaction divided by the reactants of the reaction

$$K_a = \frac{[Products]}{[Reactants]} \tag{8.5.2}$$

Based off of this general template, we plug in our concentrations from the chemical equation. The concentrations on the right side of the arrow are the products and the concentrations on the left side are the reactants. Using this information, we now can plug the concentrations in to form the K_a equation. We then write:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{8.5.3}$$

> *The concentration of the hydrogen ion ($[H^+]$) is often used synonymously with the hydrated hydronium ion ($[H_3O^+]$).*

To find a concentration of hydronium ions in solution from a pH, we use the formula:

$$[H_3O^+] = 10^{-pH} \tag{8.5.4}$$

This can be flipped to calculate pH from hydronium concentration:

$$pH = -\log[H_3O^+] \tag{8.5.5}$$

- An acidic solution is one that has an excess of H_3O^+ ions compared to OH^- ions.
- An basic (or alkaline) solution is one that has an excess of OH^- ions compared to H_3O^+ ions.
- A neutral solution is one that has equal concentrations of OH^- ions and H_3O^+ ions.

At 25 °C, we can correlate whether a solution is acidic, basic, or neutral based off of the measured pH of the solutions:

- pH = 7 is neutral
- pH > 7 is basic
- pH < 7 is acidic

However, these relationships are not valid at temperatures outside 25 °C.

cid

Calculate the pH of a weak acid solution of 0.2 M HOBr, given:

$$HOBr + H_2O \rightleftharpoons H_3O^+ + OBr^- \tag{8.5.6}$$

$$K_a = 2 \times 10^{-9} \tag{8.5.7}$$

Solution

Step 1: The ICE Table

Since we were given the initial concentration of HOBr in the equation, we can plug in that value into the Initial Concentration box of the ICE chart. Considering that no initial concentration values were given for H_3O^+ and OBr-, we can assume that none was present initially, and we indicate this by placing a zero in the corresponding boxes. M stands for molarity.

	HOBr	**H_3O^+**	**OBr^-**
Initial Concentration	0.2 M	0	0
Change in Concentration			
Equilibrium Concentration			

Because we started off without an initial concentration of H_3O^+ and OBr^-, it has to come from somewhere. In the Change in Concentration box, we add a +x because while we do not know what the numerical value of the concentration is at the moment, we do know that it has to be added and not taken away. In contrast, since we did start off with a numerical value of the initial concentration, we know that it has to be taken away to reach equilibrium. Because of this, we add a -x in the HOBr box.

	HOBr	**H_3O^+**	**OBr^-**
Initial Concentration	0.2 M	0	0
Change in Concentration	-x M	+x M	+x M
Equilibrium Concentration			

Now its time to add it all together! Go from top to bottom and add the Initial concentration boxes to the Change in concentration boxes to get the Equilibrium concentration.

	HOBr	**H_3O^+**	**OBr^-**
Initial Concentration	0.2 M	0	0
Change in Concentration	-x M	+x M	+x M
Equilibrium Concentration	(0.2 - x) M	x M	x M

Step 2: Create the K_a equation using this equation: $K_a = \dfrac{[Products]}{[Reactants]}$

$$K_a = \frac{[H_3O^+][OBr-]}{[HOBr-]}$$

Step 3: Plug in the information we found in the ICE table

$$K_a = \frac{(x)(x)}{(0.2 - x)}$$

Step 4: Set the new equation equal to the given Ka

$$2\times 10^{-9} = \frac{(x)(x)}{(0.2-x)} \tag{8.5.8}$$

Step 5: Solve for x

$$x^2 + (2\times 10^{-9})x - (4\times 10^{-10}) = 0 \tag{8.5.9}$$

To solve for x, we use the quadratic formula

- $a = 1$
- $b = 2\times 10^{-9}$
- $c = -4\times 10^{-10}$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-2\times 10^{-9}\pm\sqrt{(2\times 10^{-9})^2-4(1)(-4\times 10^{-10})}}{2(1)} \tag{8.5.10}$$

$$x = 2.0\times 10^{-5} \tag{8.5.11}$$

Step 6: Plug x back into the ICE table to find the concentration

$$x = [H_3O^+] = 2\times 10^{-5}\ M \tag{8.5.12}$$

Step 7: Use the formula using the concentration to find pH

$$pH = -\log[H_3O^+] = -\log(2\times 10^{-5}) = -(-4.69) = 4.69 \tag{8.5.13}$$

$$pH = 4.69 \tag{8.5.14}$$

✓ Example 8.5.2: Concentrated Solution of Acetic Acid (Vinegar)

For acetic acid, $HC_2H_3O_2$, the K_a value is 1.8×10^{-5}. Calculate the concentration of H_3O^+ in a 0.3 M solution of $HC_2H_3O_2$.

Solution

Step 1: The ICE Table

Since we were given the initial concentration of $HC_2H_3O_2$ in the original equation, we can plug in that value into the Initial Concentration box of the ICE chart. Considering that no initial concentration values were given for H_3O^+ and $C_2H_3O_2^-$, we assume that none was present initially, and we indicate this by placing a zero in the corresponding boxes.

	$HC_2H_3O_2$	H_3O^+	$C_2H_3O_2$
Initial Concentration	0.3 M	0	0
Change in Concentration			
Equilibrium Concentration			

Because we started off without any initial concentration of H_3O^+ and $C_2H_3O_2$-, is has to come from somewhere. For the Change in Concentration box, we add a +x because while we do not know what the numerical value of the concentration is at the moment, we do know that it has to be added and not taken away. In contrast, since we did start off with a numerical value of the initial concentration, we know that it has to be taken away to reach equilibrium. Because of this, we add a -x in the $HC_2H_3O_2$ box.

	$HC_2H_3O_2$	H_3O^+	$C_2H_3O_2$
Initial Concentration	0.3 M	0	0
Change in Concentration	-x M	+x M	+x M
Equilibrium Concentration			

Now its time to add it all together! Go from top to bottom and add the Initial concentration boxes to the Change in concentration boxes to get the Equilibrium concentration.

	$HC_2H_3O_2$	**H_3O^+**	**$C_2H_3O_2$**
Initial Concentration	0.3 M	0	0
Change in Concentration	-x M	+x M	+x M
Equilibrium Concentration	(0.3 - x) M	x M	x M

Step 2: Create the K_a equation using this equation: $K_a = \frac{[Products]}{[Reactants]}$

$$K_a = \frac{[H_3O^+][C_2H_3O_2]}{[HC_2H_3O_2]}$$

Step 3: Plug in the information we found in the ICE table

$$K_a = \frac{(x)(x)}{(0.3-x)} \tag{8.5.15}$$

Step 4: Set the new equation equal to the given K_a

$$1.8x10^{-5} = \frac{(x)(x)}{(0.3-x)} \tag{8.5.16}$$

Step 5: Solve for x

$$(x^2) + (1.8 \times 10^{-5} x) - (5.4 \times 10^{-6}) \tag{8.5.17}$$

To solve for x, we use the quadratic formula

- $a = 1$
- $b = 1.8 \times 10^{-5}$
- $c = -5.4 \times 10^{-6}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-5.4 \times 10^{-6})}}{2(1)} \tag{8.5.18}$$

$$x = 0.0023 \tag{8.5.19}$$

Step 6: Plug x back into the ICE table to find the concentration

$$x = [H_3O^+] = 0.0023\ M \tag{8.5.20}$$

Example 8.5.3: Concentrated Solution of Benzoic Acid

Find the equilibrium concentration of $HC_7H_5O_2$from a 0.43 M solution of Benzoic Acid, $HC_7H_5O_2$.

Solution

Given: K_a for $HC_7H_5O_2$= 6.4 x 10^{-5}

Step 1: The ICE Table

	$HC_7H_5O_2$	**H_3O^+**	**$C_7H_5O_2^-$**
Initial Concentration	0.43 M	0	0
Change in Concentration	-x	+x	+x

	$HC_7H_5O_2$	H_3O^+	$C_7H_5O_2^-$
Equilibrium Concentration	(0.43-x)M	x M	x M

Step 2: Create the K_a equation using this equation :$K_a = \frac{[Products]}{[Reactants]}$

$$K_a = \frac{[H_3O^+][C_7H_5O_2-]}{[HC_7H_5O_2]}$$

Step 3: Plug in the information we found in the ICE table

$$K_a = \frac{(x)(x)}{(0.43-x)}$$

Step 4: Set the new equation equal to the given Ka

$$6.4x10^{-5} = \frac{(x)(x)}{(0.43-x)}$$

Step 5: Solve for x.

x=0.0052

Step 6: Plug x back into the ICE table to find the concentration

$[HC_7H_5O_2]$= (0.43-x)M

$[HC_7H_5O_2]$= (0.43-0.0052)M

Answer: $[HC_7H_5O_2]$= 0.425 M

Example 8.5.4: Concentrated Solution of Hypochlorous acid

For a 0.2 M solution of Hypochlorous acid, calculate all equilibrium concentrations.

Solution

Given: $K_a = 3.5 \times 10^{-8}$

Step 1: The ICE Table

	HOCl	H_3O^+	OCl^-
Initial Concentration	0.2 M	0	0
Change in Concentration	-x M	+x M	+x M
Equilibrium Concentration	(0.2 - x) M	x M	x M

Step 2: Create the K_a equation using this equation: $K_a = \frac{[Products]}{[Reactants]}$

$$K_a = \frac{[H_3O^+][OCl-]}{[HOCl-]}$$

Step 3: Plug in the information we found in the ICE table

$$K_a = \frac{(x)(x)}{(0.2-x)}$$

Step 4: Set the new equation equal to the given Ka

$$3.5x10^{-8} = \frac{(x)(x)}{(0.2-x)}$$

Step 5: Solve for x

$$x=8.4 \text{ x } 10^{-5}$$

Step 6: Plug x back into the ICE table to find the concentration

$$[HOCl]= [(.2)-(8.4 \text{ x } 10^{-5})]=.199$$

$$[H_3O+]=8.4 \text{ x } 10^{-5}$$

$$[OCl-]=8.4 \text{ x } 10^{-5}$$

✓ Example 8.5.5: pH

Calculate the pH from the equilibrium concentrations of $[H_3O^+]$ in Example 8.5.4.

Solution

Given:

$$[HOCl]=0.199$$

$$[H_3O^+]=8.4 \text{ x } 10^{-5}$$

$$[OCl-]=8.4 \text{ x } 10^{-5}$$

Step 1: Use the formula using the concentration of $[H_3O^+]$ to find pH

$$pH=-\log[H3O+]=-\log(8.4x10^{-5})=4.08 \tag{8.5.21}$$

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8.6: Acid-Base Indicators

pH indicators are weak acids that exist as natural dyes and indicate the concentration of H^+ (H_3O^+) ions in a solution via color change. A pH value is determined from the negative logarithm of this concentration and is used to indicate the acidic, basic, or neutral character of the substance you are testing.

Introduction

pH indicators exist as liquid dyes and dye-infused paper strips. They are added to various solutions to determine the pH values of those solutions. Whereas the liquid form of pH indicators is usually added directly to solutions, the paper form is dipped into solutions and then removed for comparison against a color/pH key.

pH	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Color								

Very Acidic Acidic Neutral Basic Very Basic

See Figure 1 and 2 to see a color range (1) of a universal indicator (2).

The Implications of the Indicated pH via the Equation

Recall that the value of pH is related to the concentration of H^+ (H_3O^+) of a substance. pH itself is approximated as the cologarithm or negative logarithm of the H^+ ion concentration (Figure 3).

$$pH \approx -log[H_3O^+] \tag{3}$$

A pH of 7 indicates a neutral solution like water. A pH less than 7 indicates an acidic solution and a pH greater than 7 indicates a basic solution. Ultimately, the pH value indicates how much H^+ has dissociated from molecules within a solution. The lower the pH value, the higher concentration of H^+ ions in the solution and the stronger the acid. Likewise, the higher the pH value, the lower the concentration of H^+ ions in the solution and the weaker the acid.

How the Color Change of the Indicator Happens

The color change of a pH indicator is caused by the dissociation of the H^+ ion from the indicator itself. Recall that pH indicators are not only natural dyes but also weak acids. The dissociation of the weak acid indicator causes the solution to change color. The equation for the dissociation of the H^+ ion of the pH indicator is show below (Figure 4).

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^- \tag{4}$$

with

- HIn is the acidic pH indicator and
- In^- is the conjugate base of the pH indicator

It is important here to note that the equation expressed in figure 4 is in equilibrium, meaning Le Chatelier's principle applies to it. Thus, as the concentration of H_3O^+ (H^+) increases or decreases, the equilibrium shifts to the left or right accordingly. An **increase** in the HIn acid concentration causes the equilibrium to shift to the **right** (towards products), whereas an **increase** of the In^- base concentration causes the equilibrium to shift to the **left** (towards reactants).

pH Ranges of pH Indicators

pH indicators are specific to the range of pH values one wishes to observe. For example, common indicators such as phenolphthalein, methyl red, and bromothymol blue are used to indicate pH ranges of about 8 to 10, 4.5 to 6, and 6 to 7.5 accordingly. On these ranges, phenolphthalein goes from colorless to pink, methyl red goes from red to yellow, and bromothymol blue goes from yellow to blue. For universal indicators, however, the pH range is much broader and the number of color changes is much greater. See figures 1 and 2 in the introduction for visual representations. Usually, universal pH indicators are in the paper strip form.

Graphing pH vs. the H$^+$ (H_3O^+) Concentration

It is important to note that the pH scale is a **logarithmic scale**: hence an increase of 1 pH unit corresponds to a ten times increase of H_3O^+. For example, a solution with a pH of 3 will have an H$^+$ (H_3O^+) concentration ten times greater than that of a solution with a pH of 4. As pH is the negative logarithm of the H$^+$ (H_3O^+) concentration of a foreign substance, the lower the pH value, the higher the concentration of H$^+$ (H_3O^+) ions and the stronger the acid. Additionally, the higher the pH value, the lower the H$^+$ (H_3O^+) concentration and the stronger the base.

Indicators in Nature

pH indicators can be used in a variety of ways, including measuring the pH of farm soil, shampoos, fruit juices, and bodies of water. Additionally, pH indicators can be found in nature, so therefore their presence in plants and flowers can indicate the pH of the soil from which they grow.

Hydrangeas

Nature contains several natural pH indicators as well: for example, some flower petals (especially Roses and Hydrangeas), certain fruits (cherries, strawberries) and leaves can change color if the pH of the soil changes. See figure 7.

(7)

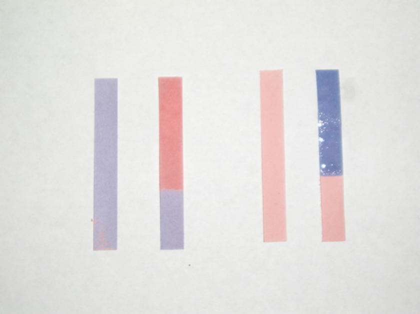
Lemon juice

In the lemon juice experiment, the pH paper turns from blue to vivid red, indicating the presence of H_3O^+ ions: lemon juice is acidic. Refer to the table of Universal Indicator Color change (figure 1 in the introduction) for clarification.

Cleaning Detergent

The household detergent contained a concentrated solution of sodium bicarbonate, commonly known as baking soda. As shown, the pH paper turns a dark blue: baking soda (in solution) is basic.Refer to the table of Universal Indicator Color change (figure 1 in the introduction) for clarification.

Here is a closer look of the pH papers before and after dipping them in the lemon juice and cleaning detergent (Figure 10):



neutral acidic neutral basic

Figure 10:

Cabbage Juices

Here is a simple demonstration that you could try in the lab or at home to get a better sense of how indicator paper works. Make sure to always wear safety glasses and gloves when performing an experiment!

Materials

- 1 cabbage
- cooking pot
- white paper coffee filters
- strainer
- water
- a bowl

Procedure

1. Peal the cabbage leaves and place them into the pot.
2. Add water into the pot, making sure the water covers the cabbage entirely.
3. Place the pot on the stove and allow to cook at medium heat for about 30 to 35 minutes.
4. Allow it to cool, then pour contents into the bowl using the strainer.
5. Soak your coffee filters in the cabbage juice for about 25 to 30 minutes.
6. Allow the filters to fully dry, then cut them into strips.
7. Now start your pH testing (starts out blue, changes to green [basic], and **red** [acidic]).

Practice Problems

1. A hair stylist walks into a store and wants to buy a shampoo with slightly acidic/neutral pH for her hair. She finds 5 brands that she really likes, but since she never took any introductory chemistry classes, she is unsure about which one to purchase. The first has a pH of 3.6, the second of 13, the third of 8.2, the fourth of 6.8 and the fifth of 9.7. Which one should she buy?

Answer: The brand that has a pH of 6.8 since it's under 7 (neutral) but very close to it, making it slightly acidic.

2. You decide to test the pH of your brand new swimming pool on your own. The instruction manual advises to keep it between 7.2-7.6. Shockingly, you realize it's set at 8.3! Horrified, you panic and are unsure whether you should add some basic or acidic chemicals in your pool (being mindful of the dose, of course. Those specific chemicals are included in the set, so no need to worry about which one you have to use and (eek!) if they are legal for public use). Which one should you add?

Answer: Since the goal is to lower the pH to its ideal value, we must add acidic solution to the pool.

3. Let's say the concentration of Hydronium ions in an aqueous solution is 0.033 mol/L. What is the corresponding pH of this solution, and based on your answer identify whether the solution is acidic, basic or neutral.

Answer: Using the formula $pH \approx -log[H_3O+]$

pH= -log[0.033]= **1.48** : The solution is highly acidic!

4. Now let's do the inverse: Say you have a solution with a pH of 9.4. What is the H_30^+ ions concentration?

Answer: $[H_3O^+]$= $10^{-9.4}$= **3.98E-10 mol/L**. Seem too low to be true? Think again, if the pH is >7, the solution will be basic, hence the hydronium ions will be low compared to the hydroxide (OH^- ions).

5. A more trickier one: 0.00026 moles of acetic acid are added to 2.5 L of water. What is the pH of the solution?

Answer: M=n/L : $M_{\text{acetic acid}}$= 0.00026/2.5 =**1.04E-4 mol/L**

pH= -log[1.04E-4]= **3.98**

Outside Links

- external link:http://www.epa.gov/acidrain/measure/ph.html
- external link:www.krampf.com/experiments/Science_Experiment16.html
- There are many common household products and garden plants that can be used or made into pH indicators. For more information on these common house hold indicators visit http://chemistry.about.com/cs/acidsandbases/a/aa060703a.htm
- commons.wikimedia.org/wiki/Ca...ndicator_paper

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8.7: Titrations of Polyatomic Acids

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8.8: Solubility Equilibria and the Solubility Product

Considering the relation between solubility and K_{sq} is important when describing the solubility of slightly ionic compounds. However, this article discusses ionic compounds that are difficult to dissolve; they are considered "slightly soluble" or "almost insoluble." Solubility product constants (K_{sq}) are given to those solutes, and these constants can be used to find the molar solubility of the compounds that make the solute. This relationship also facilitates finding the K_{sq} of a slightly soluble solute from its solubility.

Introduction

Solubility is the ability of a substance to dissolve. The two participants in the dissolution process are the solute and the solvent. The solute is the substance that is being dissolved, and the solvent is the substance that is doing the dissolving. For example, sugar is a solute and water is a solvent. Solubility is defined as the maximum amount of solute that can be dissolved in a solvent at equilibrium. Equilibrium is the state at which the concentrations of products and reactant are constant after the reaction has taken place.

The solubility product constant (K_{sq}) describes the equilibrium between a solid and its constituent ions in a solution. The value of the constant identifies the degree to which the compound can dissociate in water. For example, the higher the K_{sq}, the more soluble the compound is. K_{sq} is defined in terms of activity rather than concentration because it is a measure of a concentration that depends on certain conditions such as temperature, pressure, and composition. It is influenced by surroundings. K_{sq} is used to describe the saturated solution of ionic compounds. (A saturated solution is in a state of equilibrium between the dissolved, dissociated, undissolved solid, and the ionic compound.)

✓ Example 1: Barium Carbonate

Consider the compound barium carbonate $\mathrm{BaCO_3}$ (an ionic compound that is not very soluble):

$$\mathrm{BaCO_{3\,(s)}} \rightleftharpoons \mathrm{Ba^{2+}(aq)^{+}CO_3^{2-}(aq)}$$

Solution

First, write down the equilibrium constant expression:

$$K_c = \frac{[\mathrm{Ba^{2+}}][\mathrm{CO_3^{2-}}]}{[\mathrm{BaCO_3}]}$$

The activity of solid \(\ce{$\mathrm{BaCO}_{3\}\backslash)}$ is 1, and considering that the concentrations of these ions are small, the activities of the ions are approximated to their molar concentrations. K_{sq} is therefore equal to the product of the ion concentrations:

$$\begin{aligned} K_{sp} &= [\mathrm{Ba^{2+}}][\mathrm{CO_3^{2-}}] \\ &= 5.1 \times 10^{-9} \end{aligned}$$

How are K_{sp} and Solubility Related?

The relation between solubility and the solubility product constants is that one can be used to derive the other. In other words, there is a relationship between the solute's molarity and the solubility of the ions because K_{sq} is the product of the solubility of each ion in moles per liter.

For example, to find the K_{sq} of a slightly soluble compound from its solubility, the solubility of each ion must be converted from mass per volume to moles per liter to find the molarity of each ion. These numbers can then be substituted into the K_{sq} formula, which is the product of the solubility of each ion. An example of this process is given below:

✓ Example 2: Lead Iodide

Suppose the aqueous solubility for compound $\mathrm{PbI_2}$ is 0.54 grams/100 ml at 25 °C and calculate the K_{sq} of $\mathrm{PbI_2}$ at 25°C.

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2I^{-}_{(aq)}$$

Solution

a. Convert 0.54 grams of PbI_2 to moles:

$$0.54\ grams \times \frac{1\ mol\ PbI_2}{461.0\ grams} = 0.001171\ mol\ PbI_2$$

b. Convert ml to L:

$$\frac{100\ mL}{1000\ L} = 0.100\ L$$

c. Find the molarity:

$$\frac{0.001171\ mol}{0.100\ L} = 0.01171\ M\ PbI_2$$

d. Now find the molarity of each ion by using the stoichiometric ratio (remember there are two I$^-$ ions for each Pb^{2+} ion):

$$\begin{align} [Pb^{2+}] &= \frac{0.01171\ M}{1\ L} \times \frac{1\ mol\ Pb}{1\ mol\ PbI_2} \tag{8.8.1} \\ &= 0.011714\ M\ Pb^{2+} \tag{8.8.2} \\ [I^-] &= \frac{0.01171\ M}{1\ L} \times \frac{2\ mol\ I^-}{1\ mol\ PbI_2} \tag{8.8.3} \\ &= 0.23427\ M\ I^- \tag{8.8.4} \end{align}$$

e. Finally, plug in the molarity to find K_{sq}:

$$\begin{align} K_{sp} &= [Pb^{2+}][I^-]^2 \tag{8.8.5} \\ &= (0.011714\ M)(0.023427\ M)^2 \tag{8.8.6} \\ &= 6.4 \times 10^{-6} \tag{8.8.7} \end{align}$$

This relation facilitates solving for the molar solubility of the ionic compounds when the K_{sq} is given to us. The process involves working backwards from K_{sq} to the molarity of the ionic compound.

✓ Example 3

Suppose the K_{sq} at 25 ^{0}C is 8.5 x 10^{-17} for the compound AgI. What is the molar solubility?

$$AgI_{(s)} \rightleftharpoons Ag^+_{(aq)} + I^-_{(aq)}$$

Solution

a. Let "g" represent the number of moles:

$$\begin{align} K_{sp} &= [Ag^{2+}][I^-] \tag{8.8.8} \\ &= g^2 \tag{8.8.9} \\ &= 8.5 \times 10^{-17} \tag{8.8.10} \end{align}$$

b. Solve for "g":

$$\begin{align} g^2 &= 8.5 \times 10^{-17} \tag{8.8.11} \\ g &= (8.5 \times 10^{-17})^{\frac{1}{2}} \tag{8.8.12} \\ &= 9.0 \times 10^{-9} \tag{8.8.13} \end{align}$$

The molar solubility of AgI is 9.0 x 10^{-9}

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8.9: Precipitation and Qualitative Analysis Complex Ion Equilibria

Learning Objectives

- Calculate ion concentrations to maintain a heterogeneous equilibrium.
- Calculate pH required to precipitate a metal hydroxide.
- Design experiments to separate metal ions in a solution of mixtures of metals.

Chemical Separation by Precipitation

A mixture of metal ions in a solution can be separated by precipitation with anions such as Cl^-, Br^-, SO_4^{2-}, CO_3^{2-}, S^{2-}, $Cr_2O_4^{2-}$, PO_4^{2-}, OH^- etc. When a metal ion or a group of metal ions form insoluble salts with a particular anion, they can be separated from others by precipitation. We can also separate the anions by precipitating them with appropriate metal ions.

There are no definite dividing lines between **insoluble salts, sparingly soluble**, and **soluble salts**, but concentrations of their saturated solutions are small, medium, and large. Solubility products are usually listed for insoluble and sparingly soluble salts, but they are not given for soluble salts. Solubility products for soluble salts are very large.

What type of salts are usually soluble, sparingly soluble and insoluble? The following are some general guidelines, but these are not precise laws.

- **All nitrates are soluble.** The singly charged large NO_3^- ions form salts with high solubilities. So do ClO_4^-, ClO_3^-, NO_2^-, $HCOO^-$, and CH_3COO^-.
- **All chlorides, bromides, and iodides are soluble except those of** Ag^+**,** Hg_2^{2+}**, and** Pb^{2+}**.** CaF_2, BaF_2, and PbF_2 are also insoluble.
- **All sulfates are soluble, except those of** Ba^{2+}**,** Sr^{2+}**, and** Pb^{2+}**.** The doubly charged sulfates are usually less soluble than halides and nitrates.
- **Most singly charge cations** K^+**,** Na^+**,** NH_4^+ **form soluble salts.** However, $K_3Co(NO_2)_6$ and $(NH_4)_3Co(NO_2)_6$ are insoluble.

These are handy rules for us to have if we deal with salts often. On the other hand, solubility is an important physical property of a substance, and these properties are listed in handbooks.

Chemical Separation of Metal Ions

Formation of crystals from a saturated solution is a **heterogeneous equilibrium** phenomenon, and it can be applied to separate various chemicals or ions in a solution. When solubilities of two metal salts are very different, they can be separated by precipitation. The K_{sp} values for various salts are valuable information, and some data are given in the Handbook of this website. On the Handbook Menu, clicking the item Salts K_{sp} will give the K_{sp}'s of some salts. In the first two examples, we show how barium and strontium can be separated as chromate.

Example 1

The K_{sp} for strontium chromate is 3.6E-5 and the K_{sp} for barium chromate is 1.2E-10. What concentration of potassium chromate will precipitate the maximum amount of either the barium or the strontium chromate from an equimolar 0.30 M solution of barium and strontium ions without precipitating the other?

Solution
Since the K_{sp} for barium chromate is smaller, we know that $BaCrO_4$ will form a precipitate first as $[CrO_4^{2-}]$ increases so that Q_{sp} for $BaCrO_4$ also increases from zero to K_{sp} of $BaCrO_4$, at which point, $BaCrO_4$ precipitates. As $[CrO_4^{2-}]$ increases, $[Ba^{2+}]$ decreases. Further increase of $[CrO_4^{2-}]$ till Q_{sp} for $SrCrO_4$ increases to K_{sp} of $SrCrO_4$; it then precipitates.

Let us write the equilibrium equations and data down to help us think. Further, let *x* be the concentration of chromate to precipitate Sr^{2+}, and *y* be that to precipitate Ba^{2+}. According to the definition of K_{sp} we have,

$$\begin{array}{lcccl} SrCrO_4 & \rightarrow & Sr^{2+} & + & CrO_4^{2-}, \quad K_{sp} = 3.6 \times 10^{-5} \\ & & 0.30 & & x \end{array} \tag{8.9.1}$$

$$x = \frac{\text{3.6e-5}}{0.30} = 1.2 \times 10^{-4} M \tag{8.9.2}$$

$$\begin{array}{cccccc} \mathrm{BaCrO_4} & \rightarrow & \mathrm{Ba^{2+}} & + & \mathrm{CrO_4^{2-}}, & K_{\mathrm{sp}} = 1.2 \times 10^{-10} \\ & & 0.30 & & y & \end{array}$$

$$y = \frac{\text{1.2e-10}}{0.30} = 4.0 \times 10^{-10}\ M$$

The K_{sp}'s for the two salts indicate $\mathrm{BaCrO_4}$ to be much less soluble, and it will precipitate before any $\mathrm{SrCrO_4}$ precipitates. If chromate concentration is maintained a little less than 1.2e-4 M, $\mathrm{Sr^{2+}}$ ions will remain in the solution.

DISCUSSION

In reality, to control the increase of $[\mathrm{CrO_4^{2-}}]$ is very difficult.

✓ Example 2

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10}. Potassium chromate is added a small amount at a time to first precipitate $\mathrm{BaCrO_4}$. Calculate $[\mathrm{Ba^{2+}}]$ when the first trace of $\mathrm{SrCrO_4}$ precipitate starts to form in a solution that contains 0.30 M each of $\mathrm{Ba^{2+}}$ and $\mathrm{Sr^{2+}}$ ions.

Solution
From the solution given in **Example 1**, $[\mathrm{CrO_4^{2-}}] = 3.6 \times 10^{-4}\ M$ when $\mathrm{SrCrO_4}$ starts to form. At this concentration, the $[\mathrm{Ba^{2+}}]$ is estimated as follows.

$$[\mathrm{Ba^{2+}}]\ 3.6\backslash\mathrm{times}\ 10\hat{}\{\text{-4}\} = 1.2\backslash\mathrm{times}\ 10\hat{}\{\text{-10}\}$$

The K_{sp} of $\mathrm{BaCrO_4}$.

Thus,

$$[\mathrm{Ba^{2+}}] = \text{3.33e-7 M}$$

Very small indeed, compared to 0.30. In the fresh precipitate of $\mathrm{SrCrO_4}$, the mole ratio of $\mathrm{SrCrO_4}$ to $\mathrm{BaCrO_4}$ is 0.30 / 3.33e-7 = 9.0e5. In other words, the amount of $\mathrm{Ba^{2+}}$ ion in the solid is only 1e-6 (1 ppm) of all metal ions, providing that all the solid was removed when $[\mathrm{CrO_4^{2-}}] = \text{3.6e-4 M}$.

DISCUSSION

The calculation shown here indicates that the separation of Sr and Ba is pretty good. In practice, an impurity level of 1 ppm is a very small value.

✓ Example 3

What reagent should you use to separate silver and lead ions that are present in a solution? What data or information will be required for this task?

Solution
The K_{sp}'s for salts of silver and lead are required. We list the K_{sp}'s for chlorides and sulfates in a table here. These value are found in the Handbook Menu of our website as Salts K_{sp}.

Salt	K_{sp}	Salt	K_{sp}
AgCl	1.8×10^{-10}	$\mathrm{Ag_2SO_4}$	1.4×10^{-5}
$\mathrm{Hg_2Cl_2}$	1.3×10^{-18}	$\mathrm{BaSO_4}$	1.1×10^{-10}
$\mathrm{PbCl_2}$	1.7×10^{-5}	$\mathrm{CaSO_4}$	2.4×10^{-5}
		$\mathrm{PbSO_4}$	6.3×10^{-7}
		$\mathrm{SrSO_4}$	3.2×10^{-7}

Because the K_{sp}'s AgCl and $\mathrm{PbCl_2}$ are very different, chloride, $\mathrm{Cl^-}$, apppears a good choice of negative ions for their separation.

The literature also indicates that $\mathrm{PbCl_2}$ is rather soluble in warm water, and by heating the solution to 350 K (80°C), you can keep $\mathrm{Pb^{2+}}$ ions in solution and precipitate AgCl as a solid. The solubility of AgCl is very small even at high temperatures.

DISCUSSION

Find more detailed information about the solubility of lead chloride as a function of temperature.

Can sulfate be used to separate silver and lead ions? Which one will form a precipitate first as the sulfate ion concentration increases? What is the $[\mathrm{Pb^{2+}}]$ when $\mathrm{Ag_2SO_4}$ begins to precipitate in a solution that contains 0.10 M $\mathrm{Ag^+}$?

Questions

1. Iron(II) hydroxide is only sparingly soluble in water at 25°C; its K_{sp} is 7.9×10^{-16}. Calculate the solubility of iron(II) hydroxide in a buffer solution with pH = 7.00.
2. A solution contains 0.60 M $\mathrm{Ba^{2+}}$ and 0.30 M $\mathrm{Ca^{2+}}$; K_{sp} values for $\mathrm{BaCrO_4}$ and $\mathrm{CaCrO_4}$ are 1.2×10^{-10} and 7.1×10^{-4} respectively. What value of $[\mathrm{CrO_4^{2-}}]$ will result in a maximum separation of these two ions?
3. A solution contains 0.60 M $\mathrm{Ba^{2+}}$ and 0.30 M $\mathrm{Ca^{2+}}$; K_{sp} values for $\mathrm{BaCrO_4}$ and $\mathrm{CaCrO_4}$ are 1.2×10^{-10} and 7.1×10^{-4} respectively. Calculate the $[\mathrm{Ca^{2+}}]/[\mathrm{Ba^{2+}}]$ ratio in the solution when $[\mathrm{CrO_4^{2-}}]$ is maintained at $1.2 \times 10^{-3}\ M$.

Solutions

1. ***Answer*** $[\mathrm{Fe^{2+}}] = 0.079\ \mathrm{M}$

   Consider...

   $[\mathrm{OH^-}] = 10^{(-14+7)} = 1.00\text{e-}7\ (\text{buffer})$.

   $[\mathrm{Fe^{2+}}](1.00\text{e-}7)^2 = K_{sp};\ [\mathrm{Fe^{2+}}] = ?$

   This $\mathrm{Fe^{2+}}$ concentration is low; it is not very soluble in a neutral solution (pH = 7).

   What is $[\mathrm{Fe^{2+}}]$ in a solution whose pH = 6.00?
2. ***Answer*** $[\mathrm{CrO_4^{2-}}] = 2.37\text{e-}3\ \mathrm{M}$

   Consider...

   Solid $\mathrm{BaCrO_4}$ will form first as $[\mathrm{CrO_4^{2-}}]$ increases. The maximum $[\mathrm{CrO_4^{2-}}]$ to precipitate $\mathrm{CaCrO_4}$ is estimated as follows.

   $[\mathrm{CrO_4^{2-}}] = \dfrac{7.1\text{e-}4}{0.30} = 2.37\text{e-}3\ \mathrm{M}$

   Estimate $[\mathrm{Ba^{2+}}]$ when $[\mathrm{CrO_4^{2-}}] = 2.3\text{e-}3\ \mathrm{M}$, slightly below the maximum concentration.
3. ***Answer*** $\dfrac{[\mathrm{Ca^{2+}}]}{[\mathrm{Ba^{2+}}]} = 3\text{e}6$

   Consider...

   $[\mathrm{Ba^{2+}}] = \dfrac{1.2\text{e-}10}{1.2\text{e-}3} = 1\text{e-}7;$

   $\dfrac{[\mathrm{Ca^{2+}}]}{[\mathrm{Ba^{2+}}]} = \dfrac{0.3}{1\text{e-}7} = ?$ The ratio of three million is large!

Contributors and Attributions

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8.10: Complex Ion Equilibria

The effect of Complex Ion Formation on Solubility

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CHAPTER OVERVIEW

13: Bonding General Concepts

Chemical Principles (Zumdahl and Decoste)
Textmap Alternative

Topic hierarchy

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13.1: Types of Chemical Bonds

In the early 1900's, Paul Drüde came up with the "sea of electrons" metallic bonding theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. Metallic bonds occur among metal atoms. Whereas ionic bonds join metals to non-metals, *metallic bonding joins a bulk of metal atoms*. A sheet of aluminum foil and a copper wire are both places where you can see metallic bonding in action.

Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a soft metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table. Sodium has the electronic structure $1s^2 2s^2 2p^6 3s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. Each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium. *All* of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals that extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons (Figure 13.1.1).

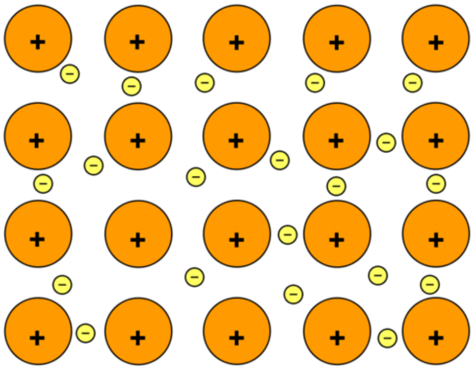

Figure 13.1.1: Metallic Bonding: The Electron Sea Model: Positive atomic nuclei (orange circles) surrounded by a sea of delocalized electrons (yellow circles).

This is sometimes described as "an array of positive ions in a sea of electrons". If you are going to use this view, beware! Is a metal made up of atoms or ions? It is made of atoms**.** Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron has not been lost - it may no longer have an attachment to a particular atom, but it's still there in the structure. Sodium metal is therefore written as Na, not Na^+.

✓ Example 13.1.1: Metallic bonding in magnesium

Use the sea of electrons model to explain why Magnesium has a higher melting point (650 °C) than sodium (97.79 °C).

Solution

If you work through the same argument above for sodium with magnesium, you end up with stronger bonds and hence a higher melting point.

Magnesium has the outer electronic structure $3s^2$. Both of these electrons become delocalized, so the "sea" has twice the electron density as it does in sodium. The remaining "ions" also have twice the charge (if you are going to use this particular view of the metal bond) and so there will be more attraction between "ions" and "sea".

More realistically, each magnesium atom has 12 protons in the nucleus compared with sodium's 11. In both cases, the nucleus is screened from the delocalized electrons by the same number of inner electrons - the 10 electrons in the $1s^2$ $2s^2$ $2p^6$ orbitals. That means that there will be a net pull from the magnesium nucleus of 2+, but only 1+ from the sodium nucleus.

So not only will there be a greater number of delocalized electrons in magnesium, but there will also be a greater attraction for them from the magnesium nuclei. Magnesium atoms also have a slightly smaller radius than sodium atoms, and so the delocalized electrons are closer to the nuclei. Each magnesium atom also has twelve near neighbors rather than sodium's eight. Both of these factors increase the strength of the bond still further.

Note: Transition metals tend to have particularly high melting points and boiling points. The reason is that they can involve the 3d electrons in the delocalization as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be.

Bulk properties of metals

Metals have several qualities that are unique, such as the ability to conduct electricity and heat, a low ionization energy, and a low electronegativity (so they will give up electrons easily to form cations). Their physical properties include a lustrous (shiny) appearance, and they are malleable and ductile. Metals have a crystal structure but can be easily deformed. In this model, the valence electrons are free, delocalized, mobile, and not associated with any particular atom. This model may account for:

- **Conductivity**: Since the electrons are free, if electrons from an outside source were pushed into a metal wire at one end (Figure $13.1.2$), the electrons would move through the wire and come out at the other end at the same rate (conductivity is the movement of charge).

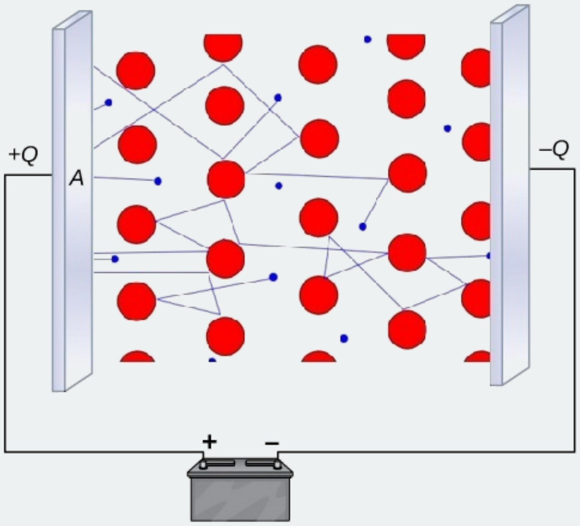

Figure $13.1.2$: The "sea of electrons" is free to flow about the crystal of positive metal ions. These flowing electron can conduct electrical change when an electric field is applied (e.g., a battery). (CC-BY-SA; OpenStax and Rafaelgarcia).

- **Malleability** and **Ductility**: The electron-sea model of metals not only explains their electrical properties but their malleability and ductility as well. The sea of electrons surrounding the protons acts like a cushion, and so when the metal is hammered on, for instance, the overall composition of the structure of the metal is not harmed or changed. The protons may be rearranged but the sea of electrons with adjust to the new formation of protons and keep the metal intact. When one layer of ions in an electron sea moves along one space with respect to the layer below it, the crystal structure does not fracture but is only deformed (Figure $13.1.3$).

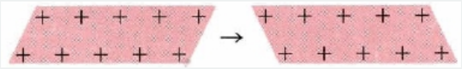

Figure $13.1.3$: Malleability of metals originate from each of moving layer of atoms with respect to each other. The final situation is much the same as the initial. Thus if we hit a metal with a hammer, the crystals do not shatter, but merely change their shape, This is very different from the behavior of ionic crystals.

- **Heat capacity**: This is explained by the ability of free electrons to move about the solid.
- **Luster**: The free electrons can absorb photons in the "sea," so metals are opaque-looking. Electrons on the surface can bounce back light at the same frequency that the light hits the surface, therefore the metal appears to be shiny.

However, these observations are only qualitative, and not quantitative, so they cannot be tested. The "Sea of Electrons" theory stands today only as an oversimplified model of how metallic bonding works.

In a molten metal, the metallic bond is still present, although the ordered structure has been broken down. The metallic bond is not fully broken until the metal boils. That means that boiling point is actually a better guide to the strength of the metallic bond than melting point is. On melting, the bond is loosened, not broken. The strength of a metallic bond depends on three things:

1. The number of electrons that become delocalized from the metal
2. The charge of the cation (metal).
3. The size of the cation.

A **strong** metallic bond will be the result of more delocalized electrons, which causes the effective nuclear charge on electrons on the cation to increase, in effect making the size of the cation smaller. Metallic bonds are strong and require a great deal of energy to break, and therefore **metals have high melting and boiling points.** A metallic bonding theory must explain how so much bonding can occur with such few electrons (since metals are located on the left side of the periodic table and do not have many electrons in their valence shells). The theory must also account for all of a metal's unique chemical and physical properties.

Expanding the Range of Bonding Possible

Previously, we argued that bonding between atoms can classified as range of possible bonding between **ionic bonds** (fully charge transfer) and **covalent bonds** (fully shared electrons). When two atoms of slightly differing electronegativities come together to form a covalent bond, one atom attracts the electrons more than the other; this is called a polar covalent bond. However, simple “ionic” and “covalent” bonding are idealized concepts and most bonds exist on a two-dimensional continuum described by the van Arkel-Ketelaar Triangle (Figure 13.1.4).

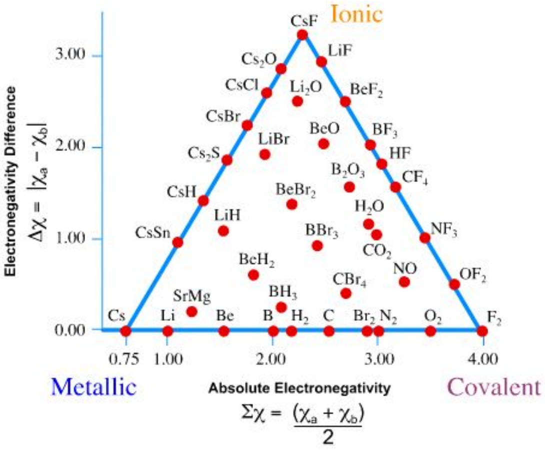

Figure 13.1.4: van Arkel-Ketelaar Triangle plots the difference in electronegativity ($\Delta\chi$) and the average electronegativity in a bond ($\sum \chi$). the top region is where bonds are mostly ionic, the lower left region is where bonding is metallic, and the lower right region is where the bonding is covalent.

Bond triangles or **van Arkel–Ketelaar** triangles (named after Anton Eduard van Arkel and J. A. A. Ketelaar) are triangles used for showing different compounds in varying degrees of ionic, metallic and covalent bonding. In 1941 van Arkel recognized three extreme materials and associated bonding types. Using 36 main group elements, such as metals, metalloids and non-metals, he placed ionic, metallic and covalent bonds on the corners of an equilateral triangle, as well as suggested intermediate species. The bond triangle shows that chemical bonds are not just particular bonds of a specific type. Rather, bond types are interconnected and different compounds have varying degrees of different bonding character (for example, polar covalent bonds).

Video 13.1.1: What is the van Arkel-Ketelaar Triangle of Bonding?

Using electronegativity - two compound average electronegativity on x-axis of Figure 13.1.4

$$\sum \chi = \frac{\chi_A + \chi_B}{2} \tag{13.1.1}$$

and electronegativity difference on y-axis,

$$\Delta \chi = |\chi_A - \chi_B| \tag{13.1.2}$$

we can rate the dominant bond between the compounds. On the right side of Figure 13.1.4 (from ionic to covalent) should be compounds with varying difference in electronegativity. The compounds with equal electronegativity, such as Cl_2 (chlorine) are placed in the covalent corner, while the ionic corner has compounds with large electronegativity difference, such as $NaCl$ (table salt). The bottom side (from metallic to covalent) contains compounds with varying degree of directionality in the bond. At one extreme is metallic bonds with delocalized bonding and at the other are covalent bonds in which the orbitals overlap in a particular direction. The left side (from ionic to metallic) is meant for delocalized bonds with varying electronegativity difference.

The Three Extremes in bonding

In general:

- Metallic bonds have low $\Delta \chi$ **and** low average $\sum \chi$.
- Ionic bonds have moderate-to-high $\Delta \chi$ and moderate values of average $\sum \chi$.
- Covalent bonds have moderate to high average $\sum \chi$ and can exist with moderately low $\Delta \chi$.

Example 13.1.2

Use the tables of electronegativities (Table A2) and Figure 13.1.4 to estimate the following values

- difference in electronegativity ($\Delta \chi$)
- average electronegativity in a bond ($\sum \chi$)
- percent ionic character
- likely bond type

for the selected compounds:

a. AsH (e.g., in arsine AsH)
b. SrLi
c. KF.

Solution

a: AsH

- The electronegativity of As is 2.18
- The electronegativity of H is 2.22

Using Equations 13.1.1 and 13.1.2:

$$\begin{aligned}\sum \chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{2.18 + 2.22}{2} \\ &= 2.2\end{aligned}$$

$$\begin{aligned}\Delta \chi &= \chi_A - \chi_B \\ &= 2.18 - 2.22 \\ &= 0.04\end{aligned}$$

- From Figure 13.1.4, the bond is fairly nonpolar and has a low ionic character (10% or less)
- The bonding is in the middle of a covalent bond and a metallic bond

b: SrLi

- The electronegativity of Sr is 0.95
- The electronegativity of Li is 0.98

Using Equations 13.1.1 and 13.1.2:

$$\begin{aligned}\sum \chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{0.95 + 0.98}{2} \\ &= 0.965\end{aligned}$$

$$\begin{aligned}\Delta \chi &= \chi_A - \chi_B \\ &= 0.98 - 0.95 \\ &= 0.025\end{aligned}$$

- From Figure 13.1.4, the bond is fairly nonpolar and has a low ionic character (~3% or less)
- The bonding is likely metallic.

c: KF

- The electronegativity of K is 0.82
- The electronegativity of F is 3.98

Using Equations 13.1.1 and 13.1.2:

$$\begin{aligned}\sum \chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{0.82 + 3.98}{2} \\ &= 2.4\end{aligned}$$

$$\begin{aligned}\Delta \chi &= \chi_A - \chi_B \\ &= |0.82 - 3.98| \\ &= 3.16\end{aligned}$$

- From Figure 13.1.4, the bond is fairly polar and has a high ionic character (~75%)
- The bonding is likely ionic.

Exercise 13.1.2

Contrast the bonding of NaCl and silicon tetrafluoride.

Answer

NaCl is an ionic crystal structure, and an electrolyte when dissolved in water; $\Delta\chi = 1.58$, average $\sum\chi = 1.79$, while silicon tetrafluoride is covalent (molecular, non-polar gas; $\Delta\chi = 2.08$, average $\sum\chi = 2.94$.

Contributors and Attributions

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13.2: Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to cesium and francium which are the least electronegative at 0.7.

What if two atoms of equal electronegativity bond together?

Consider a bond between two atoms, A and B. If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found on average half way between the two atoms:

To get a bond like this, A and B would usually have to be the same atom. You will find this sort of bond in, for example, H_2 or Cl_2 molecules. **Note:** It's important to realize that this is an average picture. The electrons are actually in a molecular orbital, and are moving around all the time within that orbital. This sort of bond could be thought of as being a "pure" covalent bond - where the electrons are shared evenly between the two atoms.

What if B is slightly more electronegative than A?

B will attract the electron pair rather more than A does.

That means that the B end of the bond has more than its fair share of electron density and so becomes slightly negative. At the same time, the A end (rather short of electrons) becomes slightly positive. In the diagram, "δ" (read as "delta") means "slightly" - so $\delta+$ means "slightly positive".

A polar bond is a covalent bond in which there is a separation of charge between one end and the other - in other words in which one end is slightly positive and the other slightly negative. Examples include most covalent bonds. The hydrogen-chlorine bond in HCl or the hydrogen-oxygen bonds in water are typical.

If B is a lot more electronegative than A, then the electron pair is dragged right over to B's end of the bond. To all intents and purposes, A has lost control of its electron, and B has complete control over both electrons. Ions have been formed. The bond is then an ionic bond rather than a covalent bond.

A "spectrum" of bonds

The implication of all this is that there is no clear-cut division between covalent and ionic bonds. In a pure covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end. How far does this dragging have to go before the bond counts as ionic? There is no real answer to that. Sodium chloride is typically considered an ionic solid, but even here the sodium has not completely lost control of its electron. Because of the properties of sodium chloride, however, we tend to count it as if it were purely ionic. Lithium iodide, on the other hand, would be described as being "ionic with some covalent character". In this case, the pair of electrons has not moved entirely over to the iodine end of the bond. Lithium iodide, for example, dissolves in organic solvents like ethanol - not something which ionic substances normally do.

Summary

- No electronegativity difference between two atoms leads to a pure non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond.
- A large electronegativity difference leads to an ionic bond.

Example 1: Polar Bonds vs. Polar Molecules

In a simple diatomic molecule like HCl, if the bond is polar, then the whole molecule is polar. What about more complicated molecules?

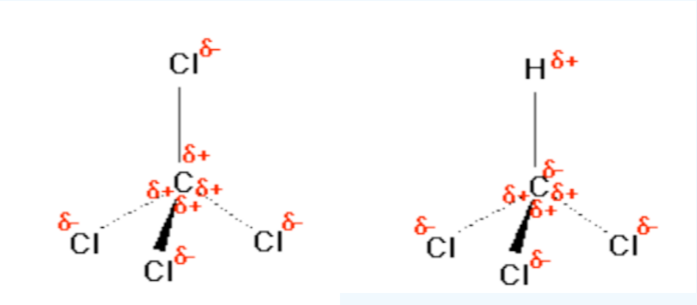


Figure 13.2.1: (left) CCl_4 (right) $CHCl_3$

Consider CCl_4, (left panel in figure above), which as a molecule is not polar - in the sense that it doesn't have an end (or a side) which is slightly negative and one which is slightly positive. The whole of the outside of the molecule is somewhat negative, but there is no overall separation of charge from top to bottom, or from left to right.

In contrast, $CHCl_3$ is a polar molecule (right panel in figure above). The hydrogen at the top of the molecule is less electronegative than carbon and so is slightly positive. This means that the molecule now has a slightly positive "top" and a slightly negative "bottom", and so is overall a polar molecule.

A polar molecule will need to be "lop-sided" in some way.

Patterns of electronegativity in the Periodic Table

The distance of the electrons from the nucleus remains relatively constant in a periodic table row, but not in a periodic table column. The force between two charges is given by Coulomb's law.

$$F = k\frac{Q_1Q_2}{r^2} \tag{13.2.1}$$

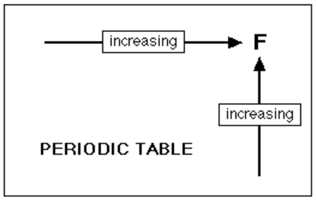
In this expression, Q represents a charge, k represents a constant and r is the distance between the charges. When r = 2, then $r^2 = 4$. When r = 3, then $r^2 = 9$. When r = 4, then $r^2 = 16$. It is readily seen from these numbers that, as the distance between the charges increases, the force decreases very rapidly. This is called a quadratic change.

The result of this change is that electronegativity increases from bottom to top in a column in the periodic table even though there are more protons in the elements at the bottom of the column. Elements at the top of a column have greater electronegativities than elements at the bottom of a given column.

The overall trend for electronegativity in the periodic table is diagonal from the lower left corner to the upper right corner. Since the electronegativity of some of the important elements cannot be determined by these trends (they lie in the wrong diagonal), we have to memorize the following order of electronegativity for some of these common elements.

F > O > Cl > N > Br > I > S > C > H > metals

The most electronegative element is fluorine. If you remember that fact, everything becomes easy, because electronegativity must always increase towards fluorine in the Periodic Table.

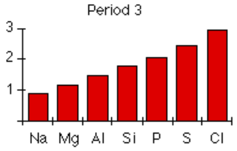


Note

This simplification ignores the noble gases. Historically this is because they were believed not to form bonds - and if they do not form bonds, they cannot have an electronegativity value. Even now that we know that some of them do form bonds, data sources still do not quote electronegativity values for them.

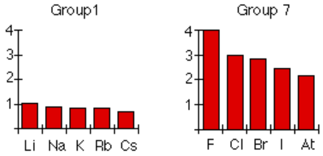
Trends in electronegativity across a period

The positively charged protons in the nucleus attract the negatively charged electrons. As the number of protons in the nucleus increases, the electronegativity or attraction will increase. Therefore electronegativity **increases** from **left to right** in a row in the periodic table. This effect only holds true for a row in the periodic table because the attraction between charges falls off rapidly with distance. The chart shows electronegativities from sodium to chlorine (ignoring argon since it does not does not form bonds).



Trends in electronegativity down a group

As you go down a group, electronegativity decreases. (If it increases up to fluorine, it must decrease as you go down.) The chart shows the patterns of electronegativity in Groups 1 and 7.



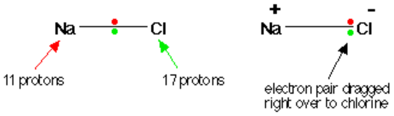
Explaining the patterns in electronegativity

The attraction that a bonding pair of electrons feels for a particular nucleus depends on:

- the number of protons in the nucleus;
- the distance from the nucleus;
- the amount of screening by inner electrons.

Why does electronegativity increase across a period?

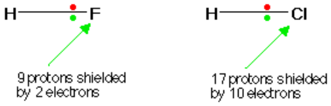
Consider sodium at the beginning of period 3 and chlorine at the end (ignoring the noble gas, argon). Think of sodium chloride as if it were covalently bonded.



Both sodium and chlorine have their bonding electrons in the 3-level. The electron pair is screened from both nuclei by the 1s, 2s and 2p electrons, but the chlorine nucleus has 6 more protons in it. It is no wonder the electron pair gets dragged so far towards the chlorine that ions are formed. Electronegativity increases across a period because the number of charges on the nucleus increases. That attracts the bonding pair of electrons more strongly.

Why does electronegativity fall as you go down a group?

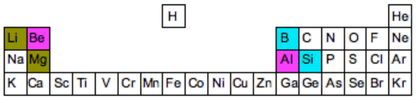
As you go **down** a group, electronegativity **decreases** because the bonding pair of electrons is increasingly distant from the attraction of the nucleus. Consider the hydrogen fluoride and hydrogen chloride molecules:



The bonding pair is shielded from the fluorine's nucleus only by the $1s^2$ electrons. In the chlorine case it is shielded by all the $1s^2 2s^2 2p^6$ electrons. In each case there is a net pull from the center of the fluorine or chlorine of +7. But fluorine has the bonding pair in the 2-level rather than the 3-level as it is in chlorine. If it is closer to the nucleus, the attraction is greater.

Diagonal relationships in the Periodic Table

At the beginning of periods 2 and 3 of the Periodic Table, there are several cases where an element at the top of one group has some similarities with an element in the next group. Three examples are shown in the diagram below. Notice that the similarities occur in elements which are diagonal to each other - not side-by-side.



For example, boron is a non-metal with some properties rather like silicon. Unlike the rest of Group 2, beryllium has some properties resembling aluminum. And lithium has some properties which differ from the other elements in Group 1, and in some ways resembles magnesium. There is said to be a diagonal relationship between these elements. There are several reasons for this, but each depends on the way atomic properties like electronegativity vary around the Periodic Table. So we will have a quick look at this with regard to electronegativity - which is probably the simplest to explain.

Explaining the diagonal relationship with regard to electronegativity

Electronegativity increases across the Periodic Table. So, for example, the electronegativities of beryllium and boron are:

Be	1.5
B	2.0

Electronegativity falls as you go down the Periodic Table. So, for example, the electronegativities of boron and aluminum are:

B	2.0
Al	1.5

So, comparing Be and Al, you find the values are (by chance) exactly the same. The increase from Group 2 to Group 3 is offset by the fall as you go down Group 3 from boron to aluminum. Something similar happens from lithium (1.0) to magnesium (1.2), and from boron (2.0) to silicon (1.8). In these cases, the electronegativities are not exactly the same, but are very close.

Similar electronegativities between the members of these diagonal pairs means that they are likely to form similar types of bonds, and that will affect their chemistry. You may well come across examples of this later on in your course.

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13.3: Bond Polarity and Dipole Moments

Dipole moments occur when there is a separation of charge. They can occur between two ions in an ionic bond or between atoms in a covalent bond; dipole moments arise from differences in electronegativity. The larger the difference in electronegativity, the larger the dipole moment. The distance between the charge separation is also a deciding factor in the size of the dipole moment. The dipole moment is a measure of the polarity of the molecule.

Introduction

When atoms in a molecule share electrons unequally, they create what is called a dipole moment. This occurs when one atom is more electronegative than another, resulting in that atom pulling more tightly on the shared pair of electrons, or when one atom has a lone pair of electrons and the difference of electronegativity vector points in the same way. One of the most common examples is the water molecule, made up of one oxygen atom and two hydrogen atoms. The differences in electronegativity and lone electrons give oxygen a partial negative charge and each hydrogen a partial positive charge.

Dipole Moment

When two electrical charges, of opposite sign and equal magnitude, are separated by a distance, an electric dipole is established. The size of a dipole is measured by its dipole moment (μ). Dipole moment is measured in Debye units, which is equal to the distance between the charges multiplied by the charge (1 Debye equals $3.34 \times 10^{-30}\ C\,m$). The dipole moment of a molecule can be calculated by Equation 13.3.1:

$$\vec{\mu} = \sum_i q_i\,\vec{r}_i \tag{13.3.1}$$

where

- $\vec{\mu}$ is the dipole moment vector
- q_i is the magnitude of the i^{th} charge, and
- $\vec{r}_i$ is the vector representing the position of i^{th} charge.

The dipole moment acts in the direction of the vector quantity. An example of a polar molecule is H_2O. Because of the lone pair on oxygen, the structure of H_2O is bent (via VSEPR theory), which means that the vectors representing the dipole moment of each bond do not cancel each other out. Hence, water is polar.

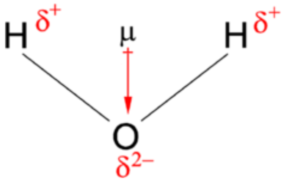

Figure 13.3.1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

The vector points from positive to negative, on both the molecular (net) dipole moment and the individual bond dipoles. Table A2 shows the electronegativity of some of the common elements. The larger the difference in electronegativity between the two atoms, the more electronegative that bond is. To be considered a polar bond, the difference in electronegativity must be large. The dipole moment points in the direction of the vector quantity of each of the bond electronegativities added together.

It is relatively easy to measure dipole moments: just place a substance between charged plates (Figure 13.3.2); polar molecules increase the charge stored on the plates, and the dipole moment can be obtained (i.e., via the capacitance of the system). Nonpolar CCl_4 is not deflected; moderately polar acetone deflects slightly; highly polar water deflects strongly. In general, polar molecules will align themselves: (1) in an electric field, (2) with respect to one another, or (3) with respect to ions (Figure 13.3.2).

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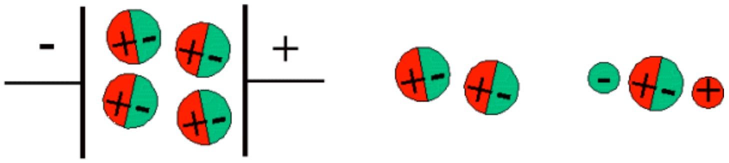


Figure 13.3.2: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

Equation 13.3.1 can be simplified for a simple separated two-charge system like diatomic molecules or when considering a bond dipole within a molecule

$$\mu_{diatomic} = Q \times r \tag{13.3.2}$$

This bond dipole is interpreted as the dipole from a charge separation over a distance r between the partial charges Q^+ and Q^- (or the more commonly used terms δ^+ - δ^-); the orientation of the dipole is along the axis of the bond. Consider a simple system of a single electron and proton separated by a fixed distance. When the proton and electron are close together, the dipole moment (degree of polarity) decreases. However, as the proton and electron get farther apart, the dipole moment increases. In this case, the dipole moment is calculated as (via Equation 13.3.2):

$$\begin{aligned} \mu &= Qr \\ &= (1.60 \times 10^{-19}\, C)(1.00 \times 10^{-10}\, m) \\ &= 1.60 \times 10^{-29}\, C \cdot m \end{aligned}$$

The Debye characterizes the size of the dipole moment. When a proton and electron are 100 pm apart, the dipole moment is $4.80\ D$:

$$\begin{aligned} \mu &= (1.60 \times 10^{-29}\, C \cdot m) \left(\frac{1\ D}{3.336 \times 10^{-30}\, C \cdot m} \right) \\ &= 4.80\ D \end{aligned}$$

$4.80\ D$ is a key reference value and represents a pure charge of +1 and -1 separated by 100 pm. If the charge separation is increased then the dipole moment increases (linearly):

- If the proton and electron are separated by 120 pm:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\, D \tag{13.3.3}$$

- If the proton and electron are separated by 150 pm:

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\, D \tag{13.3.4}$$

- If the proton and electron are separated by 200 pm:

$$\mu = \frac{200}{100}(4.80\ D) = 9.60\, D \tag{13.3.5}$$

Example 13.3.1: Water

The water molecule in Figure 13.3.1 can be used to determine the direction and magnitude of the dipole moment. From the electronegativities of oxygen and hydrogen, the difference in electronegativity is 1.2e for each of the hydrogen-oxygen bonds. Next, because the oxygen is the more electronegative atom, it exerts a greater pull on the shared electrons; it also has two lone pairs of electrons. From this, it can be concluded that the dipole moment points from between the two hydrogen atoms toward the oxygen atom. Using the equation above, the dipole moment is calculated to be 1.85 D by multiplying the distance between the oxygen and hydrogen atoms by the charge difference between them and then finding the components of each that point in the direction of the net dipole moment (the angle of the molecule is 104.5˚).

The bond moment of the O-H bond =1.5 D, so the net dipole moment is

$$\mu = 2(1.5)\cos\left(\frac{104.5^\circ}{2}\right) = 1.84\ D$$

Polarity and Structure of Molecules

The shape of a molecule and the polarity of its bonds determine the OVERALL POLARITY of that molecule. A molecule that contains polar bonds might not have any overall polarity, depending upon its shape. The simple definition of whether a complex molecule is polar or not depends upon whether its overall centers of positive and negative charges overlap. If these centers lie at the same point in space, then the molecule has no overall polarity (and is non polar). If a molecule is completely symmetric, then the dipole moment vectors on each molecule will cancel each other out, making the molecule nonpolar. A molecule can only be polar if the structure of that molecule is not symmetric.

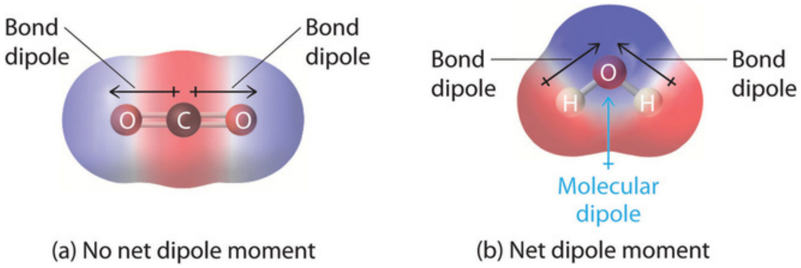


Figure 13.3.3: Charge distributions of CO_2 and H_2O\). Blue and red colored regions are negatively and positively signed regions, respectively. (CC BY-SA-NC 3.0; anonymous)

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure $13.3.3a$). This is a linear molecule and each C=O bond is, in fact, polar. The central carbon will have a net positive charge, and the two outer oxygen atoms a net negative charge. However, since the molecule is linear, these two bond dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu = 0$).

> *Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles*

For AB_n molecules, where A is the central atom and B are all the same types of atoms, there are certain molecular geometries which are symmetric. Therefore, they will have no dipole even if the bonds are polar. These geometries include linear, trigonal planar, tetrahedral, octahedral and trigonal bipyramid.

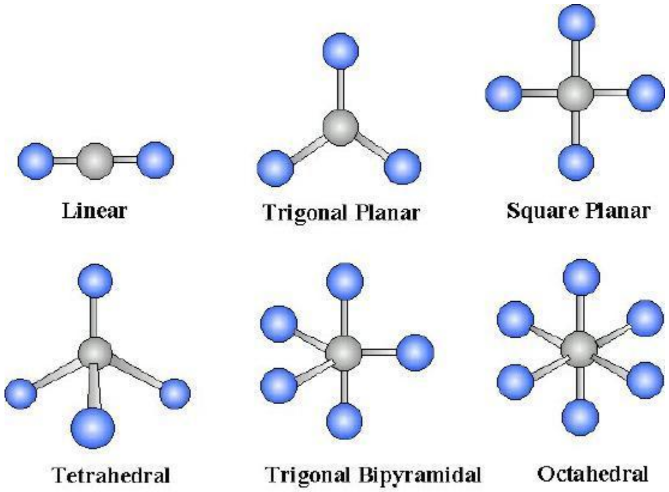
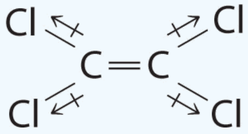


Figure 13.3.4: Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule ($\mu = 0$)

✓ Example 13.3.3: C_2Cl_4

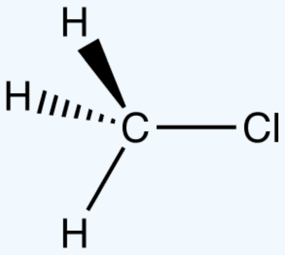
Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.



Example 13.3.3: CH_3Cl

C-Cl, the key polar bond, is 178 pm. Measurement reveals 1.87 D. From this data, % ionic character can be computed. If this bond were 100% ionic (based on proton & electron),

$$\begin{aligned}\mu &= \frac{178}{100}(4.80\ D)\\ &= 8.54\ D\end{aligned}$$



Although the bond length is ***increasing***, the dipole is ***decreasing*** as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the ***charge*** at the ends of the dipole).

Table 13.3.1: Relationship between Bond length, Electronegativity and Dipole moments in simple Diatomics

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

References

1. *Housecroft, Catherine E. and Alan G. Sharpe. Inorganic Chemistry. 3rd ed. Harlow: Pearson Education, 2008. Print. (Pages 44-46)*
2. *Tro, Nivaldo J. Chemistry: A Molecular Approach. Upper Saddle River: Pearson Education, 2008. Print. (Pages 379-386)*

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13.4: Ions: Electron Configurations and Sizes

The **electron configuration** of an atomic species (neutral or ionic) allows us to understand the shape and energy of its electrons. Many general rules are taken into consideration when assigning the "location" of the electron to its prospective energy state, however these assignments are arbitrary and it is always uncertain as to which electron is being described. Knowing the electron configuration of a species gives us a better understanding of its bonding ability, magnetism and other chemical properties.

Introduction

The **electron configuration** is the standard notation used to describe the electronic structure of an atom. Under the orbital approximation, we let each electron occupy an orbital, which can be solved by a single wavefunction. In doing so, we obtain three quantum numbers (n, l, m_l), which are the same as the ones obtained from solving the Schrödinger's equation for Bohr's hydrogen atom. Hence, many of the rules that we use to describe the electron's address in the hydrogen atom can also be used in systems involving multiple electrons. When assigning electrons to orbitals, we must follow a set of three rules: the Aufbau Principle, the Pauli-Exclusion Principle, and Hund's Rule.

The wavefunction is the solution to the Schrödinger equation. By solving the Schrödinger equation for the hydrogen atom, we obtain three quantum numbers, namely the principal quantum number (n), the orbital angular momentum quantum number (l), and the magnetic quantum number (m_l). There is a fourth quantum number, called the spin magnetic quantum number (m_s), which is not obtained from solving the Schrödinger equation. Together, these four quantum numbers can be used to describe the location of an electron in Bohr's hydrogen atom. These numbers can be thought of as an electron's "address" in the atom.

Notation

To help describe the appropriate notation for electron configuration, it is best to do so through example. For this example, we will use the iodine atom. There are two ways in which electron configuration can be written:

$$\text{I: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$$

or

$$\text{I: } [Kr] 5s^2 4d^{10} 5p^5$$

In both of these types of notations, the order of the energy levels must be written by increased energy, showing the number of electrons in each subshell as an exponent. In the short notation, you place brackets around the *preceding* noble gas element followed by the valence shell electron configuration. The periodic table shows that kyrpton (Kr) is the previous noble gas listed before iodine. The noble gas configuration encompases the energy states lower than the valence shell electrons. Therefore, in this case $[Kr]=1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$.

Quantum Numbers

Principal Quantum Number (n)

The principal quantum number n indicates the shell or energy level in which the electron is found. The value of n can be set between 1 to n, where n is the value of the outermost shell containing an electron. This quantum number can only be positive, non-zero, and integer values. That is, n=1,2,3,4,..

For example, an Iodine atom has its outmost electrons in the 5p orbital. Therefore, the principle quantum number for Iodine is 5.

Orbital Angular Momentum Quantum Number (l)

The orbital angular momentum quantum number, l, indicates the subshell of the electron. You can also tell the shape of the atomic orbital with this quantum number. An *s* subshell corresponds to l=0, a *p* subshell = 1, a *d* subshell = 2, a *f* subshell = 3, and so forth. This quantum number can only be positive and integer values, although it can take on a zero value. In general, for every value of n, there are n values of l. Furthermore, the value of l ranges from 0 to n-1. For example, if n=3, l=0,1,2.

So in regards to the example used above, the l values of Iodine for n = 5 are l = 0, 1, 2, 3, 4.

Magnetic Quantum Number (m_l)

The magnetic quantum number, m_l, represents the orbitals of a given subshell. For a given l, m_l can range from -l to +l. A p subshell (l=1), for instance, can have three orbitals corresponding to m_l = -1, 0, +1. In other words, it defines the p_x, p_y and

$p_z$orbitals of the p subshell. (However, the m_l numbers don't necessarily correspond to a given orbital. The fact that there are three orbitals simply is indicative of the three orbitals of a p subshell.) In general, for a given l, there are $2l+1$ possible values for m_l; and in a n principal shell, there are n^2 orbitals found in that energy level.

Continuing on from out example from above, the m_l values of Iodine are m_l = -4, -3, -2, -1, 0 1, 2, 3, 4. These arbitrarily correspond to the 5s, $5p_x$, $5p_y$, $5p_{z,}$ $4d_{x^2-y^2}$, $4d_{z^2}$, $4d_{xy}$, $4d_{xz}$, and $4d_{yz}$ orbitals.

Spin Magnetic Quantum Number (m_s)

The spin magnetic quantum number can only have a value of either +1/2 or -1/2. The value of 1/2 is the spin quantum number, s, which describes the electron's spin. Due to the spinning of the electron, it generates a magnetic field. In general, an electron with a m_s=+1/2 is called an alpha electron, and one with a m_s=-1/2 is called a beta electron. No two paired electrons can have the same spin value.

Out of these four quantum numbers, however, Bohr postulated that only the principal quantum number, n, determines the energy of the electron. Therefore, the 3s orbital (l=0) has the same energy as the 3p (l=1) and 3d (l=2) orbitals, regardless of a difference in l values. This postulate, however, holds true only for Bohr's hydrogen atom or other hydrogen-like atoms.

When dealing with multi-electron systems, we must consider the electron-electron interactions. Hence, the previously described postulate breaks down in that the energy of the electron is now determined by both the principal quantum number, n, and the orbital angular momentum quantum number, l. Although the Schrödinger equation for many-electron atoms is extremely difficult to solve mathematically, we can still describe their electronic structures via electron configurations.

General Rules of Electron Configuration

There are a set of general rules that are used to figure out the electron configuration of an atomic species: Aufbau Principle, Hund's Rule and the Pauli-Exclusion Principle. Before continuing, it's important to understand that each orbital can be occupied by *two* electrons of opposite spin (which will be further discussed later). The following table shows the *possible* number of electrons that can occupy each orbital in a given subshell.

subshell	number of orbitals	total number of possible electrons in each orbital
s	1	2
p	3 (p_x, p_y, p_z)	6
d	5 ($d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{xz}, d_{yz})	10
f	7 (f_{z^3}, f_{xz^2}, f_{xyz}, $f_{x(x^2-3y^2)}$, f_{yz^2}, $f_{z(x^2-y^2)}$, $f_{y(3x^2-y^2)}$)	14

Using our example, iodine, again, we see on the periodic table that its atomic number is 53 (meaning it contains 53 electrons in its neutral state). Its complete electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$. If you count up all of these electrons, you will see that it adds up to 53 electrons. Notice that each subshell can only contain the max amount of electrons as indicated in the table above.

Aufbau Principle

The word 'Aufbau' is German for 'building up'. The Aufbau Principle, also called the building-up principle, states that electron's occupy orbitals in order of increasing energy. The order of occupation is as follows:

1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f<6d<7p

Another way to view this order of increasing energy is by using **Madelung's Rule**:

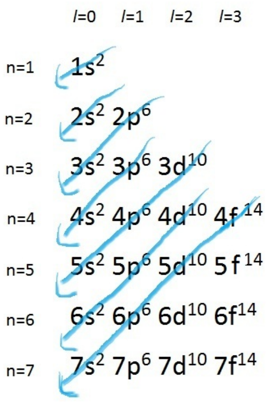

Figure 1. Madelung's Rule is a simple generalization which dictates in what order electrons should be filled in the orbitals, however there are exceptions such as copper and chromium.

This order of occupation roughly represents the increasing energy level of the orbitals. Hence, electrons occupy the orbitals in such a way that the energy is kept at a minimum. That is, the 7s, 5f, 6d, 7p subshells will not be filled with electrons unless the lower energy orbitals, 1s to 6p, are already fully occupied. Also, it is important to note that although the energy of the 3d orbital has been mathematically shown to be lower than that of the 4s orbital, electrons occupy the 4s orbital first before the 3d orbital. This observation can be ascribed to the fact that 3d electrons are more likely to be found closer to the nucleus; hence, they repel each other more strongly. Nonetheless, remembering the order of orbital energies, and hence assigning electrons to orbitals, can become rather easy when related to the periodic table.

To understand this principle, let's consider the bromine atom. Bromine (Z=35), which has 35 electrons, can be found in Period 4, Group VII of the periodic table. Since bromine has 7 valence electrons, the 4s orbital will be completely filled with 2 electrons, and the remaining five electrons will occupy the 4p orbital. Hence the full or expanded electronic configuration for bromine in accord with the Aufbau Principle is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$. If we add the exponents, we get a total of 35 electrons, confirming that our notation is correct.

Hund's Rule

Hund's Rule states that when electrons occupy degenerate orbitals (i.e. same n and *l* quantum numbers), they must first occupy the empty orbitals before double occupying them. Furthermore, the most stable configuration results when the spins are parallel (i.e. all alpha electrons or all beta electrons). Nitrogen, for example, has 3 electrons occupying the 2p orbital. According to Hund's Rule, they must first occupy each of the three degenerate p orbitals, namely the $2p_x$ orbital, $2p_y$ orbital, and the $2p_z$ orbital, and with parallel spins (Figure 2). The configuration below is incorrect because the third electron occupies does not occupy the empty $2p_z$ orbital. Instead, it occupies the half-filled $2p_x$ orbital. This, therefore, is a violation of Hund's Rule (Figure 2).

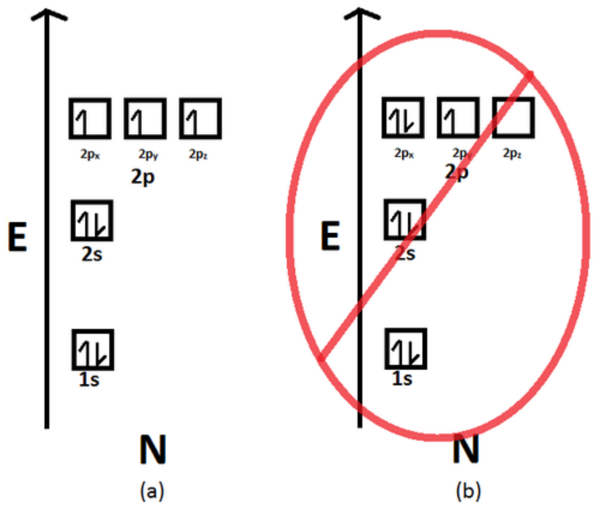

Figure 2. A visual representation of the Aufbau Principle and Hund's Rule. Note that the filling of electrons in each orbital (p_x, p_y and p_z) is arbitrary as long as the electrons are singly filled before having two electrons occupy the same orbital. (a)This diagram represents the *correct* filling of electrons for the nitrogen atom. (b) This diagramrepresents the *incorrect* filling of the electrons for the nitrogen atom.

Pauli-Exclusion Principle

Wolfgang Pauli postulated that each electron can be described with a unique set of four quantum numbers. Therefore, if two electrons occupy the same orbital, such as the 3s orbital, their spins must be paired. Although they have the same principal quantum number (n=3), the same orbital angular momentum quantum number (l=0), and the same magnetic quantum number (m_l=0), they have different spin magnetic quantum numbers (m_s=+1/2 and m_s=-1/2).

Electronic Configurations of Cations and Anions

The way we designate electronic configurations for cations and anions is essentially similar to that for neutral atoms in their ground state. That is, we follow the three important rules: Aufbau Principle, Pauli-exclusion Principle, and Hund's Rule. The electronic configuration of cations is assigned by removing electrons first in the outermost p orbital, followed by the s orbital and finally the d orbitals (if any more electrons need to be removed). For instance, the ground state electronic configuration of calcium (Z=20) is $1s^22s^22p^63s^23p^64s^2$. The calcium ion (Ca^{2+}), however, has two electrons less. Hence, the electron configuration for Ca^{2+} is $1s^22s^22p^63s^23p^6$. Since we need to take away two electrons, we first remove electrons from the outermost shell (n=4). In this case, all the 4p subshells are empty; hence, we start by removing from the s orbital, which is the 4s orbital. The electron configuration for Ca^{2+} is the same as that for Argon, which has 18 electrons. Hence, we can say that both are isoelectronic.

The electronic configuration of anions is assigned by adding electrons according to Aufbau Principle. We add electrons to fill the outermost orbital that is occupied, and then add more electrons to the next higher orbital. The neutral atom chlorine (Z=17), for instance has 17 electrons. Therefore, its ground state electronic configuration can be written as $1s^22s^22p^63s^23p^5$. The chloride ion (Cl^-), on the other hand, has an additional electron for a total of 18 electrons. Following Aufbau Principle, the electron occupies the partially filled 3p subshell first, making the 3p orbital completely filled. The electronic configuration for Cl^- can, therefore, be designated as $1s^22s^22p^63s^23p^6$. Again, the electron configuration for the chloride ion is the same as that for Ca^{2+} and Argon. Hence, they are all isoelectronic to each other.

Problems

1. Which of the princples explained above tells us that electrons that are paired cannot have the same spin value?

2. Find the values of n, *l*, m_l, and m_s for the following:

   a. Mg

   b. Ga

   c. Co

3. What is a possible combination for the quantum numbers of the 5d orbital? Give an example of an element which has the 5d orbital as it's most outer orbital.

4. Which of the following cannot exist (there may be more than one answer):

   a. $n = 4; l = 4; m_l = -2; m_s = +1/2$

   b. $n = 3; l = 2; m_l = 1; m_s = 1$

   c. $n = 4; l = 3; m_l = 0; m_s = +1/2$

   d. $n = 1; l = 0; m_l = 0; m_s = +1/2$

   e. $n = 0; l = 0; m_l = 0; m_s = +1/2$

5. Write electron configurations for the following:

   a. P

   b. S^{2-}

   c. Zn^{3+}

Answers

1. Pauli-exclusion Principle

2. a. $n = 3; l = 0, 1, 2; m_l = -2, -1, 0, 1, 2; m_s$ can be either +1/2 or -1/2

b. $n = 4; l = 0, 1, 2, 3; m_l = -3, -2, -1, 0, 1, 2, 3; m_s$ can be either +1/2 or -1/2

c. $n = 3; l = 0, 1, 2; m_l = -2, -1, 0, 1, 2, 3; m_s$ can be either +1/2 or -1/2

3. $n = 5; l = 3; m_l = 0; m_s = +1/2$. Osmium (Os) is an example.

4. a. The value of *l* cannot be 4, because *l* ranges from (0 - n-1)

b. m_s can only be +1/2 or -1/2

c. Okay

d. Okay

e. The value of n cannot be zero.

5. a. $1s^2 2s^2 2p^6 3s^2 3p^3$

b. $1s^2 2s^2 2p^6 3s^2 3p^6$

c. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$

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13.5: Formation of Binary Ionic Compounds

Ionic bonding is the complete transfer of valence electron(s) between atoms and is a type of chemical bond that generates two oppositely charged ions. It is observed because metals with few electrons in its outer-most orbital. By losing those electrons, these metals can achieve noble-gas configuration and satisfy the octet rule. Similarly, nonmetals that have close to 8 electrons in its valence shell tend to readily accept electrons to achieve its noble gas configuration.

Introduction

In ionic bonding, electrons are transferred from one atom to another resulting in the formation of positive and negative ions. The electrostatic attractions between the positive and negative ions hold the compound together. The predicted overall energy of the ionic bonding process, which includes the ionization energy of the metal and electron affinity of the nonmetal, is usually positive, indicating that the reaction is endothermic and unfavorable. However, this reaction is highly favorable because of their electrostatic attraction. At the most ideal inter-atomic distance, attraction between these particles releases enough energy to facilitate the reaction. Most ionic compounds tend to dissociate in polar solvents because they are often polar. This phenomenon is due to the opposite charges on each ions.

At a simple level, a lot of importance is attached to the electronic structures of noble gases like neon or argon which have eight electrons in their outer energy levels (or two in the case of helium). These noble gas structures are thought of as being in some way a "desirable" thing for an atom to have. One may well have been left with the strong impression that when other atoms react, they try to organize things such that their outer levels are either completely full or completely empty.

✓ Example: Bonding in NaCl

Sodium Chloride:

- Sodium (2,8,1) has 1 electron more than a stable noble gas structure (2,8). If it gave away that electron it would become more stable.
- Chlorine (2,8,7) has 1 electron short of a stable noble gas structure (2,8,8). If it could gain an electron from somewhere it too would become more stable.

The answer is obvious. If a sodium atom gives an electron to a chlorine atom, both become more stable.

The sodium has lost an electron, so it no longer has equal numbers of electrons and protons. Because it has one more proton than electron, it has a charge of 1+. If electrons are lost from an atom, positive ions are formed. Positive ions are sometimes called **cations**.

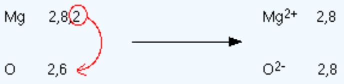
The chlorine has gained an electron, so it now has one more electron than proton. It therefore has a charge of 1-. If electrons are gained by an atom, negative ions are formed. A negative ion is sometimes called an **anion**.

The nature of the bond

The sodium ions and chloride ions are held together by the strong electrostatic attractions between the positive and negative charges. You need one sodium atom to provide the extra electron for one chlorine atom, so they combine together 1:1. The formula is therefore NaCl.

✓ Example 1: Bonding in MgO

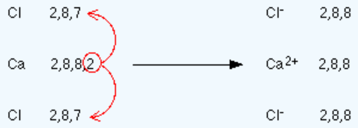
Magnesium Oxide:



Again, noble gas structures are formed, and the magnesium oxide is held together by very strong attractions between the ions. The ionic bonding is stronger than in sodium chloride because this time you have 2+ ions attracting 2- ions. The greater the charge, the greater the attraction. The formula of magnesium oxide is MgO.

✓ 2

Calcium Chloride:



This time you need two chlorines to use up the two outer electrons in the calcium. The formula of calcium chloride is therefore $CaCl_2$.

✓ O

Potassium Oxide:

Again, noble gas structures are formed. It takes two potassiums to supply the electrons the oxygen needs. The formula of potassium oxide is K_2O.

Some Stable Ions do not have Noble Gas Configurations

You may have come across some of the following ions, which are all perfectly stable, but not one of them has a noble gas structure.

Fe^{3+}		$[Ar]3d^5$
Cu^{2+}		$[Ar]3d^9$
Zn^{2+}		$[Ar]3d^{10}$
Ag^+		$[Kr]4d^{10}$
Pb^{2+}		$[Xe]4f^{14}5d^{10}6s^2$

What needs modifying is the view that there is something magic about noble gas structures. There are far more ions which do not have noble gas structures than there are which do.

- Noble gases (apart from helium) have an outer electronic structure ns^2np^6. Apart from some elements at the beginning of a transition series (scandium forming Sc^{3+} with an argon structure, for example), all transition metal elements and any metals following a transition series (like tin and lead in Group 4, for example) will have structures like those above.
- That means that the only elements to form positive ions with noble gas structures (apart from odd ones like scandium) are those in groups 1 and 2 of the Periodic Table and aluminum in group 3 (boron in group 3 does not form ions).
- Negative ions are tidier! Those elements in Groups 5, 6 and 7 which form simple negative ions all have noble gas structures.

If elements are not aiming for noble gas structures when they form ions, what decides how many electrons are transferred? The answer lies in the energetics of the process by which the compound is made.

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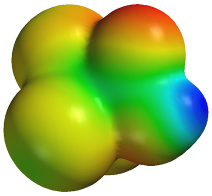
13.6: Partial Ionic Character of Covalent Bonds

Electrostatic potential maps, also known as electrostatic potential energy maps, or molecular electrical potential surfaces, illustrate the charge distributions of molecules three dimensionally. These maps allow us to visualize variably charged regions of a molecule. Knowledge of the charge distributions can be used to determine how molecules interact with one another.

Introduction

Electrostatic potential maps are very useful three dimensional diagrams of molecules. They enable us to visualize the charge distributions of molecules and charge related properties of molecules. They also allow us to visualize the size and shape of molecules. In organic chemistry, electrostatic potential maps are invaluable in predicting the behavior of complex molecules.



The first step involved in creating an electrostatic potential map is collecting a very specific type of data: electrostatic potential energy. An advanced computer program calculates the electrostatic potential energy at a set distance from the nuclei of the molecule. Electrostatic potential energy is fundamentally a measure of the strength of the nearby charges, nuclei and electrons, at a particular position.

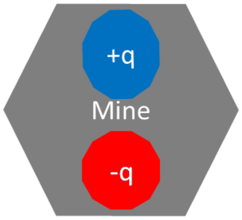
To accurately analyze the charge distribution of a molecule, a very large quantity of electrostatic potential energy values must be calculated. The best way to convey this data is to visually represent it, as in an electrostatic potential map. A computer program then imposes the calculated data onto an electron density model of the molecule derived from the Schrödinger equation. To make the electrostatic potential energy data easy to interpret, a color spectrum, with red as the lowest electrostatic potential energy value and blue as the highest, is employed to convey the varying intensities of the electrostatic potential energy values.

Analogous System

Electrostatic potential maps involve a number of basic concepts. The actual process of mapping the electrostatic potentials of a molecule, however, involves factors that complicate these fundamental concepts. An analogous system will be employed to introduce these basic concepts.

Imagine that there is a special type of mine. This mine is simply an explosive with some charged components on top of it. The circles with positive and negative charges in them are the charged components. If the electric field of the electric components are significantly disturbed, the mine triggers and explodes. The disarming device is positively charged. To disarm the mine, the disarming device must take the path of least electric resistance and touch the first charged mine component on this path. Deviating from this minimal energy path will cause a significant disturbance and the mine will explode. The specific charged components within the mine are known.

Q. How do you disarm the following mine?



The mine with positive charge and negative charge.

A. Touch the bottom most portion of negatively charged component, red, with the disarming device.

Introduction to Coulomb's Law and Electrostatic Energy

Coulomb's Law Formula

$$F = k\frac{q_a q_b}{r^2} \tag{13.6.1}$$

with

- Molecular electrostatic potential maps also illustrate information about the charge distribution of a molecule. Electrostatic potential maps convey information about the charge distribution of a molecule because of the properties of the nucleus and nature of electrostatic potential energy. For simplicity, consider moving a positively charged test charge along the spherical isosurface of an atom. The positively charged nucleus emits a radially constant electric field. A region of higher than average electrostatic potential energy indicates the presence of a stronger positive charge or a weaker negative charger. Given the consistency of the nucleuses positive charge, the higher potential energy value indicates the absence of negative charges, which would mean that there are fewer electrons in this region. The converse is also true. Thus a high electrostatic potential indicates the relative absence of electrons and a low electrostatic potential indicates an abundance of electrons. This property of electrostatic potentials can be extrapolated to molecules as well.

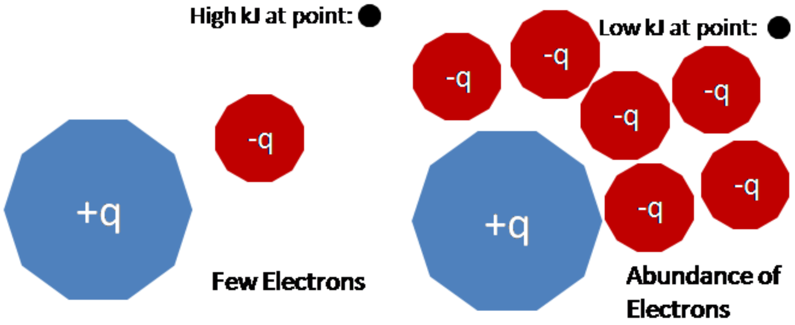
  Here is a simplified visual representation of the relationship between charge distribution and electrostatic potential. Keep in mind the equation used to find the electrostatic potential.

  \text{Total Electrostatic Potential Energy= \sum_i \text{Electrostatic Potential Energy}

  where

$$\text{Potential Energy} = K\frac{q_1 q_2}{r} \tag{13.6.2}$$

  and $K = \text{Coulomb's Constant}$.



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13.7: The Covalent Chemical Bond: A Model

Covalent bonding occurs when pairs of electrons are shared by atoms. Atoms will covalently bond with other atoms in order to gain more stability, which is gained by forming a full electron shell. By sharing their outer most (valence) electrons, atoms can fill up their outer electron shell and gain stability. Nonmetals will readily form covalent bonds with other nonmetals in order to obtain stability, and can form anywhere between one to three covalent bonds with other nonmetals depending on how many valence electrons they posses. Although it is said that atoms share electrons when they form covalent bonds, they do not usually share the electrons equally.

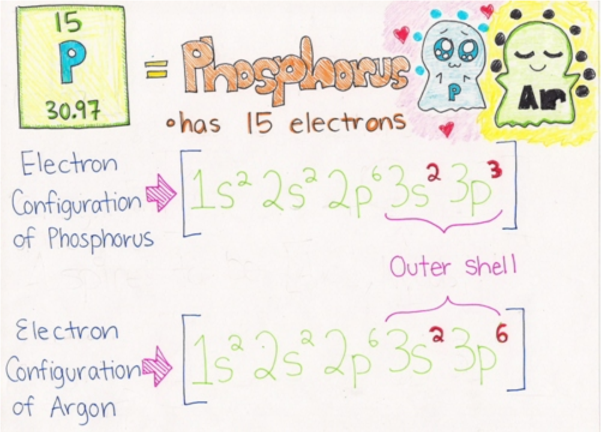
Introduction

Only when two atoms of the same element form a covalent bond are the shared electrons actually shared equally between the atoms. When atoms of different elements share electrons through covalent bonding, the electron will be drawn more toward the atom with the higher electronegativity resulting in a polar covalent bond. When compared to ionic compounds, covalent compounds usually have a lower melting and boiling point, and have less of a tendency to dissolve in water. Covalent compounds can be in a gas, liquid, or solid state and do not conduct electricity or heat well. The types of covalent bonds can be distinguished by looking at the Lewis dot structure of the molecule. For each molecule, there are different names for pairs of electrons, depending if it is shared or not. A pair of electrons that is shared between two atoms is called a **bond pair**. A pair of electrons that is *not* shared between two atoms is called a **lone pair**.

Octet Rule

The **Octet Rule** requires all atoms in a molecule to have 8 valence electrons--either by sharing, losing or gaining electrons--to become stable. For Covalent bonds, atoms tend to share their electrons with each other to satisfy the Octet Rule. It requires 8 electrons because that is the amount of electrons needed to fill a *s*- and *p*- orbital (electron configuration); also known as a noble gas configuration. Each atom wants to become as stable as the noble gases that have their outer valence shell filled because noble gases have a charge of 0. Although it is important to remember the "magic number", 8, note that there are many Octet rule exceptions.

Example: As you can see from the picture below, Phosphorus has only 5 electrons in its outer shell (bolded in red). Argon has a total of 8 electrons (bolded in red), which satisfies the Octet Rule. Phosphorus needs to gain 3 electrons to fulfill the Octet Rule. It wants to be like Argon who has a full outer valence shell.



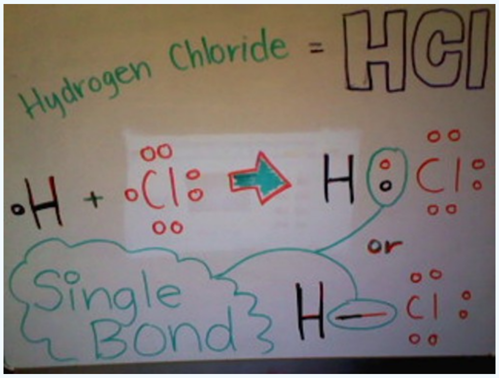
More examples can be found here.

Single Bonds

A **single bond** is when two electrons--one pair of electrons--are shared between two atoms. It is depicted by a single line between the two atoms. Although this form of bond is weaker and has a smaller density than a double bond and a triple bond, it is the most stable because it has a lower level of reactivity meaning less vulnerability in losing electrons to atoms that want to steal electrons.

✓ Example 1: HCl

Below is a Lewis dot structure of Hydrogen Chloride demonstrating a single bond. As we can see from the picture below, Hydrogen Chloride has 1 Hydrogen atom and 1 Chlorine atom. Hydrogen has only 1 valence electron whereas Chlorine has 7 valence electrons. To satisfy the Octet Rule, each atom gives out 1 electron to share with each other; thus making a single bond.

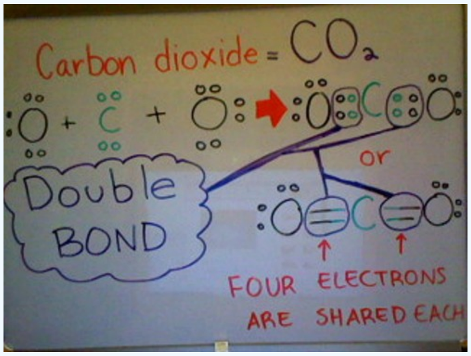


Double Bonds

A **Double bond** is when two atoms share two pairs of electrons with each other. It is depicted by two horizontal lines between two atoms in a molecule. This type of bond is much stronger than a single bond, but less stable; this is due to its greater amount of reactivity compared to a single bond.

✓ 2

Below is a Lewis dot structure of Carbon dioxide demonstrating a double bond. As you can see from the picture below, Carbon dioxide has a total of 1 Carbon atom and 2 Oxygen atoms. Each Oxygen atom has 6 valence electrons whereas the Carbon atom only has 4 valence electrons. To satisfy the Octet Rule, Carbon needs 4 more valence electrons. Since each Oxygen atom has 3 lone pairs of electrons, they can each share 1 pair of electrons with Carbon; as a result, filling Carbon's outer valence shell (Satisfying the Octet Rule).

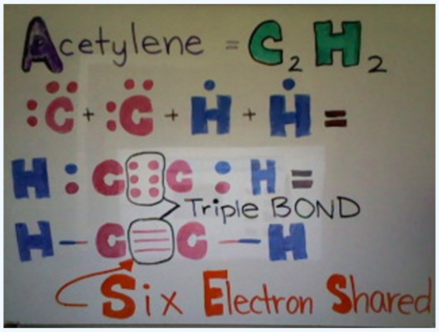


Triple Bond

A **Triple bond** is when three pairs of electrons are shared between two atoms in a molecule. It is the least stable out of the three general types of covalent bonds. It is very vulnerable to electron thieves!

✓ Example 3: Acetylene

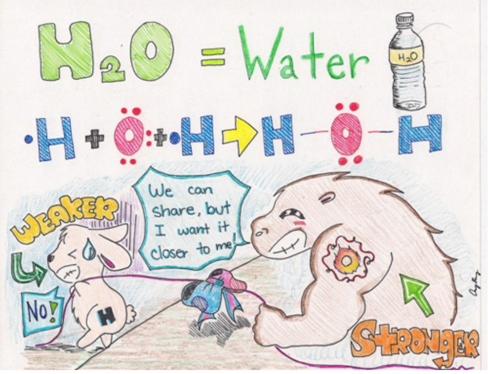
Below is a Lewis dot structure of Acetylene demonstrating a triple bond. As you can see from the picture below, Acetylene has a total of 2 Carbon atoms and 2 Hydrogen atoms. Each Hydrogen atom has 1 valence electron whereas each Carbon atom has 4 valence electrons. Each Carbon needs 4 more electrons and each Hydrogen needs 1 more electron. Hydrogen shares its only electron with Carbon to get a full valence shell. Now Carbon has 5 electrons. Because each Carbon atom has 5 electrons--1 single bond and 3 unpaired electrons--the two Carbons can share their unpaired electrons, forming a triple bond. Now all the atoms are happy with their full outer valence shell.



Polar Covalent Bond

A **Polar Covalent Bond** is created when the shared electrons between atoms are not equally shared. This occurs when one atom has a higher electronegativity than the atom it is sharing with. The atom with the higher electronegativity will have a stronger pull for electrons (Similiar to a Tug-O-War game, whoever is stronger usually wins). As a result, the shared electrons will be closer to the atom with the higher electronegativity, making it unequally shared. A polar covalent bond will result in the molecule having a slightly positive side (the side containing the atom with a lower electronegativity) and a slightly negative side (containing the atom with the higher electronegativity) because the shared electrons will be displaced toward the atom with the higher electronegativity. As a result of polar covalent bonds, the covalent compound that forms will have an electrostatic potential. This potential will make the resulting molecule slightly polar, allowing it to form weak bonds with other polar molecules. One example of molecules forming weak bonds with each other as a result of an unbalanced electrostatic potential is hydrogen bonding, where a hydrogen atom will interact with an electronegative hydrogen, fluorine, or oxygen atom from another molecule or chemical group.

Example: Water, Sulfide, Ozone, etc.

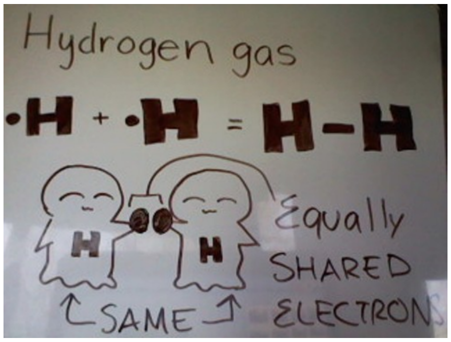


As you can see from the picture above, Oxygen is the big buff creature with the tattoo of "O" on its arm. The little bunny represents a Hydrogen atom. The blue and red bow tied in the middle of the rope, pulled by the two creatures represents--the shared pair of electrons--a single bond. Because the Hydrogen atom is weaker, the shared pair of electrons will be pulled closer to the Oxygen atom.

Nonpolar Covalent Bond

A **Nonpolar Covalent Bond** is created when atoms share their electrons equally. This usually occurs when two atoms have similar or the same electron affinity. The closer the values of their electron affinity, the stronger the attraction. This occurs in gas molecules; also known as diatomic elements. Nonpolar covalent bonds have a similar concept as polar covalent bonds; the atom with the higher electronegativity will draw away the electron from the weaker one. Since this statement is true--if we apply this to our diatomic molecules--all the atoms will have the same electronegativity since they are the same kind of element; thus, the electronegativities will cancel each other out and will have a charge of 0 (i.e., a nonpolar covalent bond).

Examples of gas molecules that have a nonpolar covalent bond: Hydrogen gas atom, Nitrogen gas atoms, etc.



As you can see from the picture above, Hydrogen gas has a total of 2 Hydrogen atoms. Each Hydrogen atom has 1 valence electron. Since Hydrogen can only fit a max of 2 valence electrons in its orbital, each Hydrogen atom only needs 1 electron. Each atom has 1 valence electron, so they can just share, giving each atom two electrons each.

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Outside Links

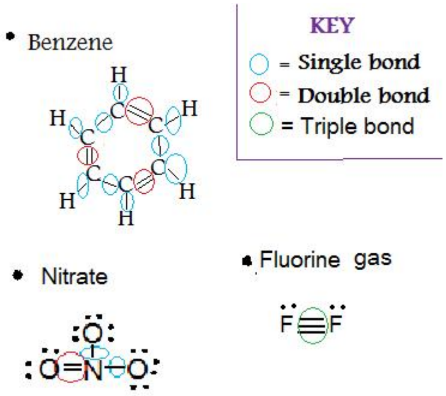
- Covalent Bond - Wikipedia: en.Wikipedia.org/wiki/Covalent_bond
- Electron Sharing and Covalent Bonds - http://www.chem.ox.ac.uk/vrchemistry...nds/intro1.htm
- Bond Stability - Newton BBS: www.newton.dep.anl.gov/askasc.../chem03155.htm
- Covalent Radii - Wikipedia: http://en.Wikipedia.org/wiki/Covalent_radius

Problems

1. Determine the type(s) of bond(s) in

- Benzene (C_6H_6)
- NO_3 (Nitrate)
- F_2(Fluorine gas)

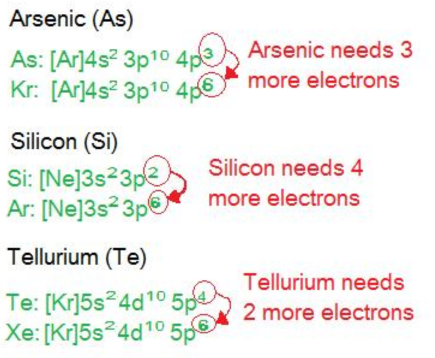
Solution:



2. Write the electron configuration and determine how many electrons are needed to achieve the nearest noble-gas configuration for the following:

- Arsenic (As)
- Silicon (Si)
- Tellurium (Te)

Solution:



Arsenic (As)

As: $[Ar]4s^2 3p^{10} 4p^3$

Kr: $[Ar]4s^2 3p^{10} 4p^6$

Arsenic needs 3 more electrons

Silicon (Si)

Si: $[Ne]3s^2 3p^2$

Ar: $[Ne]3s^2 3p^6$

Silicon needs 4 more electrons

Tellurium (Te)

Te: $[Kr]5s^2 4d^{10} 5p^4$

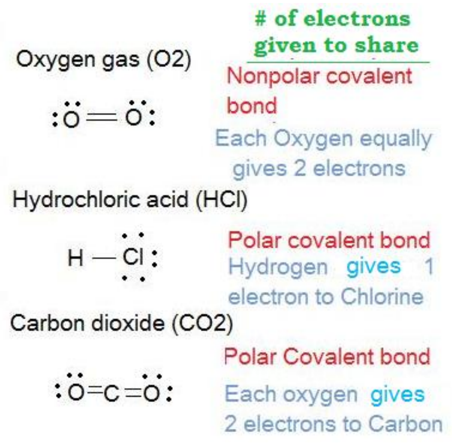
Xe: $[Kr]5s^2 4d^{10} 5p^6$

Tellurium needs 2 more electrons

3. Determine which molecules are polar and which molecules are nonpolar for the following:

- Oxygen gas (O_2)
- Hydrochloric acid (HCl)
- Carbon dioxide ($CO_{2)}$

Solution:



# of electrons given to share

Oxygen gas (O2)

Nonpolar covalent bond

Each Oxygen equally gives 2 electrons

Hydrochloric acid (HCl)

Polar covalent bond

Hydrogen gives 1 electron to Chlorine

Carbon dioxide (CO2)

Polar Covalent bond

Each oxygen gives 2 electrons to Carbon

4. Which of the following statements are true? (There can be more than one true statement.)

a. A covalent bond is the same as a ionic bond.
b. The Octet rule only applys to molecules with covalent bonds.
c. A molecule is polar if the shared electrons are equally shared.
d. A molecule is nonpolar if the shared electrons are are equally shared.
e. Methane gas (CH_4) has a nonpolar covalent bond because it is a gas.

Solution: Only d) is true.

5. Match each atom or molecule with its corresponding letter(s):

- Nitrogen gas
- Argon
- Carbon monoxide

- Hydrogen gas

a) Nonpolar covalent bond

b) Polar covalent bond

c) Follows the Octet Rule

d) Noble gas

e) Two lone pairs

f) Single bond

Solution:

- Nitrogen gas: a), c), e)
- Argon: c), d)
- Carbon monoxide: b), c), e)
- Hydrogen gas: c), f)

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13.8: Covalent Bond Energies and Chemical Reactions

Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.*

When a chemical reaction occurs, molecular bonds are broken and other bonds are formed to make different molecules. For example, the bonds of two water molecules are broken to form hydrogen and oxygen.

$$2H_2O \rightarrow 2H_2 + O_2 \tag{13.8.1}$$

Energy is always required to break a bond, which is known as bond energy. While the concept may seem simple, bond energy serves a very important purpose in describing the structure and characteristics of a molecule. It can be used to determine which Lewis Dot Structure is most suitable when there are multiple Lewis Dot Structures.

> *Energy is always required to break a bond. Energy is released when a bond is made.*

Although each molecule has its own characteristic bond energy, some generalizations are possible. For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 100 kcal of energy to break 1 mol of C–H bonds, so we speak of the bond energy of a C–H bond as being about 100 kcal/mol. A C–C bond has an approximate bond energy of 80 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. We can calculate a more general bond energy by finding the average of the bond energies of a specific bond in different molecules to get the average bond energy.

Table 1: Average Bond Energies (kJ/mol)

Single Bonds						Multiple Bonds	
H—H	432	**N—H**	391	**I—I**	149	**C = C**	614
H—F	565	**N—N**	160	**I—Cl**	208	**C ≡ C**	839
H—Cl	427	**N—F**	272	**I—Br**	175	**O = O**	495
H—Br	363	**N—Cl**	200			**C = O***	745
H—I	295	**N—Br**	243	**S—H**	347	**C ≡ O**	1072
		N—O	201	**S—F**	327	**N = O**	607
C—H	413	**O—H**	467	**S—Cl**	253	**N = N**	418
C—C	347	**O—O**	146	**S—Br**	218	**N ≡ N**	941
C—N	305	**O—F**	190	**S—S**	266	**C ≡ N**	891
C—O	358	**O—Cl**	203			**C = N**	615
C—F	485	**O—I**	234	**Si—Si**	340		
C—Cl	339			**Si—H**	393		
C—Br	276	**F—F**	154	**Si—C**	360		
C—I	240	**F—Cl**	253	**Si—O**	452		
C—S	259	**F—Br**	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C == O(CO_2) = 799

When a bond is strong, there is a higher bond energy because it takes more energy to break a strong bond. This correlates with bond order and bond length. When the Bond order is higher, bond length is shorter, and the shorter the bond length means a greater the Bond Energy because of increased electric attraction. In general, **the shorter the bond length, the greater the bond energy.**

> The average bond energies in Table T3 are the averages of bond dissociation energies. For example the average bond energy of O-H in H_2O is 464 kJ/mol. This is due to the fact that the H-OH bond requires 498.7 kJ/mol to dissociate, while the O-H bond needs 428 kJ/mol.
>
> $$\dfrac{498.7\ kJ/mol + 428\ kJ/mol}{2} = 464\ kJ/mol \tag{13.8.2}$$
>
> When more bond energies of the bond in different molecules that are taken into consideration, the average will be more accurate. However,
>
> - Average bonds values are not as accurate as a molecule specific bond-dissociation energies.
> - Double bonds are higher energy bonds in comparison to a single bond (but not necessarily 2-fold higher).
> - Triple bonds are even higher energy bonds than double and single bonds (but not necessarily 3-fold higher).

Bond Breakage and Formation

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*.

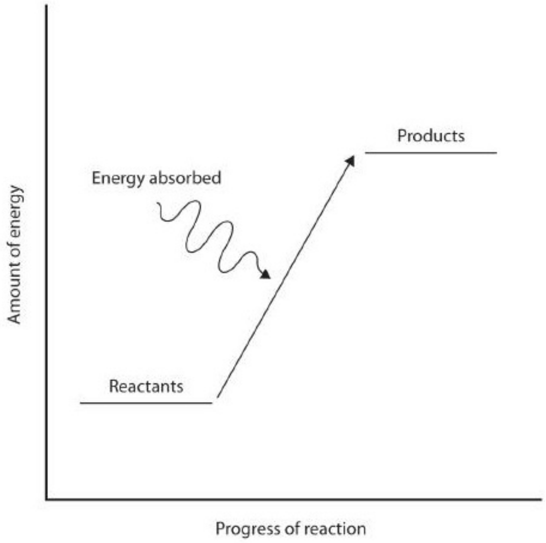

Figure 1: (**left**) Exothermic Reactions. For an exothermic chemical reaction, energy is given off as reactants are converted to products. **(right)** Endothermic Reactions. For an endothermic chemical reaction, energy is absorbed as reactants are converted to products.

In some reactions, the energy of the products is lower than the energy of the reactants. Thus, in the course of the reaction, the substances lose energy to the surrounding environment. Such reactions are exothermic and can be represented by an *energy-level diagram* in Figure 1 (left). In most cases, the energy is given off as heat (although a few reactions give off energy as light). In chemical reactions where the products have a higher energy than the reactants, the reactants must absorb energy from their environment to react. These reactions are endothermic and can be represented by an energy-level diagrams like Figure 1 (right).

Technically Temperature is Neither a Reactant nor Product

It is not uncommon that textbooks and instructors to consider heat as a independent "species" in a reaction. While this is rigorously incorrect because one cannot "add or remove heat" to a reaction as with species, it serves as a convenient mechanism to predict the shift of reactions with changing temperature. For example, if heat is a "reactant" ($\Delta H > 0$), then the

> reaction favors the formation of products at elevated temperature. Similarly, if heat is a "product" ($\Delta H < 0$), then the reaction favors the formation of reactants. A more accurate, and hence preferred, description is discussed below.

Exothermic and endothermic reactions can be thought of as having energy as either a "product" of the reaction or a "reactant." Exothermic reactions releases energy, so energy is a product. Endothermic reactions require energy, so energy is a reactant.

✓ Example 13.8.1: Exothermic vs. Endothermic

Is each chemical reaction exothermic or endothermic?

a. $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)} + 135 \text{ kcal}$
b. $N_{2(g)} + O_{2(g)} + 45 \text{ kcal} \rightarrow 2NO_{(g)}$

Solution

No calculates are required to address this question. Just look at where the "heat" is in the chemical reaction.

a. Because energy is released; this reaction is exothermic.
b. Because energy is absorbed; this reaction is endothermic.

? Exercise 13.8.1

If the bond energy for H-Cl is 431 kJ/mol. What is the overall bond energy of 2 moles of HCl?

Answer

Simply multiply the average bond energy of H-Cl by 2. This leaves you with 862 kJ (Table T3).

✓ Example 13.8.2: Generation of Hydrogen Iodide

What is the enthalpy change for this reaction and is it endothermic or exothermic?

$$H_2(g) + I_2(g) \rightarrow 2HI(g) \tag{13.8.3}$$

Solution

First look at the equation and identify which bonds exist on in the reactants.

- one H-H bond and
- one I-I bond

Now do the same for the products

- two H-I bonds

Then identify the bond energies of these bonds from the table above:

- H-H bonds: 436 kJ/mol
- I-I bonds: 151 kJ/mol

The sum of enthalpies on the reaction side is:

436 kJ/mole + 151 kJ/mole = 587 kJ/mol.

This is how much energy is needed to break the bonds on the reactant side. Then we look at the bond formation which is on the product side:

- 2 mol H-I bonds: 297 kJ/mol

The sum of enthalpies on the product side is:

2 x 297 kJ/mol= 594 kJ/mol

This is how much energy is released when the bonds on the product side are formed. The net change of the reaction is therefore

587-594= -7 kJ/mol.

Since this is negative, the reaction is *exothermic*.

✓ Example 13.8.2: Decomposition of Water

Using the bond energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$2H_2O(g) \rightarrow 2H_2 + O_2(g) \tag{13.8.4}$$

Is the reaction written above exothermic or endothermic? Explain.

Solution

The enthalpy change deals with breaking two mole of O-H bonds and the formation of 1 mole of O-O bonds and two moles of H-H bonds (Table T3).

- The sum of the energies required to break the bonds on the reactants side is 4 x 460 kJ/mol = 1840 kJ/mol.
- The sum of the energies released to form the bonds on the products side is
  - 2 moles of H-H bonds = 2 x 436.4 kJ/mol = 872.8 kJ/mol
  - 1 moles of O=O bond = 1 x 498.7 kJ/mil = 498.7 kJ/mol

which is an output (released) energy = 872.8 kJ/mol + 498.7 kJ/mol = 1371.5 kJ/mol.

Total energy difference is 1840 kJ/mol – 1371.5 kJ/mol = 469 kJ/mol, which indicates that the reaction is *endothermic* and that 469 kJ of heat is needed to be supplied to carry out this reaction.

This reaction is endothermic since it requires energy in order to create bonds.

Summary

Energy is released to generate bonds, which is why the enthalpy change for breaking bonds is positive. Energy is required to break bonds. Atoms are much happier when they are "married" and release energy because it is easier and more stable to be in a relationship (e.g., to generate *octet electronic configurations*). The enthalpy change is negative because the system is releasing energy when forming bond.

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3. For more practice problems: http://www.chalkbored.com/lessons/chemistry-11/bond-energies-worksheet.pdf

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SECTION OVERVIEW

13.9: The Localized Electron Bonding Model

Valence bond (VB) theory assumes that all bonds are localized bonds formed between two atoms by the donation of an electron from each atom. This is actually an invalid assumption because many atoms bond using delocalized electrons. In molecular oxygen VB theory predict that there are no unpaired electrons. VB theory does a good job of qualitatively describing the shapes of covalent compounds. While Molecular Orbital (MO) theory is good for understanding bonding in general. It is more difficult to learn, but predicts the actual properties of molecules better than VB theory. MO theory actually predicts electron transitions because of the differences in the energy levels of orbitals in the molecule. MO theory has been more correct in numerous instances and for this reason it is preferred.

Valence Bond theory describes covalent bond formation as well as the electronic structure of molecules. The theory assumes that electrons occupy atomic orbitals of individual atoms within a molecule, and that the electrons of one atom are attracted to the nucleus of another atom. This attraction increases as the atoms approach one another until the atoms reach a minimum distance where the electron density begins to cause repulsion between the two atoms. This electron density at the minimum distance between the two atoms is where the lowest potential energy is acquired, and it can be considered to be what holds the two atoms together in a chemical bond.

Topic hierarchy

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13.10: Lewis Structures

Lewis Structures are visual representations of the bonds between atoms and illustrate the lone pairs of electrons in molecules. They can also be called Lewis dot diagrams and are used as a simple way to show the configuration of atoms within a molecule. Between 1916 and 1919, Gilbert Newton Lewis, Walther Kossel, and Irving Langmuir came up with a theory to explain chemical bonding. This theory would be later called **Lewis Theory** and it is based on the following principles:

1. **Valence electrons**, or the electrons in the outermost electron shell, have an essential role in chemical bonding.
2. **Ionic bonds** are formed between atoms when electrons are transferred from one atom to another. Ionic bond is a bond between nonmetals and metals .
3. **Covalent bonds** are formed between atoms when pairs of electrons are shared between atoms. A covalent bond is between two nonmetals.
4. Electrons are transferred/shared so that each atom may reach a more stable electron configuration i.e. the noble gas configuration which contains 8 valence electrons. This is called **octet rule**.

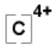
Lewis Symbols and Lewis Structures

A **Lewis Symbol** for an element is composed of a chemical symbol surrounded by dots that are used to represent valence electrons. An example of a Lewis symbol is shown below with the element Carbon, which has the electron configuration of $1s^2 2s^2 2p^2$:

This Lewis symbol shows that carbon has four valence electrons in its outer orbital and these four electrons play a major role in bonding of carbon molecules.

Lewis symbols differ slightly for ions. When forming a Lewis symbol for an ion, the chemical symbol is surrounded by dots that are used to represent valence electrons, and the whole structure is placed in square brackets with superscript representing the charge of the ion. An example of a Lewis symbol for the cation and anion of Carbon is shown below:

Cation of Carbon



Anion of Carbon

Constructing Lewis Structures

To construct Lewis Structures one can generally abide by the following steps:

1. Find how many valence electrons (N) are in the molecule that needs to be shown on the Lewis Structure by using the periodic table. Find the charge, add an electron for every negative charge and remove an electron for every positive charge.
2. Draw out the single bonds and initial framework, called the skeleton, of the molecule.
3. Complete the octets around the non-central atoms i.e. the terminal atoms by using the lone-pairs of electrons.
4. Compare the number of electrons currently depicted to the number needed (N) in the central atom and add electrons to it if less the number is less than N.
5. If there are extra lone-pair electrons and the octet rule is not filled for the central atom, use the extra electrons to form double or triple bonds around the central atom.
6. Check the formal charge of each atom (Formal Charge explained below).

When constructing the structures keep in mind the following:

- The dots surrounding the chemical symbol are the valence electrons, and each dash represents one covalent bond (consisting of two valence electrons)
- Hydrogen is always terminal in the structure
- The atom with the lowest ionization energy is typically the central atom in the structure
- The octet rule means there are 8 valence electrons around the atoms, but for hydrogen the maximum is 2 electrons

Lewis Structures can differ based on whether the electrons are shared through ionic or covalent bonds.

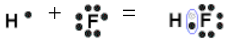
Example 1: Ionic Bonding in NaCl

An example of ionic bonding can be seen below in the instance of the reaction of Sodium and Chlorine:

$$2Na_{(s)} + 2Cl_{2(g)} \rightarrow 2NaCl_{s} \tag{13.10.1}$$

Sodium has one valence electron and Chlorine has seven valence electrons; the two elements together form the noble gas configuration. The Chlorine atom takes the valence electron from the Sodium atom leaving the Chlorine atom with one extra electron and thus negatively charged and the Sodium atom without an electron and thus positively charged. The two atoms then become ions and because of their opposite charges the ions are held together in an ionic bond.

An **example** of covalent bonding can be seen below with the reaction of Hydrogen and Fluorine:



Hydrogen has one valence electron and Fluorine has seven valence electrons; together the elements form the noble gas configuration. The Hydrogen atom shares its electron with Fluorine atom so that the Hydrogen atom has 2 electrons and the Fluorine atom has 8 electrons. Therefore both atoms have their outermost shells completely filled.

Example 2: The Chlorate Ion

Try the Chlorate ion: (ClO_3^-)

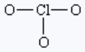
SOLUTION

First, lets find the how many valence electrons chlorate has:

ClO_3^- : 7 e^-(from Cl) + 3(6) e^-(from 3 O atoms) + 1 (from the total charge of -1) = 26

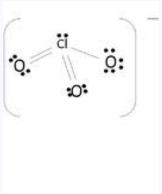
There are 26 valence electrons.

Next lets draw the basic framework of the molecule:



The molecule uses covalent bonds to hold together the atoms to the central Chlorine. The remaining electrons become non-bonding electrons. Since 6 electrons were used for the bonds, the 20 others become those un-bonding electrons to complete the octet:

The oxygen atom's shells fill up with 18 electrons, and the other 2 complete Chlorine's octet.



Example 3: Formaldehyde

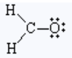
Constructing the Lewis Structure of the formaldehyde (H_2CO) molecule.

SOLUTION

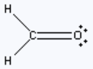
First find the valence electrons:

H_2CO: 2(1) e^- (from the H atoms) + 4 e^- (from the C atom) + 6 e^- (from the O atom)

There are 12 valence electrons. Next draw out the framework of the molecule:



To satisfy the octet of Carbon, one of the pairs of electrons on Oxygen must be moved to create a double bond with Carbon. Therefore our Lewis Structure would look as it does below:



The Hydrogen atoms are each filled up with their two electrons and both the Carbon and the Oxygen atoms' octets are filled.

Formal Charge

The charge on each atom in a molecule is called the formal charge. The formal charge can be calculated if the electrons in the bonds of the molecule are equally shared between atoms. This is not the same thing as the net charge of the ion.

In calculating formal charge, the following steps can be extremely helpful:

1. Determine the number of valence electrons that should be present for each atom in the structure.
2. Count the electrons around each atom in the structure (each lone pair = 2 electrons, each single bond =1 electron, each double bond = 2 electrons, each triple bond = 3 electrons).
3. Subtract the number of valence electrons that should be present (from step 1) from the electrons counted in step 2 for each atom. This is the formal charge for each atom.
4. Check that the formal charges add up to equal the overall charge of the molecule.

Formal charge = (number of valence electrons) - (number of non-bonding electrons + 1/2 number of bonding electrons)

In Lewis structures, the most favorable structure has the smallest formal charge for the atoms, and negative formal charges tend to come from more electronegative atoms.

An **example** of determining formal charge can be seen below with the nitrate ion, NO_3^-:

- The double bonded O atom has *6 electrons*: 4 non-bonding and 2 bonding (one electron for each bond). Since O should have 6 electrons, the *formal charge is 0*.
- The two singly bonded O atoms each have *7 electrons*: 6 non-bonding and 1 bonding electron. Since O should have 6 electrons, and there is one extra electron, those O atoms each have *formal charges of -1*.
- The N atom has 4 electrons: 4 bonding and 0 non-bonding electrons. Since N should have 5 electrons and there are only 4 electrons for this N, the N atom has a *formal charge of +1*.
- The charges add up to the overall charge of the ion. 0 + (-1) + (-1) + 1 = -1. Thus, these charges are correct, as the overall charge of nitrate is -1.

Resonance

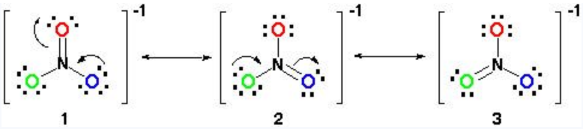
There are times when more than one acceptable Lewis structure can be drawn for a molecule and no single structure can represent the molecule entirely. When this occurs the molecule/ion is said to have **resonance**. The combination of the various plausible Lewis structures is called a **resonance hybrid**.

Some rules for drawing resonance structures are as follows:

1. The same number of electrons must be present for all resonance structures.
2. The octet rule must be obeyed.
3. Nuclei (or the chemical symbol in the structure's representation) cannot be rearranged; only the valence electrons differ for resonance structures.

Example 4: Nitrate Ion

Consider the nitrate ion, NO_3^-



- Each structure differs based on the movement of two electrons.
- From structure 1 to structure 2 one of the lone pairs on the blue O moves to form a double bond with N. One of the electrons shared in the double bond between the red O and N then moves to be a lone pair on the red O because the N cannot have 10 electrons surrounding it.
- This is the same process that occurs from structure 2 to structure 3 except the changes occur in the green O and blue O.

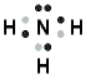
Problems

1. Draw the Lewis structure for water.
2. Find the formal charge for each of the atoms in water.
3. Draw the Lewis structure for ammonia.
4. Find the formal charge for each of the atoms in ammonia.

Answers:

1.

2. All atoms in water have a formal charge of 0.

3. 

4. The formal charge for each H is 0 and for N is 0.

References

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2. Petrucci, Ralph H., et al. General Chemistry: Principles and Modern Applications. Upper Saddle River, NJ: Pearson Prentice Hall, 2007.

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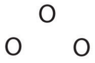
13.11: Resonance

Resonance is a mental exercise within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. It involves constructing multiple Lewis structures that, when combined, represent the full electronic structure of the molecule. **Resonance structures** are used when a single Lewis structure cannot fully describe the bonding; the combination of possible resonance structures is defined as a **resonance hybrid**, which represents the overall delocalization of electrons within the molecule. In general, molecules with multiple resonance structures will be more stable than one with fewer and some resonance structures contribute more to the stability of the molecule than others - formal charges aid in determining this.

Introduction

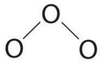
Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several resonance structures. The nuclear skeleton of the Lewis Structure of these resonance structures remains the same, only the electron locations differ. Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°. Let's motivate the discussion by building the Lewis structure for ozone.

1. We know that ozone has a V-shaped structure, so one O atom is central:



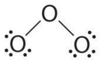
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



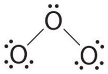
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain



and have 2 electrons left over.

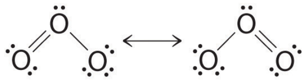
5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either

Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> *When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.*

The electrons appear to "shift" between different resonance structures and while not strictly correct as each resonance structure is just a limitation of using the Lewis structure perspective to describe these molecules. A more accurate description of the electron structure of the molecule requires considering multiple resonance structures simultaneously.

Delocalization and Resonance Structures Rules

1. Resonance structures should have the same number of electrons, do not add or subtract any electrons. (check the number of electrons by simply counting them).
2. Each resonance structures follows the rules of writing Lewis Structures.
3. The hybridization of the structure must stay the same.
4. The skeleton of the structure can not be changed (only the electrons move).
5. Resonance structures must also have the same number of lone pairs.

"Pick the Correct Arrow for the Job"

Most arrows in chemistry cannot be used interchangeably and care must be given to selecting the correct arrow for the job.

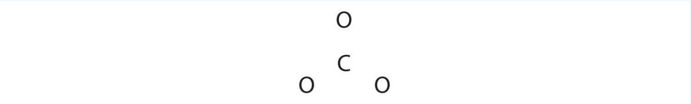
- ↔: A double headed arrow on both ends of the arrow between Lewis structures is used to show resonance
- ⇌: Double harpoons are used to designate equilibria
- ⇀: A single harpoon on one end indicates the movement of **one** electron
- →: A double headed arrow on one end is used to indicate the movement of **two** electrons

Example 13.11.2: Carbonate Ion

Identify the resonance structures for the carbonate ion: CO_3^{2-}.

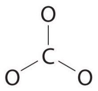
Solution

1. Because carbon is the least electronegative element, we place it in the central position:

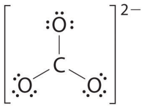


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

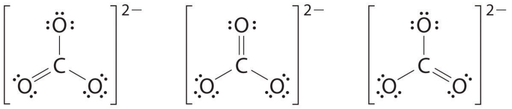


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:

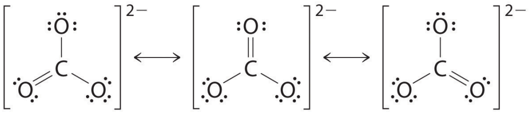


5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



The actual structure is an average of these three resonance structures.

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

Using Formal Charges to Identify viable Resonance Structures

While each resonance structure contributes to the total electronic structure of the molecule, they may not contribute equally. Assigning Formal charges to atoms in the molecules is one mechanism to identify the viability of a resonance structure and determine its relative magnitude among other structures. The formal charge on an atom in a covalent species is the net charge the atom would bear if the electrons in all the bonds to the atom were equally shared. Alternatively the formal charge on an atom in a covalent species is the net charge the atom would bear if all bonds to the atom were nonpolar covalent bonds. To determine the formal charge on a given atom in a covalent species, use the following formula:

$$\begin{aligned}\text{Formal Charge} = (\text{number of valence electrons in free orbital}) - (\text{number of lone-pair electrons}) \\ -\frac{1}{2}(\text{ number bond pair electrons})\end{aligned} \tag{13.11.1}$$

Rules for estimating stability of resonance structures

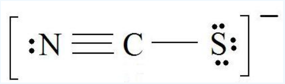
1. The **greater the number of covalent bonds**, the greater the stability since more atoms will have complete octets
2. The structure with the **least number of formal charges** is more stable
3. The structure with the **least separation of formal charge** is more stable
4. A structure with a **negative charge on the more electronegative atom** will be more stable
5. **Positive charges on the least electronegative atom** (most electropositive) is more stable
6. Resonance forms that are equivalent have no difference in stability and contribute equally (eg. benzene)

Example 13.11.3: Thiocyanate Ion

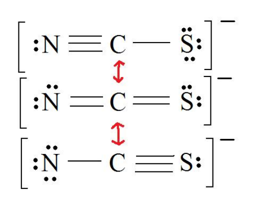
Consider the thiocyanate (CNS^{-}) ion.

Solution

1. Find the Lewis Structure of the molecule. (Remember the Lewis Structure rules.)



2. Resonance: All elements want an octet, and we can do that in multiple ways by moving the terminal atom's electrons around (bonds too).

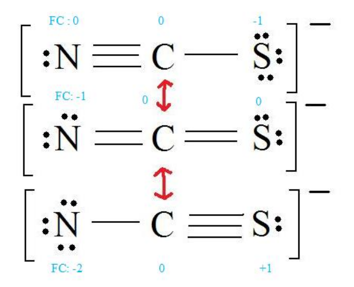


3. Assign Formal Charges via Equation 13.11.1.

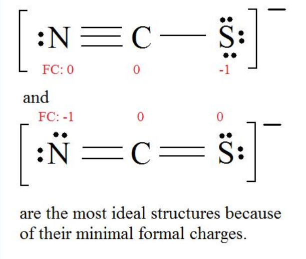
Formal Charge = (number of valence electrons in free orbital) - (number of lone-pair electrons) - ($\frac{1}{2}$ number bond pair electrons)

Remember to determine the number of valence electron each atom has before assigning Formal Charges

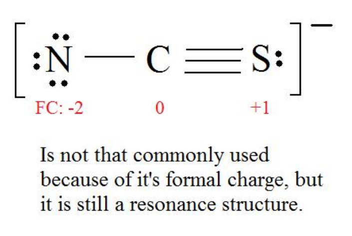
C = 4 valence e^-, N = 5 valence e^-, S = 6 valence e^-, also add an extra electron for the (-1) charge. The total of valence electrons is 16.



4. Find the most ideal resonance structure. (Note: It is the one with the least formal charges that adds up to zero or to the molecule's overall charge.)



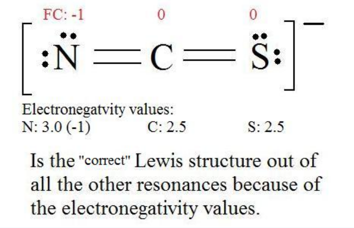
are the most ideal structures because of their minimal formal charges.



Is not that commonly used because of it's formal charge, but it is still a resonance structure.

5. Now we have to look at electronegativity for the "Correct" Lewis structure.

The most electronegative atom usually has the negative formal charge, while the least electronegative atom usually has the positive formal charges.



Is the "correct" Lewis structure out of all the other resonances because of the electronegativity values.

It is useful to combine the resonance structures into a single structure called the **Resonance Hybrid** that describes the bonding of the molecule. The general approach is described below:

1. Draw the Lewis Structure & Resonance for the molecule (using solid lines for bonds).

2. Where there **can** be a double or triple bond, draw a dotted line (-----) for the bond.
3. Draw only the lone pairs found in all resonance structures, do not include the lone pairs that are not on all of the resonance structures.

✔ Example 13.11.4: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

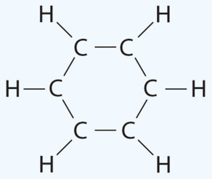
Asked for: resonance structures

Strategy:

A. Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.
B. Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.
C. Draw the resonance structures for benzene.

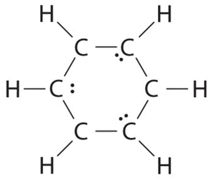
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



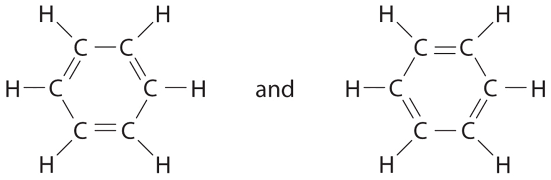
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

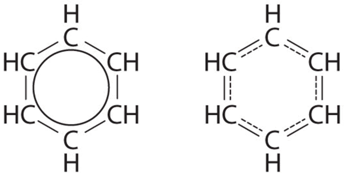


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



Benzene

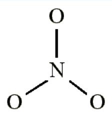
✓ Example 13.11.5: Nitrate Ion

Draw the possible resonance structures for the Nitrate ion NO_3^-.

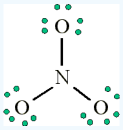
Solution

1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

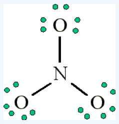
2. Draw the bond connectivities:



3. Add octet electrons to the atoms bonded to the center atom:

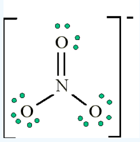


4. Place any leftover electrons (24-24 = **0**) on the center atom:



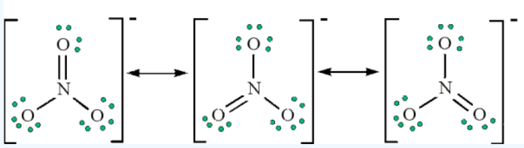
5. Does the central atom have an octet?

- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



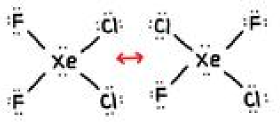
Note: We would expect that the bond lengths in the NO_3^- ion to be somewhat shorter than a single bond.

References

1. Petrucci, Ralph H., et al. *General Chemistry: Principles and Modern Applications*. New Jersey: Pearson Prentice Hall, 2007.
2. Ahmad, Wan-Yaacob and Zakaria, Mat B. "Drawing Lewis Structures from Lewis Symbols: A Direct Electron Pairing Approach." Journal of Chemical Education: Journal 77.3.

Problems

1. True or False, The picture below is a resonance structure?

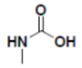


2. Draw the Lewis Dot Structure for **SO_4^{2-}** and all possible resonance structures. Which of the following resonance structure is not favored among the Lewis Structures? Explain why. Assign Formal Charges.
3. Draw the Lewis Dot Structure for **CH_3COO^-** and all possible resonance structures. Assign Formal Charges. Choose the most favorable Lewis Structure.
4. Draw the Lewis Dot Structure for **HPO_3^{2-}** and all possible resonance structures. Assign Formal Charges.
5. Draw the Lewis Dot Structure for **CHO_2^{1-}** and all possible resonance structures. Assign Formal Charges.
6. Draw the Resonance Hybrid Structure for **PO_4^{3-}**.
7. Draw the Resonance Hybrid Structure for **NO_3^-**.

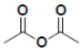
Problems #2

Problems: Draw the resonance forms for the following structures

1.



2



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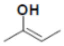

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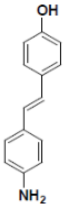

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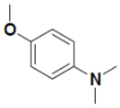
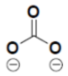
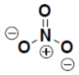


Based on resonance conformation which structure is more stable?

6

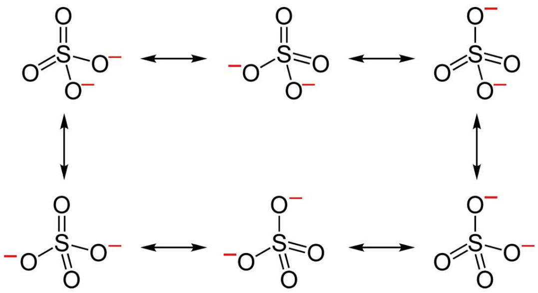




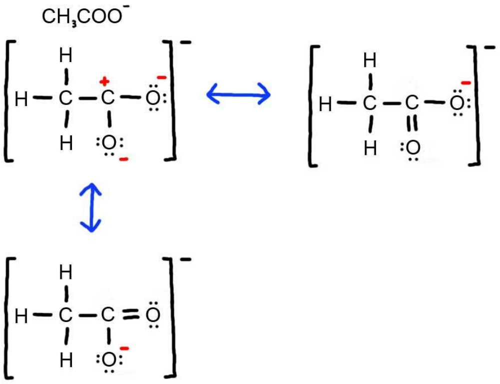
Answers

1. False, because the electrons were not moved around, only the atoms (this violates the Resonance Structure Rules).

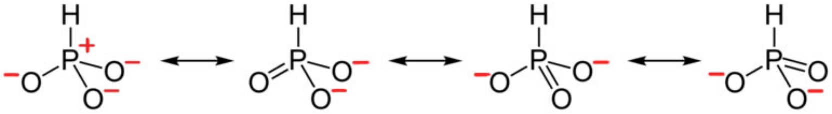
2. Below are the all Lewis dot structure with formal charges (in red) for Sulfate (**SO_4^{2-}**). There isn't a most favorable resonance of the Sulfate ion because they are all identical in charge and there is no change in Electronegativity between the Oxygen atoms.



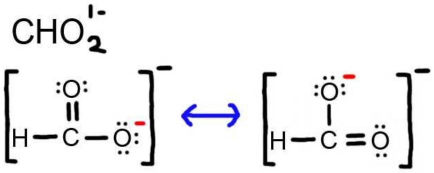
3. Below is the resonance for **CH_3COO^-**, formal charges are displayed in red. The Lewis Structure with the most formal charges is not desirable, because we want the Lewis Structure with the least formal charge.



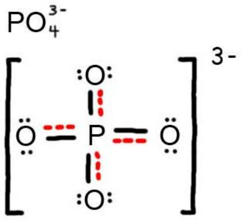
4. The resonance for **HPO_3^{2-}**, and the formal charges (in red).



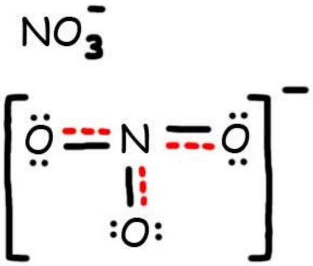
5. The resonance for **CHO_2^{1-}**, and the formal charges (in red).



6. The resonance hybrid for **PO_4^{3-}**, hybrid bonds are in red.

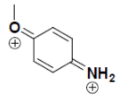


7. The resonance hybrid for **NO_3^-**, hybrid bonds are in red.



Problems #2

5



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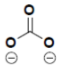

This is more stable

Contributors and Attributions

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13.12: Exceptions to the Octet Rule

Three cases can be constructed that do not follow the Octet Rule, and as such, they are known as the exceptions to the Octet Rule. Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. However, it is hard to imagine that one rule could be followed by all molecules. There is always an exception, and in this case, three exceptions. The Octet Rule is violated in these three scenarios:

1. When there are an odd number of valence electrons
2. When there are too few valence electrons
3. When there are too many valence electrons

> *Reminder: Always use the Octet Rule when drawing Lewis Dot Structures, these exceptions will only occur when necessary.*

Exception 1: Species with Odd Numbers of Electrons

The first exception to the Octet Rule is when there are an odd number of valence electrons. An example of this would be the nitrogen (II) oxide molecule (NO). Nitrogen atom has 5 valence electrons while the oxygen atom has 6 electrons. The total would be 11 valence electrons to be used. The Octet Rule for this molecule is fulfilled in the above example, however that is with 10 valence electrons. The last one does not know where to go. The lone electron is called an unpaired electron. But where should the unpaired electron go? The unpaired electron is usually placed in the Lewis Dot Structure so that each element in the structure will have the *lowest* formal charge possible. The formal charge is *the perceived charge on an individual atom in a molecule when atoms do not contribute equal numbers of electrons to the bonds they participate in*. The formula to find a formal charge is:

Formal Charge= [# of valence e$^-$ the atom would have on its own] - [# of lone pair electrons on that atom] - [# of bonds that atom participates in]

No formal charge at all is the most ideal situation. An example of a stable molecule with an odd number of valence electrons would be nitrogen monoxide. Nitrogen monoxide has 11 valence electrons (Figure 1). If you need more information about formal charges, see Lewis Structures. If we were to consider the nitrogen monoxide cation (NO^+ with ten valence electrons, then the following Lewis structure would be constructed:

Figure 1. Lewis dot structure for the NO^+ ion with ten valence electrons.

Nitrogen normally has five valence electrons. In Figure 1, it has two lone pair electrons and it participates in two bonds (a double bond) with oxygen. This results in nitrogen having a formal charge of +1. Oxygen normally has six valence electrons. In Figure 1, oxygen has four lone pair electrons and it participates in two bonds with nitrogen. Oxygen therefore has a formal charge of 0. The overall molecule here has a formal charge of +1 (+1 for nitrogen, 0 for oxygen. +1 + 0 = +1). However, if we add the eleventh electron to nitrogen (because we want the molecule to have the *lowest* total formal charge), it will bring both the nitrogen and the molecule's overall charges to zero, the most ideal formal charge situation. That is exactly what is done to get the correct Lewis structure for nitrogen monoxide:

Figure 2. The proper Lewis structure for NO molecule with 11 valence electrons

Free Radicals

There are actually very few stable molecules with odd numbers of electrons that exist, since that unpaired electron is willing to react with other unpaired electrons. Most odd electron species are highly reactive, which we call **Free Radicals**. Because of their instability, free radicals bond to atoms in which they can take an electron from in order to become stable, making them very chemically reactive. Radicals are found as both reactants and products, but generally react to form more stable molecules as soon as they can. To emphasize the existence of the unpaired electron, radicals are denoted with a dot in front of their

> chemical symbol as with $\cdot OH$, the hydroxyl radical. An example of a radical you may by familiar with already is the gaseous chlorine atom, denoted $\cdot Cl$. Interestingly, molecules with an odd number of Valence electrons will *always* be paramagnetic.

Exception 2: Incomplete Octets

The second exception to the Octet Rule is when there are too few valence electrons that results in an incomplete Octet. There are even more occasions where the octet rule does not give the most correct depiction of a molecule or ion. This is also the case with incomplete octets. Species with incomplete octets are pretty rare and generally are only found in some beryllium, aluminum, and boron compounds including the boron hydrides. Let's take a look at one such hydride, BH_3 (Borane).

If one was to make a Lewis structure for BH_3 following the basic strategies for drawing Lewis structures, one would probably come up with this structure (Figure 3):

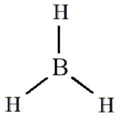


Figure 3: **The structure of the Borane molecule.**

The problem with this structure is that boron has an incomplete octet; it only has **six electrons** around it. Hydrogen atoms can naturally only have only 2 electrons in their outermost shell (their version of an octet), and as such there are no spare electrons to form a double bond with boron. One might surmise that the failure of this structure to form complete octets must mean that this bond should be ionic instead of covalent. However, boron has an electronegativity that is very similar to hydrogen, meaning there is likely very little ionic character in the hydrogen to boron bonds, and as such this Lewis structure, though it does not fulfill the octet rule, is likely the best structure possible for depicting BH_3 with Lewis theory. One of the things that may account for BH_3's incomplete octet is that it is commonly a transitory species, formed temporarily in reactions that involve multiple steps.

Let's take a look at another incomplete octet situation dealing with boron, BF_3 (Boron trifluorine). Like with BH_3, the initial drawing of a Lewis structure of BF_3 will form a structure where boron has only six electrons around it (Figure 4).

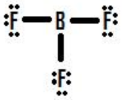


Figure 4

If you look Figure 4, you can see that the fluorine atoms possess extra lone pairs that they can use to make additional bonds with boron, and you might think that all you have to do is make one lone pair into a bond and the structure will be correct. If we add one double bond between boron and one of the fluorines we get the following Lewis Structure (Figure 5):

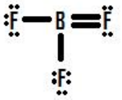


Figure 5

Each fluorine has eight electrons, and the boron atom has eight as well! Each atom has a perfect octet, right? Not so fast. We must examine the formal charges of this structure. The fluorine that shares a double bond with boron has six electrons around it (four from its two lone pairs of electrons and one each from its two bonds with boron). This is one less electron than the number of valence electrons it would have naturally (Group seven elements have seven valence electrons), so it has a formal charge of +1. The two flourines that share single bonds with boron have seven electrons around them (six from their three lone pairs and one from their single bonds with boron). This is the same amount as the number of valence electrons they would have on their own, so they both have a formal charge of zero. Finally, boron has four electrons around it (one from each of its four bonds shared with fluorine). This is one more electron than the number of valence electrons that boron would have on its own, and as such boron has a formal charge of -1.

This structure is supported by the fact that the experimentally determined bond length of the boron to fluorine bonds in BF_3 is less than what would be typical for a single bond (see Bond Order and Lengths). However, this structure contradicts one of the major rules of formal charges: Negative formal charges are supposed to be found on the more electronegative atom(s) in a bond, but in the structure depicted in Figure 5, a *positive* formal charge is found on fluorine, which not only is the most electronegative element in the structure, but the most electronegative element in the entire periodic table ($\chi = 4.0$). Boron on the other hand, with the much lower electronegativity of 2.0, has the negative formal charge in this structure. This formal charge-electronegativity disagreement makes this double-bonded structure impossible.

However the large electronegativity difference here, as opposed to in BH_3, signifies significant polar bonds between boron and fluorine, which means there is a high ionic character to this molecule. This suggests the possibility of a semi-ionic structure such as seen in Figure 6:

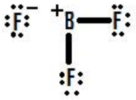


Figure 6

None of these three structures is the "correct" structure in this instance. The most "correct" structure is most likely a resonance of all three structures: the one with the incomplete octet (Figure 4), the one with the double bond (Figure 5), and the one with the ionic bond (Figure 6). The most contributing structure is probably the incomplete octet structure (due to Figure 5 being basically impossible and Figure 6 not matching up with the behavior and properties of BF_3). As you can see even when other possibilities exist, incomplete octets may best portray a molecular structure.

As a side note, it is important to note that BF_3 frequently bonds with a F^- ion in order to form BF_4^- rather than staying as BF_3. This structure completes boron's octet and it is more common in nature. This exemplifies the fact that incomplete octets are rare, and other configurations are typically more favorable, including bonding with additional ions as in the case of BF_3 .

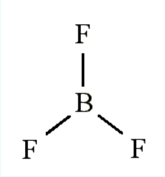
Example: BF_3

Draw the Lewis structure for boron trifluoride (BF_3).

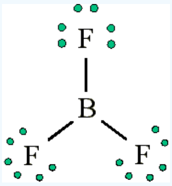
Solution

1. Add electrons (3*7) + 3 = **24**

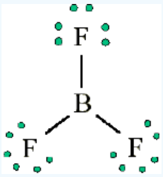
2. Draw connectivities:



3. Add octets to outer atoms:

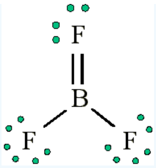


4. Add extra electrons (24-24=0) to central atom:



5. Does central electron have octet?

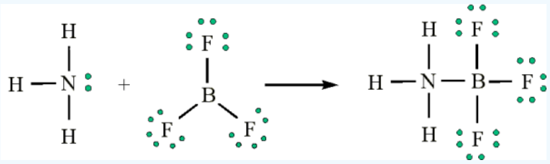
- NO. It has 6 electrons
- Add a multiple bond (double bond) to see if central atom can achieve an octet:



6. The central Boron now has an octet (there would be three resonance Lewis structures)

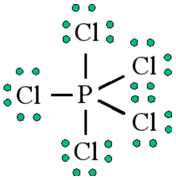
However...

- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single bonds, and 6 valence electrons around the central boron is the most likely structure***
- BF_3 reacts strongly with compounds which have an unshared pair of electrons which can be used to form a bond with the boron:



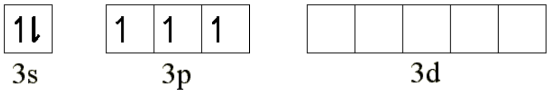
Exception 3: Expanded Valence Shells

More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, and a nonmetal central atom found in the third period or below*, which those terminal atoms bond to. For example, PCl_5 is a legitimate compound (whereas NCl_5) is not:



> Expanded valence shells are observed **only** for elements in period 3 (i.e. n=3) and beyond

The 'octet' rule is based upon available n*s* and n*p* orbitals for valence electrons (2 electrons in the *s* orbitals, and 6 in the *p* orbitals). Beginning with the n=3 principle quantum number, the d orbitals become available (*l*=2). The orbital diagram for the valence shell of phosphorous is:



Hence, the third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons. Size is also an important consideration:

- The larger the central atom, the larger the number of electrons which can surround it
- Expanded valence shells occur most often when the central atom is bonded to small electronegative atoms, such as F, Cl and O.

There is currently much scientific exploration and inquiry into the reason why expanded valence shells are found. The top area of interest is figuring out where the extra pair(s) of electrons are found. Many chemists think that there is not a very large energy difference between the 3p and 3d orbitals, and as such it is plausible for extra electrons to easily fill the 3d orbital when an expanded octet is more favorable than having a complete octet. This matter is still under hot debate, however and there is even debate as to what makes an expanded octet more favorable than a configuration that follows the octet rule.

One of the situations where expanded octet structures are treated as more favorable than Lewis structures that follow the octet rule is when the formal charges in the expanded octet structure are smaller than in a structure that adheres to the octet rule, or when there are less formal charges in the expanded octet than in the structure a structure that adheres to the octet rule.

The sulfate ion, SO_4^{-2}. is an ion that prefers an expanded octet structure. A strict adherence to the octet rule forms the following Lewis structure:

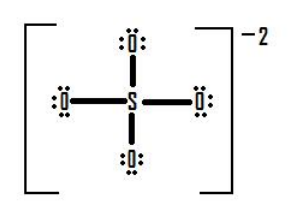


Figure 12

If we look at the formal charges on this molecule, we can see that all of the oxygen atoms have seven electrons around them (six from the three lone pairs and one from the bond with sulfur). This is one more electron than the number of valence electrons then they would have normally, and as such each of the oxygen atoms in this structure has a formal charge of -1. Sulfur has four electrons around it in this structure (one from each of its four bonds) which is two electrons fewer than the number of valence electrons it would have normally, and as such it carries a formal charge of +2.

If instead we made a structure for the sulfate ion with an expanded octet, it would look like this:

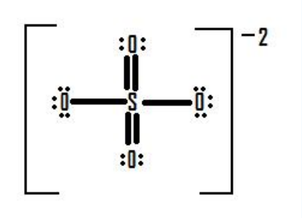


Figure 13

Looking at the formal charges for this structure, the sulfur ion has six electrons around it (one from each of its bonds). This is the same amount as the number of valence electrons it would have naturally. This leaves sulfur with a formal charge of zero. The two oxygens that have double bonds to sulfur have six electrons each around them (four from the two lone pairs and one each from the two bonds with sulfur). This is the same amount of electrons as the number of valence electrons that oxygen atoms have on their own, and as such both of these oxygen atoms have a formal charge of zero. The two oxygens with the single bonds to sulfur have seven electrons around them in this structure (six from the three lone pairs and one from the bond to sulfur). That is one electron more than the number of valence electrons that oxygen would have on its own, and as such those two oxygens carry a formal charge of -1. Remember that with formal charges, the goal is to keep the formal charges (or the difference between the formal charges of each atom) as small as possible. The number of and values of the formal charges on this structure (-1 and 0 (difference of 1) in Figure 12, as opposed to +2 and -1 (difference of 3) in Figure 12) is significantly lower than on the structure that follows the octet rule, and as such an expanded octet is plausible, and even preferred to a normal octet, in this case.

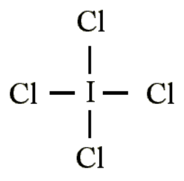
✓ Example 3: The ICl_4^- Ion

Draw the Lewis structure for ICl_4^- ion.

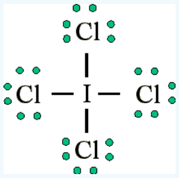
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

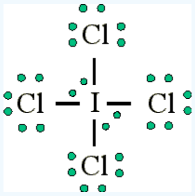
2. Draw the connectivities:



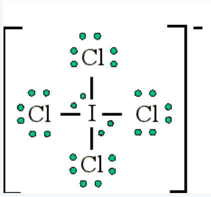
3. Add octet of electrons to outer atoms:



4. Add extra electrons (36-32=**4**) to central atom:



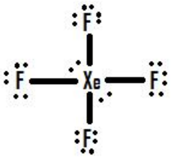
5. The ICl_4^- ion thus has 12 valence electrons around the central Iodine (in the 5*d* orbitals)

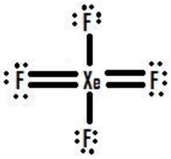


Expanded Lewis structures are also plausible depictions of molecules when experimentally determined bond lengths suggest partial double bond characters even when single bonds would already fully fill the octet of the central atom. Despite the cases for expanded octets, as mentioned for incomplete octets, it is important to keep in mind that, in general, the octet rule applies.

Practice Problems

1. Draw the Lewis structure for the molecule I_3^-.
2. Draw the molecule ClF_3.
3. The central atom for an expanded octet must have an atomic number larger than what?
4. Draw the Lewis structure for the molecule NO_2.
5. Which Lewis structure is more likely?

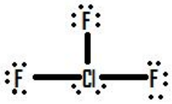




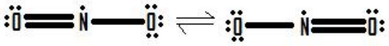
or

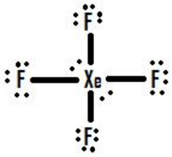
Answers

1.

2. 

3. 10 (Sodium and higher)

4. 

5. 

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1. Petrucci, Ralph H.; Harwood, William S.; Herring, F. G.; Madura, Jeffrey D. General Chemistry: Principles & Modern Applications. 9th Ed. New Jersey. Pearson Education, Inc. 2007.
2. Moore, John W.; Stanitski, Conrad L.; Jurs, Peter C. Chemistry; The Molecular Science. 2nd Ed. 2004.

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13.13: Molecular Structure: The VSEPR Model

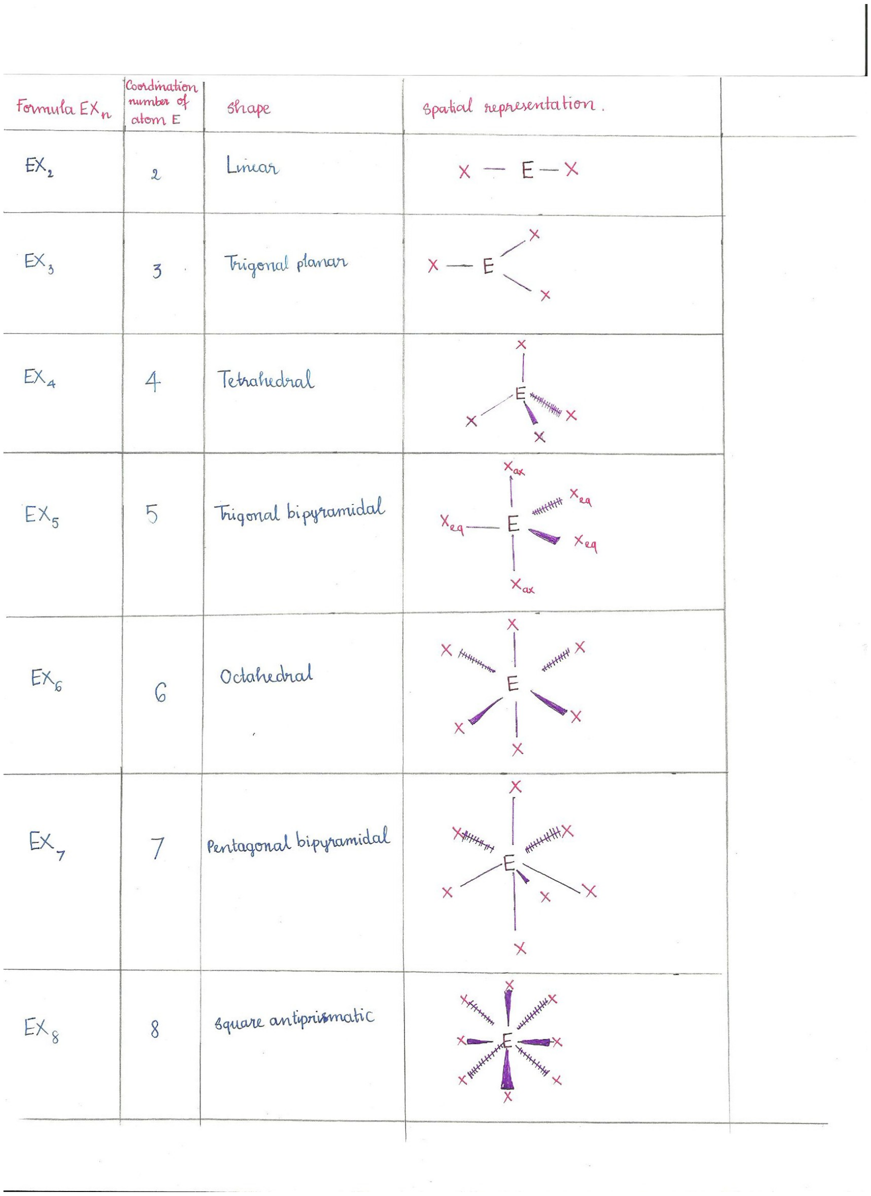
Valence Shell Electron Pair Repulsion (VSPER) theory is used to predict the geometric shape of the molecules based on the electron repulsive force. There are some limitation to VSEPR.

Introduction

The shapes of the molecules is determined mainly by the electrons surrounding the central atom. Therefore, VSEPR theory gives simple directions on how to predict the shape of the molecules. The VSEPR model combines the original ideas of Sidwick and Powell and further development of Nyholm and Gillespie.

How VSEPR works

In a molecule EX_n, the valence shell electron pair around the central atom E and the E-X single bonds are very important due to the repulsion in which determine the shape of the molecule. The repulsions decrease in order of: lone pair-lone pair, lone pair-bonding pair, bonding pair-bonding pair. At the same time, the repulsion would decrease in order of: triple bond-single bond, double bond-single bond, and single bond-single bond if the central atom E has multiple bonds. The difference between the electronegativities of E and X also determine the repulsive force between the bonding pairs. If electron-electron repulsive force is less, then more electron density is drawn away from the central atom E.



Formula EX_n	Coordination number of atom E	Shape	Spatial representation.
EX_2	2	Linear	X — E — X
EX_3	3	Trigonal planar	
EX_4	4	Tetrahedral	
EX_5	5	Trigonal bipyramidal	
EX_6	6	Octahedral	
EX_7	7	Pentagonal bipyramidal	
EX_8	8	square antiprismatic	

Shape determination:

VSEPR model works better for simple halides of the p-block elements but can also be used with other substituents. It does not take steric factors, size of the substituents into account. Therefore, the shape of the molecules are arranged so that the energy is minimized. For example:

- BeCl2 has minimum energy when it is a linear molecule.
- BCl3 takes the shape of trigonal planar.

Lone pair electrons are also taken into account. When lone pair electrons are present, the "parent structure" are used as a guideline for determining the shape..

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1. Li, Kee W., Gong D. zhou, and Thomas Chung W. Mak. *Advanced structural inorganic chemistry*. Oxford, New York: Oxford University Press, 2008. Print.
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Problems

1. What is VSEPR used in chemistry?

It is used to predict the molecular shape of molecules

2. How to predict a molecule structure using VSEPR theory?

First step is to count the total number of valence electrons. After the total number of electrons is determined, this number is divided by two to give the total number of electron pairs. With the electron pairs of the molecule, the shape of the molecule is determined based on the table shown above.

3. What is the shape of PF_5 ?

It is trigonal bipyramidal because it has total of 20 electron pairs. Each Fluorine atom give 1 electron to the Phosphorus central atom which creates total of 5 pairs. Also, each Fluorine atom has 3 electron pairs. With the presence of 5 Fluorine atom, there are 15 more electron pairs so there are 20 electron pairs total.

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CHAPTER OVERVIEW

14: Covalent Bonding

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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SECTION OVERVIEW

14.1: Hybridization and the Localized Electron Model

When molecules share electrons, they form bonds. Atoms can share one, two, or three pairs of electrons, forming single, double, and triple bonds, respectively. Although it is impossible to determine the exact position of the electron, it is possible to calculate the probability that one will find the electron in a point around the nucleus.

14.2: The Molecular Orbital Model

Hybridization is the idea that atomic orbitals fuse to form newly hybridized orbitals, which in turn, influences molecular geometry and bonding properties. Hybridization is also an expansion of the valence bond theory. In order to explore this idea further, we will utilize three types of hydrocarbon compounds to illustrate sp^3, sp^2, and sp hybridization.

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SECTION OVERVIEW

14.3: Bonding in Homonuclear Diatomic Molecules

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14.4: Bonding in Heteronuclear Diatomic Molecules

1.1 Chemistry in the Modern World

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14.5: Combining the Localized Electron and Molecular Orbital Models

1.1 Chemistry in the Modern World

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CHAPTER OVERVIEW

10: Entropy, Gibbs Energy, and Spontaneity

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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SECTION OVERVIEW

10.1: Spontaneous Processes

Entropy is a state function that is often erroneously referred to as the 'state of disorder' of a system. Qualitatively, entropy is simply a measure how much the energy of atoms and molecules become more spread out in a process and can be defined in terms of statistical probabilities of a system or in terms of the other thermodynamic quantities. Entropy is also the subject of the Second and Third laws of thermodynamics, which describe the changes in entropy of the universe with respect to the system and surroundings, and the entropy of substances, respectively.

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10.2: Isothermal Expansions and Compressions of Ideal Gases

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10.3: Definition of Entropy

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10.4: Entropy and Physical Changes

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10.5: Entropy and the Second Law of Thermodynamics

The Second Law of Thermodynamics states that the state of entropy of the entire universe, as an isolated system, will always increase over time. The second law also states that the changes in the entropy in the universe can never be negative.

Introduction

Why is it that when you leave an ice cube at room temperature, it begins to melt? Why do we get older and never younger? And, why is it whenever rooms are cleaned, they become messy again in the future? Certain things happen in one direction and not the other, this is called the "arrow of time" and it encompasses every area of science. The thermodynamic arrow of time (entropy) is the measurement of disorder within a system. Denoted as ΔS, the change of entropy suggests that time itself is asymmetric with respect to order of an isolated system, meaning: a system will become more disordered, as time increases.

Major players in developing the Second Law

- Nicolas Léonard Sadi Carnot was a French physicist, who is considered to be the "father of thermodynamics," for he is responsible for the origins of the Second Law of Thermodynamics, as well as various other concepts. The current form of the second law uses entropy rather than caloric, which is what Sadi Carnot used to describe the law. Caloric relates to heat and Sadi Carnot came to realize that some caloric is always lost in the motion cycle. Thus, the thermodynamic reversibility concept was proven wrong, proving that irreversibility is the result of every system involving work.
- Rudolf Clausius was a German physicist, and he developed the Clausius statement, which says "Heat generally **cannot flow spontaneously** from a material at a lower temperature to a material at a higher temperature."
- William Thompson, also known as Lord Kelvin, formulated the Kelvin statement, which states "It is **impossible** to convert heat completely in a cyclic process." This means that there is no way for one to convert all the energy of a system into work, without losing energy.
- Constantin Carathéodory, a Greek mathematician, created his own statement of the second low arguing that "In the neighborhood of any initial state, there are states which **cannot** be approached arbitrarily close through adiabatic changes of state."

Figure 10.5.1: Nicolas Carnot (left), Rudolf Clausius (second on left), William Thompson (second on right), Constantin Carathéodory (right)

Probabilities

If a given state can be accomplished in more ways, then it is more probable than the state that can only be accomplished in a fewer/one way.

Assume a box filled with jigsaw pieces were jumbled in its box, the probability that a jigsaw piece will land randomly, away from where it fits perfectly, is very high. Almost every jigsaw piece will land somewhere away from its ideal position. The probability of a jigsaw piece landing correctly in its position, is very low, as it can only happened one way. Thus, the misplaced jigsaw pieces have a much higher multiplicity than the correctly placed jigsaw piece, and we can correctly assume the misplaced jigsaw pieces represent a higher entropy.

Derivation and Explanation

To understand why entropy increases and decreases, it is important to recognize that two changes in entropy have to considered at all times. The entropy change of the surroundings and the entropy change of the system itself. Given the entropy change of the universe is equivalent to the sums of the changes in entropy of the system and surroundings:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \frac{q_{sys}}{T} + \frac{q_{surr}}{T} \tag{10.5.1}$$

In an isothermal reversible expansion, the heat q absorbed by the system from the surroundings is

$$q_{rev} = nRT \ln \frac{V_2}{V_1} \tag{10.5.2}$$

Since the heat absorbed by the system is the amount lost by the surroundings, $q_{sys} = -q_{surr}$ .Therefore, for a truly reversible process, the entropy change is

$$\Delta S_{univ} = \frac{nRT \ln \frac{V_2}{V_1}}{T} + \frac{-nRT \ln \frac{V_2}{V_1}}{T} = 0 \tag{10.5.3}$$

If the process is irreversible however, the entropy change is

$$\Delta S_{univ} = \frac{nRT \ln \frac{V_2}{V_1}}{T} > 0 \tag{10.5.4}$$

If we put the two equations for ΔS_{univ}together for both types of processes, we are left with the second law of thermodynamics,

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0 \tag{10.5.5}$$

where ΔS_{univ} equals zero for a truly reversible process and is greater than zero for an irreversible process. In reality, however, truly reversible processes never happen (or will take an infinitely long time to happen), so it is safe to say all thermodynamic processes we encounter everyday are irreversible in the direction they occur.

> The second law of thermodynamics can also be stated that "all **spontaneous** processes produce an **increase** in the entropy of the universe".

Gibbs Free Energy

Given another equation:

$$\Delta S_{total} = \Delta S_{univ} = \Delta S_{surr} + \Delta S sys \tag{10.5.6}$$

The formula for the entropy change in the surroundings is $\Delta S_{surr} = -\Delta H_{sys}/T$. If this equation is replaced in the previous formula, and the equation is then multiplied by T and by -1 it results in the following formula.

$$-T\,\Delta S_{univ} = \Delta H_{sys} - T\,\Delta S_{sys} \tag{10.5.7}$$

If the left side of the equation is replaced by G, which is know as Gibbs energy or free energy, the equation becomes

$$\Delta G = \Delta H - T\Delta S \tag{10.5.8}$$

Now it is much simpler to conclude whether a system is spontaneous, non-spontaneous, or at equilibrium.

- ΔH refers to the heat change for a reaction. A positive ΔH means that heat is taken from the environment (endothermic). A negative ΔH means that heat is emitted or given the environment (exothermic).
- ΔG is a measure for the change of a system's free energy in which a reaction takes place at **constant** pressure (P) and temperature (T).

According to the equation, when the entropy decreases and enthalpy increases the free energy change, ΔG, is positive and not spontaneous, and it does not matter what the temperature of the system is. Temperature comes into play when the entropy and enthalpy both increase or both decrease. The reaction is not spontaneous when both entropy and enthalpy are positive and at low temperatures, and the reaction is spontaneous when both entropy and enthalpy are positive and at high temperatures. The reactions are spontaneous when the entropy and enthalpy are negative at low temperatures, and the reaction is not spontaneous when the entropy and enthalpy are negative at high temperatures. Because all spontaneous reactions increase entropy, one can determine if the entropy changes according to the spontaneous nature of the reaction (Equation 10.5.8).

Table 10.5.1: Matrix of Conditions Dictating Spontaneity

Case	ΔH	ΔS	ΔG	Answer
high temperature	-	+	-	Spontaneous
low temperature	-	+	-	Spontaneous
high temperature	-	-	+	Nonspontaneous
low temperature	-	-	-	Spontaneous
high temperature	+	+	-	Spontaneous
low temperature	+	+	+	Nonspontaneous
high temperature	+	-	+	Nonspontaneous
low temperature	+	-	+	Nonspontaneous

✓ Example 10.5.1

Lets start with an easy reaction:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$$

The enthalpy, ΔH, for this reaction is -241.82 kJ, and the entropy, ΔS, of this reaction is -233.7 J/K. If the temperature is at 25º C, then there is enough information to calculate the standard free energy change, ΔG.

The first step is to convert the temperature to Kelvin, so add 273.15 to 25 and the temperature is at 298.15 K. Next plug ΔH, ΔS, and the temperature into the $\Delta G = \Delta H - T\Delta S$.

ΔG= -241.8 kJ + (298.15 K)(-233.7 J/K)

= -241.8 kJ + -69.68 kJ (Don't forget to convert Joules to Kilojoules)

= -311.5 kJ

✓ Example 10.5.2

Here is a little more complex reaction:

$$2ZnO_{(s)} + 2C_{(g)} \rightarrow 2Zn_{(s)} + 2CO_{(g)}$$

If this reaction occurs at room temperature (25º C) and the enthalpy, ΔH, and standard free energy, ΔG, is given at -957.8 kJ and -935.3 kJ, respectively. One must work backwards somewhat using the same equation from Example 1 for the free energy is given.

-935.3 kJ = -957.8 kJ + (298.15 K) (ΔS)

22.47 kJ = (298.15 K) (ΔS) (Add -957.8 kJ to both sides)

0.07538 kJ/K = ΔS (Divide by 298.15 K to both sides)

Multiply the entropy by 1000 to convert the answer to Joules, and the new answer is 75.38 J/K.

✓ Example 10.5.3

For the following dissociation reaction

$$O_{2(g)} \rightarrow 2O_{(g)}$$

under what temperature conditions will it occurs spontaneously?

Solution

By simply viewing the reaction one can determine that the reaction increases in the number of moles, so the entropy increases. Now all one has to do is to figure out the enthalpy of the reaction. The enthalpy is positive, because covalent bonds are broken. When covalent bonds are broken energy is absorbed, which means that the enthalpy of the reaction is positive. Another way to determine if enthalpy is positive is to to use the formation data and subtract the enthalpy of the reactants from the enthalpy of the products to calculate the total enthalpy. So, if the temperature is low it is probable that ΔH is more than $T * \Delta S$, which means the reaction is not spontaneous. If the temperature is large then $T * \Delta S$ will be larger than the enthalpy, which means the reaction is spontaneous.

✓ Example 10.5.4

The following reaction

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

occurs spontaneously under what temperature conditions? The enthalpy of the reaction is -40 kJ.

Solution

One may have to calculate the enthalpy of the reaction, but in this case it is given. If the enthalpy is negative then the reaction is exothermic. Now one must find if the entropy is greater than zero to answer the question. Using the entropy of formation data and the enthalpy of formation data, one can determine that the entropy of the reaction is -42.1 J/K and the enthalpy is -41.2 kJ. Because both enthalpy and entropy are negative, the spontaneous nature varies with the temperature of the reaction. The temperature would also determine the spontaneous nature of a reaction if both enthalpy and entropy were positive. When the reaction occurs at a low temperature the free energy change is also negative, which means the reaction is spontaneous. However, if the reaction occurs at high temperature the reaction becomes nonspontaneous, for the free energy change becomes positive when the high temperature is multiplied with a negative entropy as the enthalpy is not as large as the product.

✓ Example 10.5.5

Under what temperature conditions does the following reaction occurs spontaneously ?

$$H_{2(g)} + I_{(g)} \rightleftharpoons 2HI_{(g)}$$

Solution

Only after calculating the enthalpy and entropy of the reaction is it possible for one can answer the question. The enthalpy of the reaction is calculated to be -53.84 kJ, and the entropy of the reaction is 101.7 J/K. Unlike the previous two examples, the temperature has no affect on the spontaneous nature of the reaction. If the reaction occurs at a high temperature, the free energy change is still negative, and ΔG is still negative if the temperature is low. Looking at the formula for spontaneous change one can easily come to the same conclusion, for there is no possible way for the free energy change to be positive. Hence, the reaction is spontaneous at all temperatures.

Application of the Second Law

The second law occurs all around us all of the time, existing as the biggest, most powerful, general idea in all of science.

Explanation of Earth's Age

When scientists were trying to determine the age of the Earth during 1800s they failed to even come close to the value accepted today. They also were incapable of understanding how the earth transformed. Lord Kelvin, who was mentioned earlier, first hypothesized that the earth's surface was extremely hot, similar to the surface of the sun. He believed that the earth was cooling at a slow pace. Using this information, Kelvin used thermodynamics to come to the conclusion that the earth was at least twenty million years, for it would take about that long for the earth to cool to its current state. Twenty million years was not even close to the actual age of the Earth, but this is because scientists during Kelvin's time were not aware of radioactivity. Even though Kelvin was incorrect about the age of the planet, his use of the second law allowed him to predict a more accurate value than the other scientists at the time.

Evolution and the Second Law

Some critics claim that evolution violates the Second Law of Thermodynamics, because organization and complexity increases in evolution. However, this law is referring to isolated systems only, and the earth is not an isolated system or closed system. This is evident for constant energy increases on earth due to the heat coming from the sun. So, order may be becoming more organized, the universe as a whole becomes more disorganized for the sun releases energy and becomes disordered. This connects to how the second law and cosmology are related, which is explained well in the video below.

Problems

1. Predict the entropy changes of the converse of SO_2 to SO_3: 2 SO_2 (g) + O_2 (g) --> 2 SO_3 (g)
2. True/False: $\Delta G > 0$, the process is spontaneous
3. State the conditions when ΔG is nonspontaneous.
4. True/False: A nonspontaneous process cannot occur with external intervention.

Answers

1. Entropy decreases
2. False
3. Case 3, Case 6, Case 7, Case 8 (Table above)
4. True

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1. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, California: University Science Books, 2005.
2. *How the Earth Was Made*. Dir. Peter Chin. A&E Home Video, 2008. DVD.
3. Petrucci, Ralph H., William S. Harwood, F. G. Herring, and Jeffry D. Madura. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, NJ: Pearson Prentice Hall, 2007. 791-796.

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SECTION OVERVIEW

10.6: The Effect of Temperature on Spontaneity

The concept of an ideal solution is fundamental to chemical thermodynamics and its applications, such as the use of colligative properties. An **ideal solution** or ideal mixture is a solution in which the enthalpy of solution ($\Delta H_{solution} = 0$) is zero; with the closer to zero the enthalpy of solution, the more "ideal" the behavior of the solution becomes. Since the enthalpy of mixing (solution) is zero, the change in Gibbs energy on mixing is determined solely by the entropy of mixing ($\Delta S_{solution}$).

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10.7: Gibbs (Free) Energy

Gibbs Free Energy

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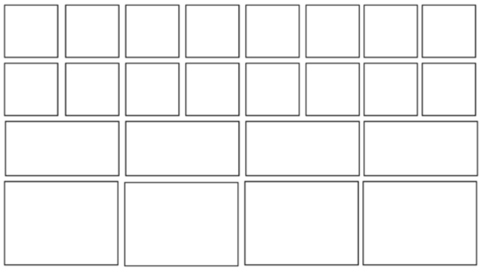
10.8: Entropy Changes in Chemical Reactions

Entropy is another important aspect of thermodynamics. Enthalpy has something to do with the energetic content of a system or a molecule. Entropy has something to do with how that energy is stored. We sometimes speak of the energy in a system as being "partitioned" or divided into various "states". How this energy is divided up is the concern of entropy.

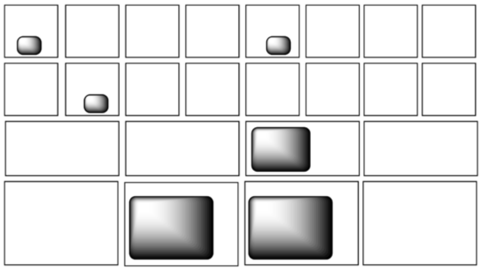
By way of analogy, picture a set of mailboxes. You may have a wall of them in your dormitory or your apartment building. The mailboxes are of several different sizes: maybe there are a few rows of small ones, a couple of rows of medium sized ones, and a row of big mailboxes on the bottom.



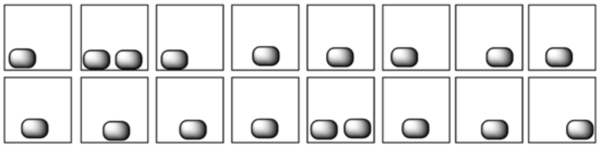
Instead of putting mail in these boxes, we're going to use them to hold little packages of energy. Later on, you might take the energy packages out of your own mailbox and use them to take a trip to the mall or the gym. But how does the mail get to your mailbox in the first place?

The energy packages don't arrive in your molecular dormitory with addresses on them. The packages come in different sizes, because they contain different amounts of energy, but other than that there is no identifying information on them.

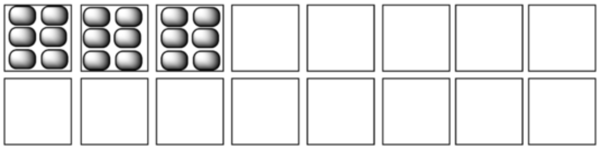
Some of the packages don't fit into some of the mailboxes, because some of the packages are too big and some of the mailboxes are smaller than the others. The energy packages need to go into mailboxes that they will fit into.



Still, there are an awful lot of mailboxes that most of the energy packages could still fit into. There needs to be some system of deciding where to put all of these packages. It turns out that, in the molecular world, there is such a system, and it follows a pretty simple rule. When a whole pile of energy packages arrive, the postmaster does her best to put one package into every mailbox. Then, when every mailbox has one, she starts putting a second one into each box, and so on.



It didn't have to be that way. It could have been the case that all the energy was simply put into the first couple of mailboxes and the rest were left empty. In other words, the rule could have been that all the energy must be sorted into the same place, instead of being spread around. But that's not how it is.



- Energy is always partitioned into the maximum number of states possible.

Entropy is the sorting of energy into different modes or states. When energy is partitioned or sorted into additional states, entropy is said to increase. When energy is bundled into a smaller number of states, entropy is said to decrease. Nature's bias is towards an increase in entropy.

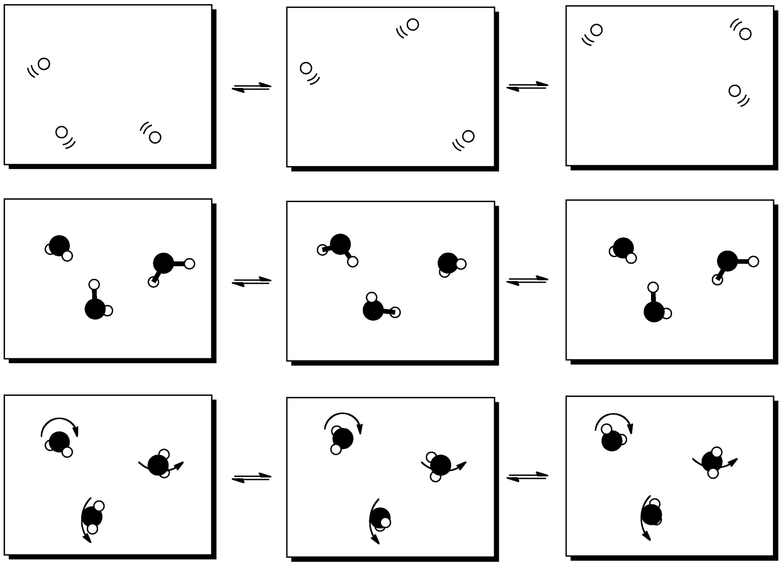
This is a fundamental law of the universe; there is no reason that can be used to explain why nature prefers high entropy to low entropy. Instead, increasing entropy is itself the basic reason for a wide range of things that happen in the universe.

Entropy is popularly described in terms of "disorder". That can be a useful idea, although it doesn't really describe what is happening energetically.

A better picture of entropy can be built by looking at how a goup of molecules might sort some energy that is added to them. In other words, what are some examples of "states" in which energy can be sorted?

If you get more energy -- maybe by eating breakfast -- one of the immediate benefits is being able to increase your physical activity. You have more energy to move around, to run, to jump. A similar situation is true with molecules.

Molecules have a variety of ways in which they can move, if they are given some energy. They can zip around; this kind of motion is usually called translation. They can tumble and roll; this kind of motion is referred to as rotation. Also, they can wiggle, letting their bonds get longer and shorter by moving individual atoms around a little bit. This type of motion is called vibration.

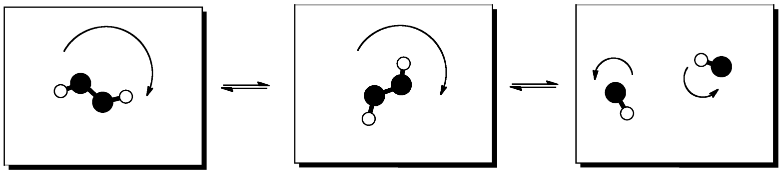


When molecules absorb extra energy, they may be able to sort the energy into rotational, vibrational and translational states. This only works with energy packages of a certain size; other packages would be sorted into other kinds of states. However, these are just a few examples of what we mean by states.

Okay, so energy is stored in states, and it is sorted into the maximum possible number of states. But how does entropy change in a reaction? We know that enthalpy may change by breaking or forming certain bonds, but how does the energy get sorted again?

The changes in internal entropy during a reaction are often very small. In other words, the energy remaining at the end of the reaction gets sorted more or less the way it was before the reaction. However, there are some very common exceptions.

The most common case in which internal entropy changes a lot is when the number of molecules involved changes between the start of the reaction and the end of the reaction. Maybe two molecules react together to form one, new molecule. Maybe one molecule splits apart to make two, new molecules.



If one molecule splits apart in the reaction, entropy generally increases. Two molecules can rotate, vibrate and translate (or tumble, wiggle and zip around) independently of each other. That means the number of states available for partitioning energy increases when one molecule splits into two.

- Entropy generally increases when a reaction produces more molecules than it started with.
- Entropy generally decreases when a reaction produces fewer molecules than it started with.

Apart from a factor like a change in the number of molecules involved, internal entropy changes are often fairly subtle. They are not as easy to predict as enthalpy changes.

Nevertheless, there may sometimes be a trade-off between enthalpy and entropy. If a reaction splits a molecule into two, it seems likely that an increase in enthalpy will be involved, so that the bond that held the two pieces together can be broken. That's not favourable. However, when that happens, we've just seen that there will be an increase in entropy, because energy can then be sorted into additional modes in the two, independent molecules.

So we have two different factors to balance. There is a tool we often use to decide which factor wins out. It's called free energy, and we will look at it next.

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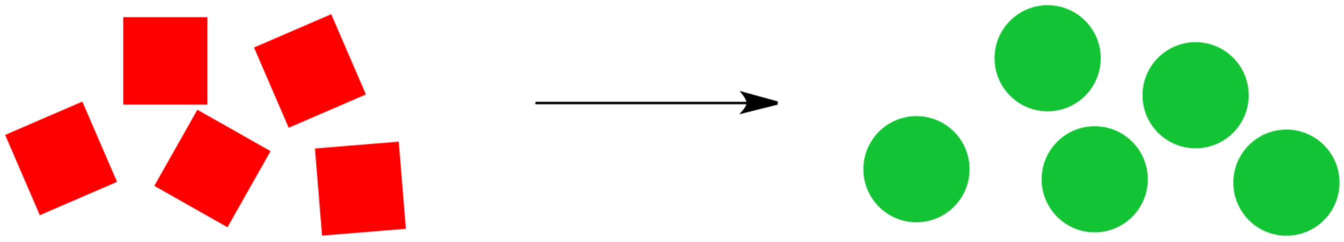
10.9: Gibbs Energy and Reactions

Entropy and enthalpy are two of the basic factors of thermodynamics. Enthalpy has something to do with the energetic content of a system or a molecule. Entropy has something to do with how that energy is stored.

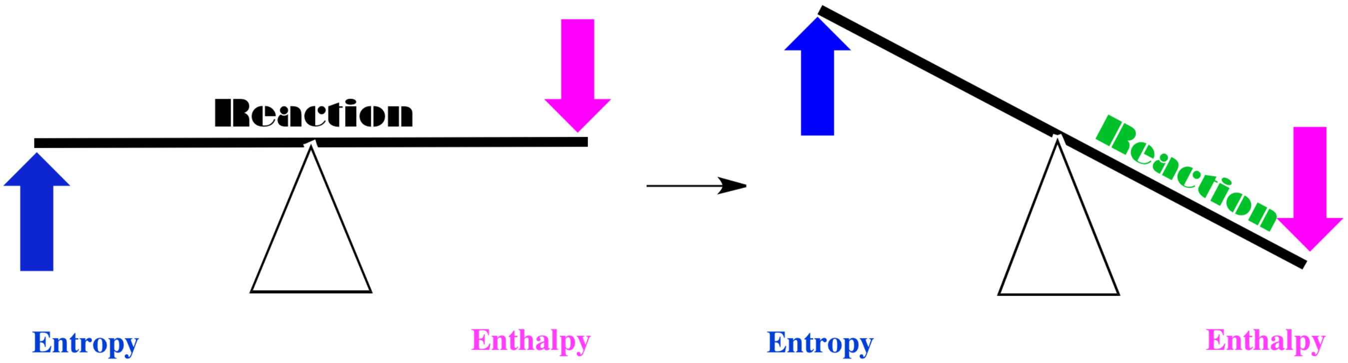
- **A reaction is favored if enthalpy decreases:** There is a bias in nature toward decreasing enthalpy in a system. Reactions can happen when enthalpy is transferred to the surroundings.
- **A reaction is favored if entropy increases:** There is also a bias in nature toward increasing entropy in a system. Reactions can happen when entropy increases.

Consider the cartoon reaction below. Red squares are being converted to green circles, provided the reaction proceeds from left to right as shown.

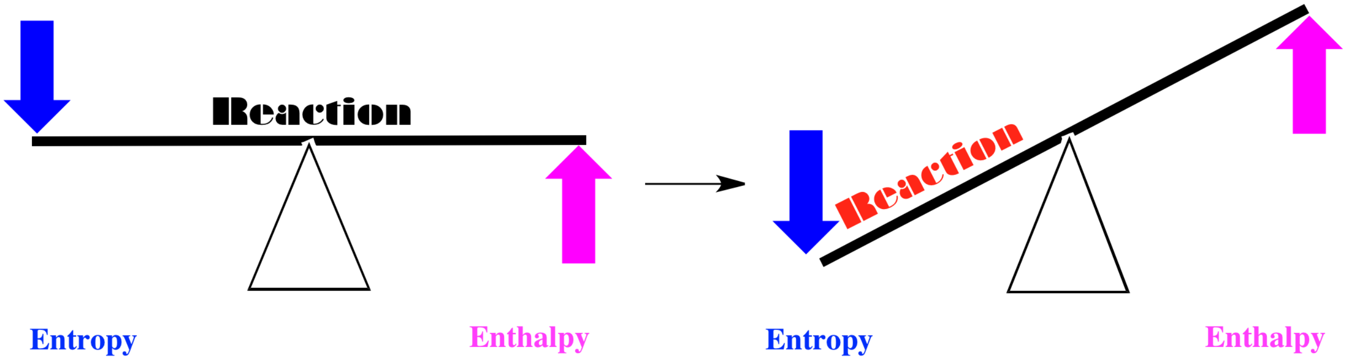


Whether or not the reaction proceeds to the right depends on the balance between enthalpy and entropy. There are several combinations possible.

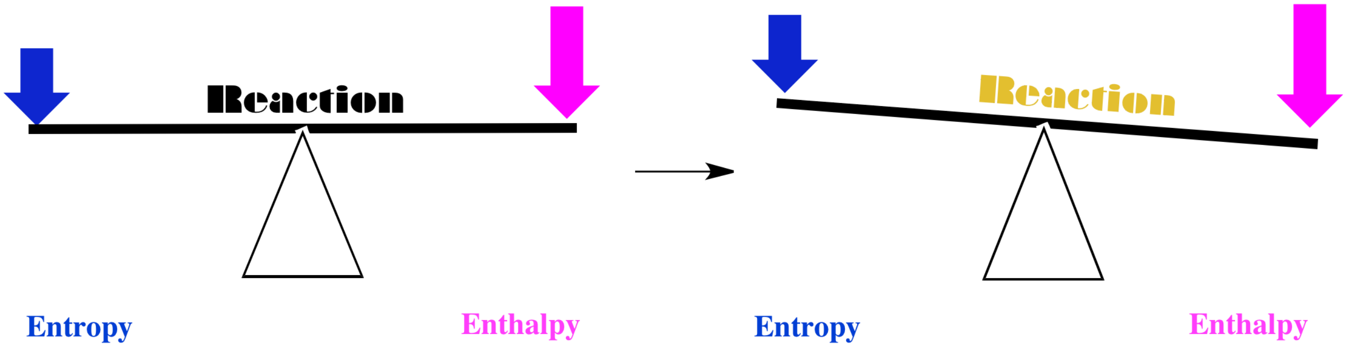
In one case, maybe entropy increases when the red squares turn into green circles, and the enthalpy decreases. If we think of the balance between these two factors, we come to a simple conclusion. Both factors tilt the balance of the reaction to the right. In this case, the red squares will be converted into green circles.



Alternatively, maybe entropy decreases when the red squares turn into green circles, and enthalpy increases. If we think of the balance between these two factors, we come to another simple conclusion. Both factors tilt the balance of the reaction to the left. In this case, the red squares will remain just as they are.



Having two factors may lead to complications. For example, what if enthalpy decreases, but so does entropy? Does the reaction happen, or doesn't it? In that case, we may need quantitation to make a decision. How much does the enthalpy decrease? How much does the entropy decrease? If the effect of the enthalpy decrease is greater than that of the entropy decrease, the reaction may still go forward.



The combined effects of enthalpy and entropy are often combined in what is called "free energy." Free energy is just a way to keep track of the sum of the two effects. Mathematically, the symbol for the internal enthalpy change is "ΔH" and the symbol for the internal entropy change is "ΔS." Free energy is symbolized by "ΔG," and the relationship is given by the following expression:

$$\Delta G = \Delta H - T\Delta S \tag{10.9.1}$$

T in this expression stands for the temperature (in Kelvin, rather than Celsius or Fahrenheit). The temperature acts as a scaling factor in the expression, putting the entropy and enthalpy on equivalent footing so that their effects can be compared directly.

How do we use free energy? It works the same way we were using enthalpy earlier (that's why the free energy has the same sign as the enthalpy in the mathematical expression, whereas the entropy has an opposite sign). If free energy decreases, the reaction can proceed. If the free energy increases, the reaction can't proceed.

- A reaction is favored if the free energy of the system decreases.
- A reaction is not favored if the free energy of the system increases.

Because free energy takes into consideration both the enthalpy and entropy changes, we don't have to consider anything else to decide if the reaction occurs. Both factors have already been taken into account.

Remember the terms "endothermic" and "exothermic" from our discussion of enthalpy. Exothermic reactions were favored (in which enthalpy decreases). Endothermic ones were not. In free energy terms, we say that exergonic reactions are favored(in which free energy decreases). Endergonic ones (in which free energy increases) are not.

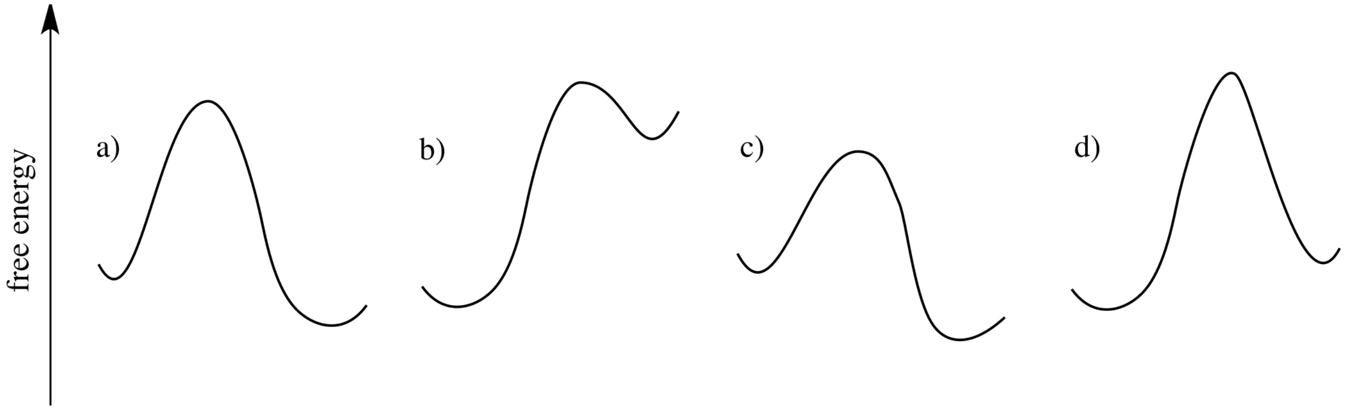
Problem TD4.1.

Imagine a reaction in which the effects of enthalpy and entropy are opposite and almost equally balanced, so that there is no preference for whether the reaction proceeds or not. Looking at the expression for free energy, how do you think the situation will change under the following conditions:

1. the temperature is very cold (0.09 K)
2. the temperature is very warm (500 K)

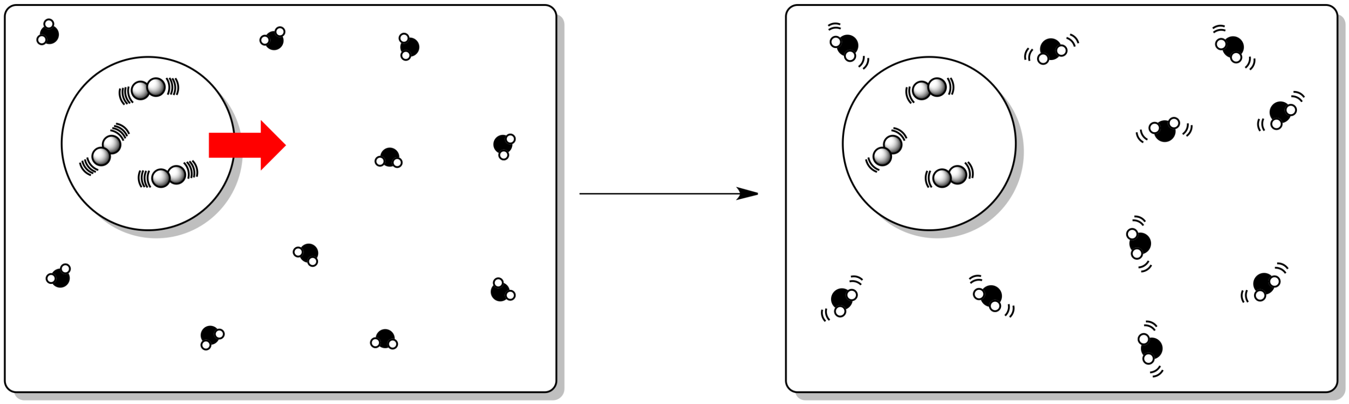
Problem TD4.2.

Which of the following reaction profiles describe reactions that will proceed? Which ones describe reactions that will not proceed?



How Entropy Rules Thermodynamics

Sometimes it is said that entropy governs the universe. As it happens, enthalpy and entropy changes in a reaction are partly related to each other. The reason for this relationship is that if energy is added to or released from the system, it has to be partitioned into new states. Thus, an enthalpy change can also have an effect on entropy.

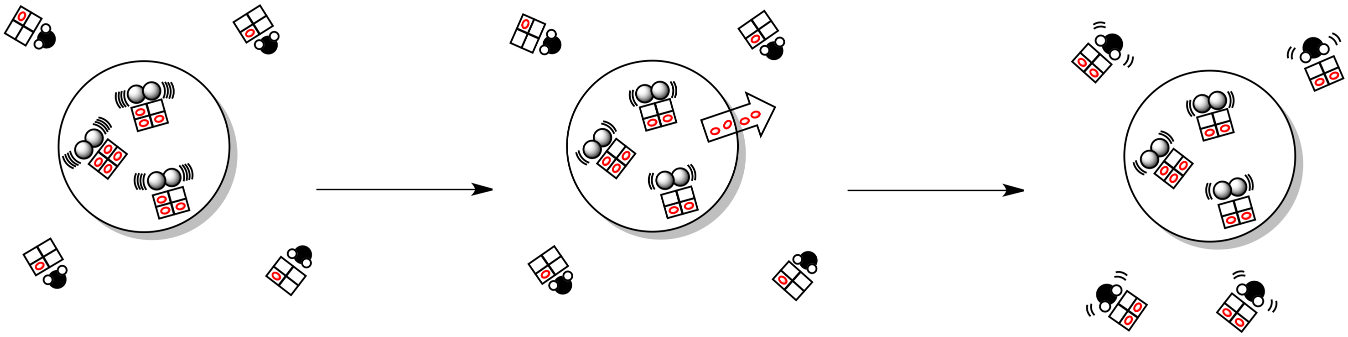


Specifically, the internal enthalpy change that we discussed earlier has an effect on the entropy of the surroundings. So far, we have just considered internal entropy changes.

- In an exothermic reaction, the external entropy (entropy of the surroundings) increases.
- In an endothermic reaction, the external entropy (entropy of the surroundings) decreases.

Free energy takes into account both the entropy of the system and the entropy changes that arise because of heat exchange with the surroundings. Together, the system and the surroundings are called "the universe". That's because the system is just everything involved in the reaction, and the surroundings are everything that isn't involved in the reaction.

Enthalpy changes in the system lead to additional partitioning of energy. We might visualize that with the mailbox analogy we used for entropy earlier. In this case, each molecule has its own set of mailboxes, into which it sorts incoming energy.



Looked at in this way, thermodynamics boils down to one major consideration, and that is the combined entropy of both the system and its surroundings (together known as the universe).

- For a reaction to proceed, the entropy of the universe must increase.

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SECTION OVERVIEW

10.10: The Dependence of Free Energy on Pressure

The concept of an ideal solution is fundamental to chemical thermodynamics and its applications, such as the use of colligative properties. An **ideal solution** or ideal mixture is a solution in which the enthalpy of solution ($\Delta H_{solution} = 0$) is zero; with the closer to zero the enthalpy of solution, the more "ideal" the behavior of the solution becomes. Since the enthalpy of mixing (solution) is zero, the change in Gibbs energy on mixing is determined solely by the entropy of mixing ($\Delta S_{solution}$).

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SECTION OVERVIEW

10.11: Gibbs Energy and Equilibrium

The concept of an ideal solution is fundamental to chemical thermodynamics and its applications, such as the use of colligative properties. An **ideal solution** or ideal mixture is a solution in which the enthalpy of solution ($\Delta H_{solution} = 0$) is zero; with the closer to zero the enthalpy of solution, the more "ideal" the behavior of the solution becomes. Since the enthalpy of mixing (solution) is zero, the change in Gibbs energy on mixing is determined solely by the entropy of mixing ($\Delta S_{solution}$).

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SECTION OVERVIEW

10.12: Free Energy and Work

The concept of an ideal solution is fundamental to chemical thermodynamics and its applications, such as the use of colligative properties. An **ideal solution** or ideal mixture is a solution in which the enthalpy of solution ($\Delta H_{solution} = 0$) is zero; with the closer to zero the enthalpy of solution, the more "ideal" the behavior of the solution becomes. Since the enthalpy of mixing (solution) is zero, the change in Gibbs energy on mixing is determined solely by the entropy of mixing ($\Delta S_{solution}$).

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CHAPTER OVERVIEW

11: Electrochemistry

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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CHAPTER OVERVIEW

Front Matter

11: Electrochemistry

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11.1: Galvanic Cells

Skills to Develop

- To understand the basics of voltaic cells
- To connect voltage from a voltaic cell to underlying REDOX chemistry

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** 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**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$Zn_{(s)} + Br_{2(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Br^-_{(aq)} \tag{11.1.1}$$

The half-reactions are as follows:

reduction half-reaction:

$$Br_{2(aq)} + 2e^- \rightarrow 2Br^-_{(aq)} \tag{11.1.2}$$

oxidation half-reaction:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \tag{11.1.3}$$

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 11.1.1). 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.

> *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**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. 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. A **galvanic (voltaic) cell** 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 cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 11.1.1). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**). 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.

Figure 11.1.1: 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.

Voltaic (Galvanic) 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:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{11.1.4}$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. 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.

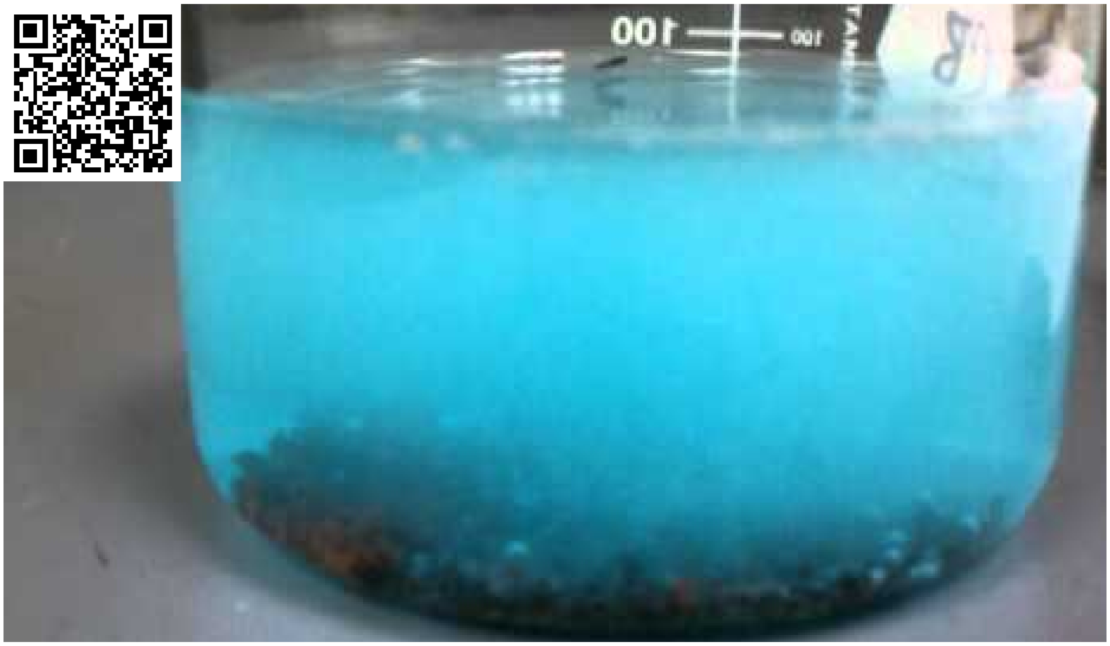

Figure 11.1.2: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give Zn^{2+}(aq) ions, while Cu^{2+}(aq) 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.

This same reaction can be carried out using the galvanic cell illustrated in Figure 11.1.3*a*. 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 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 (Figure 11.1.3*b*). 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 11.1.3: 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.

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})** 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 (Figure 11.1.3*a*). 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 11.1.1.

> *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 11.1.1

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:

$$3Sn_{(s)} + 2NO^-_{3(aq)} + 8H^+_{(aq)} \rightarrow 3Sn^{2+}_{(aq)} + 2NO_{(g)} + 4H_2O_{(l)} \tag{11.1.5}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. 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:

a. **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:

$$\text{reduction: } NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$$

$$\text{oxidation: } Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

b. 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.
c. **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 11.1.1

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:

$$2MnO^-_{4(aq)} + 5Sn^{2+}_{(aq)} + 16H^+_{(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 5Sn^{4+}_{(aq)} + 8H_2O_{(l)} \tag{11.1.6}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is positive and which is negative.

Answer:

a. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$; $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$
b. The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.
c. 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.

Cell Potential

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. Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper. 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.

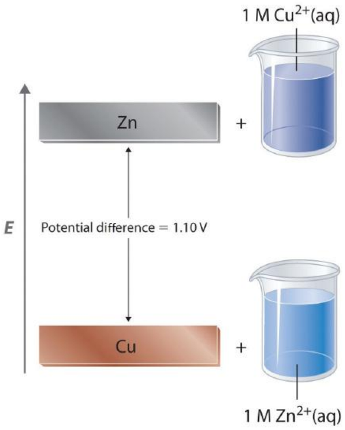

Figure 11.1.1: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic Zn and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous Zn^{2+} *ions. Much of this potential energy difference is because 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 11.1.1 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 potential** (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.

> *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 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:

$$Co_{(s)} \mid Co^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E^{\circ} = 0.59\ V \tag{11.1.7}$$

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 (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:

$$E^{\circ}{}_{cell} = E^{\circ}{}_{cathode} - E^{\circ}{}_{anode} \tag{11.1.8}$$

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 11.1.8, 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.

The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials:

$$E^{\circ}{}_{cell} = E^{\circ}{}_{cathode} - E^{\circ}{}_{anode} \tag{11.1.9}$$

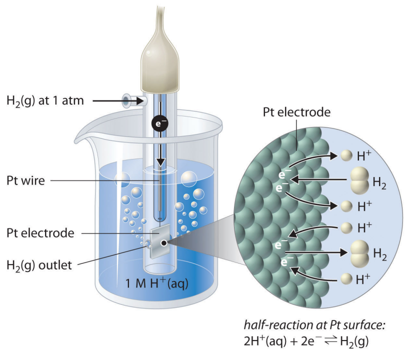

Figure 11.1.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules 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.

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)** 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 11.1.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{11.1.10}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

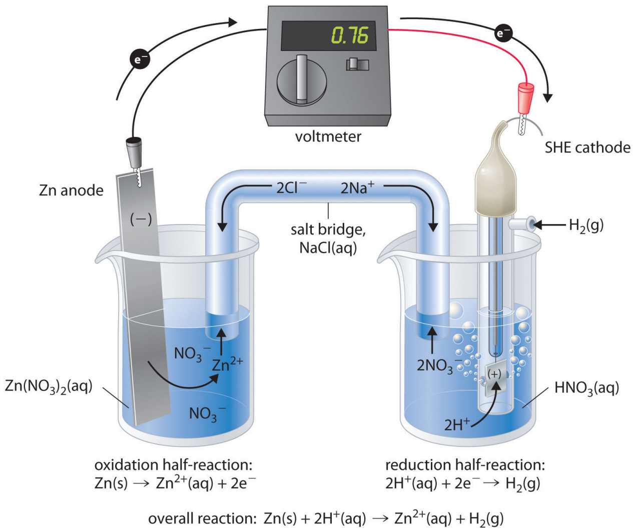

Figure 11.1.3: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is E°_{cell} = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to 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.

Figure 11.1.3 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:

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel H^+(aq, 1M) \mid H_2(g, 1atm) \mid Pt_{(s)} \tag{11.1.11}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ{}_{cathode} = 0V \tag{11.1.12}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E^\circ{}_{anode} = -0.76\ V \tag{11.1.13}$$

- overall:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{11.1.14}$$

$$E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode} = 0.76\ V \tag{11.1.15}$$

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 potential** 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

$$E^\circ{}_{cell} : 0\,V - (-0.76\,V) = 0.76\,V \tag{11.1.16}$$

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.

> *E° values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.*

Summary

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. 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.

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11.2: Standard Reduction Potential

Learning Objectives

- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

The cell potential results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is shown in Figure 17.4.1 and is called the standard hydrogen electrode (SHE). The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

$$2\,\mathrm{H^+}(aq,\ 1\ M) + 2\,\mathrm{e^-} \rightleftharpoons \mathrm{H_2}(g,\ 1\ \mathrm{atm}) \quad E^\circ = 0\ \mathrm{V}$$

$E°$ is the standard reduction potential. The superscript “°” on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). The voltage is defined as zero for all temperatures.

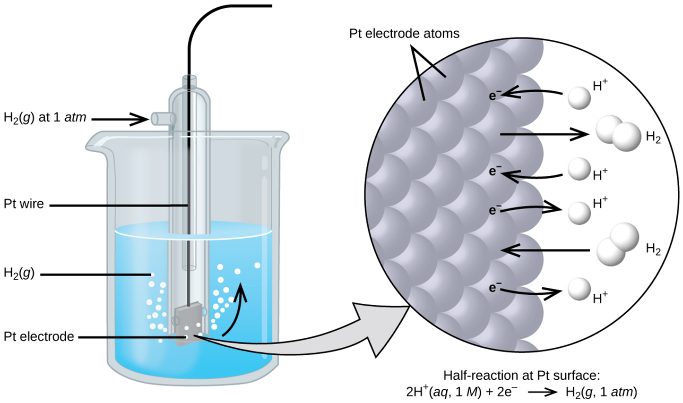

Figure 11.2.1: Hydrogen gas at 1 atm is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure 11.2.2). In cell notation, the reaction is

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,|\,\mathrm{Cu}(s)$$

Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{array}{l}\text{Anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \\ \text{Cathode (reduction): } \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu}(s) \\ \hline \text{Overall: } \mathrm{Cu^{2+}}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + \mathrm{Cu}(s)\end{array}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.34\ \mathrm{V} = E^\circ_{\mathrm{Cu^{2+}/Cu}} - E^\circ_{\mathrm{H^+/H_2}} = E^\circ_{\mathrm{Cu^{2+}/Cu}} - 0 = E^\circ_{\mathrm{Cu^{2+}/Cu}}$$

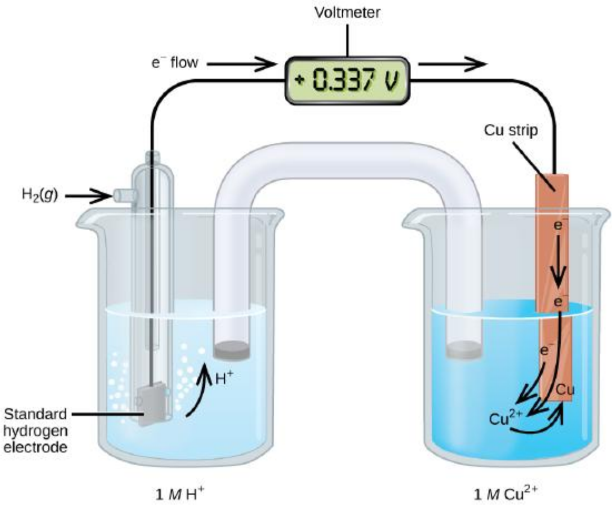

Figure 11.2.2: A galvanic cell can be used to determine the standard reduction potential of Cu^{2+}.

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in Figure 11.2.2, where

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

Electrons flow from left to right, and the reactions are

$$\begin{array}{l}\text{anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \\ \text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s) \\ \hline \text{overall: } 2\,\mathrm{Ag^+}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{Ag}(s)\end{array}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.80\ \mathrm{V} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{H^+/H_2}} = E^\circ_{\mathrm{Ag^+/Ag}} - 0 = E^\circ_{\mathrm{Ag^+/Ag}}$$

It is important to note that the potential is *not* doubled for the cathode reaction.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the standard cell potential, E°_{cell}, for any cell. For example, for the following cell:

$$\mathrm{Cu}(s)\,|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

$$\begin{array}{l}\text{anode (oxidation): } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-} \\ \text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s) \\ \hline \text{overall: } \mathrm{Cu}(s) + 2\,\mathrm{Ag^+}(aq) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{Ag}(s)\end{array}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{Cu^{2+}/Cu}} = 0.80\ \mathrm{V} - 0.34\ \mathrm{V} = 0.46\ \mathrm{V}$$

Again, note that when calculating E°_{cell}, standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in Table 11.2.1. A more complete list is provided in Tables P1 or P2.

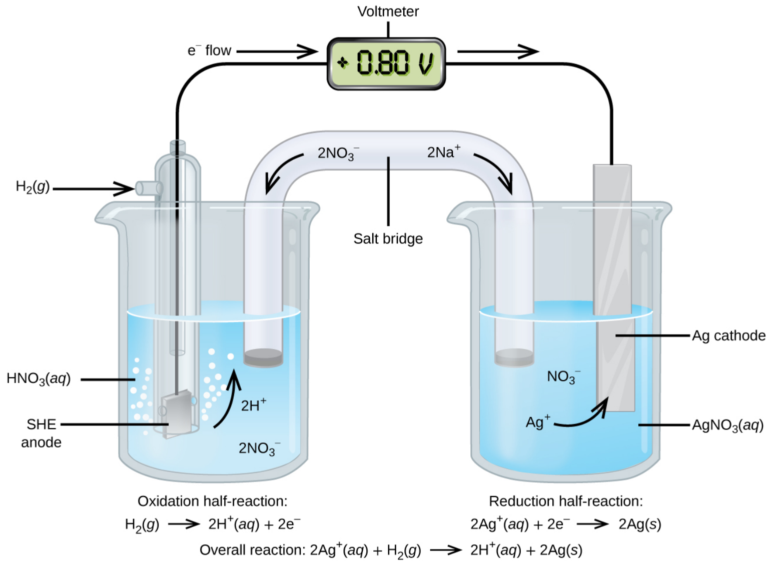

Figure 11.2.3: A galvanic cell can be used to determine the standard reduction potential of Ag^+. The SHE on the left is the anode and assigned a standard reduction potential of zero.

Table 11.2.1: Selected Standard Reduction Potentials at 25 °C

Half-Reaction	**E° (V)**
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$	+1.69
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.507
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.35827
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.558
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.5355
$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$	+0.26808
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.151
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.1262
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.1375

Half-Reaction	E° (V)
$\mathrm{Ni^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ni}(s)$	−0.257
$\mathrm{Co^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Co}(s)$	−0.28
$\mathrm{PbSO_4}(s) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Pb}(s) + \mathrm{SO_4^{2-}}(aq)$	−0.3505
$\mathrm{Cd^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cd}(s)$	−0.4030
$\mathrm{Fe^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Fe}(s)$	−0.447
$\mathrm{Cr^{3+}}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Cr}(s)$	−0.744
$\mathrm{Mn^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn}(s)$	−1.185
$\mathrm{Zn(OH)_2}(s) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Zn}(s) + 2\,\mathrm{OH^-}(aq)$	−1.245
$\mathrm{Zn^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Zn}(s)$	−0.7618
$\mathrm{Al^{3+}}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Al}(s)$	−1.662
$\mathrm{Mg^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mg}(s)$	−2.372
$\mathrm{Na^{+}}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Na}(s)$	−2.71
$\mathrm{Ca^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ca}(s)$	−2.868
$\mathrm{Ba^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ba}(s)$	−2.912
$\mathrm{K^{+}}(aq) + \mathrm{e^-} \longrightarrow \mathrm{K}(s)$	−2.931
$\mathrm{Li^{+}}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Li}(s)$	−3.04

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions.

✓ Example 11.2.1: Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of $\mathrm{Au^{3+}/Au}$ and $\mathrm{Ni^{2+}/Ni}$ half-cells? Identify the oxidizing and reducing agents.

Solution

Using Table $11.2.1$, the reactions involved in the galvanic cell, both written as reductions, are

$$\mathrm{Au^{3+}}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Au}(s) \qquad E^\circ_{\mathrm{Au^{3+}/Au}} = +1.498\ \mathrm{V}$$

$$\mathrm{Ni^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ni}(s) \qquad E^\circ_{\mathrm{Ni^{2+}/Ni}} = -0.257\ \mathrm{V}$$

Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

$$\text{Anode (oxidation): } \mathrm{Ni}(s) \longrightarrow \mathrm{Ni^{2+}}(aq) + 2\,\mathrm{e^-} \qquad E^\circ_{\text{anode}} = E^\circ_{\mathrm{Ni^{2+}/Ni}} = -0.257\ \mathrm{V}$$

$$\text{Cathode (reduction): } \mathrm{Au^{3+}}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Au}(s) \qquad E^\circ_{\text{cathode}} = E^\circ_{\mathrm{Au^{3+}/Au}} = +1.498\ \mathrm{V}$$

The least common factor is six, so the overall reaction is

$$3\,\mathrm{Ni}(s) + 2\,\mathrm{Au^{3+}}(aq) \longrightarrow 3\,\mathrm{Ni^{2+}}(aq) + 2\,\mathrm{Au}(s)$$

The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.498\ \mathrm{V} - (-0.257\ \mathrm{V}) = 1.755\ \mathrm{V}$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au^{3+} is reduced, so it is the oxidizing agent.

Exercise 11.2.1

A galvanic cell consists of a Mg electrode in 1 *M* $Mg(NO_3)_2$ solution and a Ag electrode in 1 *M* $AgNO_3$ solution. Calculate the standard cell potential at 25 °C.

Answer

$$\mathrm{Mg}(s) + 2\,\mathrm{Ag}^+(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) + 2\,\mathrm{Ag}(s) \qquad E^\circ_{\text{cell}} = 0.7996\ \mathrm{V} - (-2.372\ \mathrm{V}) = 3.172\ \mathrm{V}$$

Summary

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, $E°$, for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 *M* for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction for the reaction at the cathode. When calculating the standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

Key Equations

- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

Glossary

standard cell potential (E°_{cell})

the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

standard hydrogen electrode (SHE)

the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

standard reduction potential (*E*°)

the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

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11.3: Cell Potential, Electrical Work, and Gibbs Energy

Learning Objectives

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of $\mathrm{Co(s)}$ with $\mathrm{Ni^{2+}(aq)}$ to form $\mathrm{Ni(s)}$ and $\mathrm{Co^{2+}(aq)}$ occurs spontaneously, but if we reduce the concentration of $\mathrm{Ni^{2+}}$ by a factor of 100, so that $[\mathrm{Ni^{2+}}]$ 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 & Gibbs 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)**, 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)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ \mathrm{J}}{1\ \mathrm{V}} = 1\ \mathrm{C} = \mathrm{A \cdot s}$$

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)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$\begin{aligned} F &= (1.60218 \times 10^{-19}\ \mathrm{C}) \left(\frac{6.02214 \times 10^{23}\ J}{1\ \mathrm{mol\ e^-}}\right) \\ &= 9.64833212 \times 10^{4}\ \mathrm{C/mol\ e^-} \\ &\simeq 96,485\ J/(\mathrm{V \cdot mol\ e^-}) \end{aligned}$$

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.

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; 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 ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{11.3.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°$_{cell}$.

Example 11.3.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table P2, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG^o for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E^o, write the overall reaction and calculate E°_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Then use Equation 11.3.1 to calculate ΔG^o. If ΔG^o 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^o. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E^o values:

$$\begin{array}{lll} \text{cathode:} & \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} & E^\circ_{\text{cathode}} = 1.36\text{ V} \\ \text{anode:} & \mathrm{2Br^-(aq) \rightarrow Br_2(aq) + 2e^-} & E^\circ_{\text{anode}} = 1.09\text{ V} \end{array}$$

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^o is not affected:

$$\begin{array}{lll} \text{cathode:} & \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} & E^\circ_{\text{cathode}} = 1.36\text{ V} \\ \text{anode:} & \mathrm{6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-} & E^\circ_{\text{anode}} = 1.09\text{ V} \\ \hline \text{overall:} & \mathrm{Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)} & E^\circ_{\text{cell}} = 0.27\text{ V} \end{array}$$

B

We can now calculate ΔG° using Equation 11.3.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned} \Delta G^\circ &= -(n)(F)(E^\circ_{\text{cell}}) \\ &= -(6\text{ mole})[96,485\text{ J}/(\text{V}\cdot\text{mol})(0.27\text{ V})] \\ &= -15.6\ \times 10^4\text{ J} \\ &= -156\text{ kJ/mol }\mathrm{Cr_2O_7^{2-}} \end{aligned}$$

Thus ΔG^o is −168 kJ/mol for the reaction as written, and the reaction is spontaneous.

Exercise 11.3.1

Use the data in Table P2 to calculate ΔG^o for the reduction of ferric ion by iodide:

$$\mathrm{2\,Fe^{3+}(aq) + 2\,I^-(aq) \rightarrow 2\,Fe^{2+}(aq) + I_2(s)}$$

> Is the reaction spontaneous?
>
> **Answer**
>
> −44 kJ/mol I_2; yes

Potentials for the Sums of Half-Reactions

Although Table P2 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 $\mathrm{Fe^{3+}(aq)}$ to $\mathrm{Fe(s)}$ is not listed in the table, but two related reductions are given:

$$\mathrm{Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)} \quad E^\circ = +0.77V$$

$$\mathrm{Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)} \quad E^\circ = -0.45V$$

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^o is not a state function. However, because ΔG^o is a state function, the sum of the ΔG^o values for the individual reactions gives us ΔG^o for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E^o for the overall half-reaction, we first must add the values of $\Delta G^o (= -nFE^o)$ for each individual half-reaction to obtain ΔG^o for the overall half-reaction:

$$\begin{aligned} &\mathrm{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)} && \Delta G^\circ = -(1)(F)(0.77\text{ V}) \\ &\mathrm{Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)} && \Delta G^\circ = -(2)(F)(-0.45\text{ V}) \\ &\mathrm{Fe^{3+}(aq) + 3\,e^- \rightarrow Fe(s)} && \Delta G^\circ = [-(1)(F)(0.77\text{ V})] + [-(2)(F)(-0.45\text{ V})] \end{aligned}$$

Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^\circ = F[(-0.77V) + (-2)(-0.45V)] = F(0.13V)$$

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 11.3.1 and solving for E^o gives the following:

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ F(0.13\text{ V}) &= -(3)(F)(E^\circ_{\text{cell}}) \\ E^\circ &= -\frac{0.13\text{ V}}{3} = -0.043\text{ V} \end{aligned}$$

This value of E^o 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.

> *Values of E^o for half-reactions cannot be added to give E^o for the sum of the half-reactions; only values of $\Delta G^o = -nFE^\circ_{cell}$ for half-reactions can be added.*

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, 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:

$$\Delta G^\circ = -RT \ln K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 11.3.1), we can write

$$-nFE^\circ_{cell} = -RT \ln K$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right)\ln K \tag{11.3.2}$$

For $T = 298\ K$, Equation 11.3.2can be simplified as follows:

$$\begin{aligned} E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right)\ln K \\ &= \left[\frac{[8.314\ \text{J}/(\text{mol}\cdot\text{K})(298\ \text{K})]}{n[96,485\ \text{J}/(\text{V}\cdot\text{mol})]}\right] 2.303 \log K \\ &= \left(\frac{0.0592\ \text{V}}{n}\right)\log K \end{aligned} \tag{11.3.3}$$

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 11.3.2

Use the data in Table P2 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^o_{cell}.
B. Determine the number of electrons transferred in the overall reaction. Use Equation 11.3.3to solve for log K and then K.

Solution

A The relevant half-reactions and potentials from Table P2 are as follows:

cathode:	$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	$E^\circ_{\text{cathode}} = 1.69\ \text{V}$
anode:	$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$	$E^\circ_{\text{anode}} = -0.36\ \text{V}$
overall:	$Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$	$E^\circ_{\text{cell}} = 2.05\ \text{V}$

B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 11.3.3for log K and inserting the values of n and E^o,

$$\begin{aligned} \log K &= \frac{nE^\circ}{0.0591\ \text{V}} = \frac{2(2.05\ \text{V})}{0.0591\ \text{V}} = 69.37 \\ K &= 2.3 \times 10^{69} \end{aligned}$$

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 11.3.2

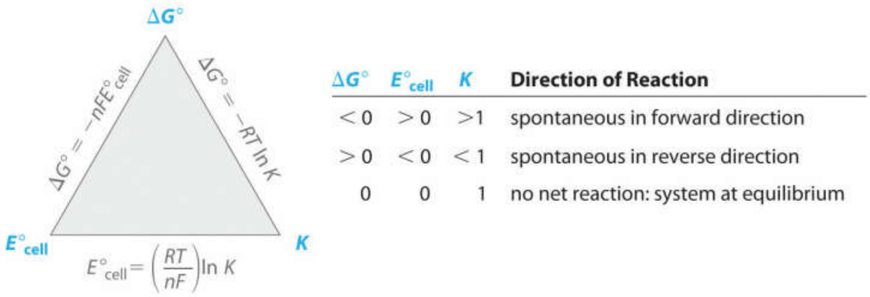
Use the data in Table P2 to calculate the equilibrium constant for the reaction of $Sn^{2+}(aq)$ with oxygen to produce $Sn^{4+}(aq)$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2\,Sn^{2+}(aq) + O_2(g) + 4\,H^+(aq) \rightleftharpoons 2\,Sn^{4+}(aq) + 2\,H_2O(l)$$

Answer

5.7×10^{72}

Figure 11.3.1 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 (ΔG° < 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.



ΔG°	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 11.3.1: 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, ΔG°, 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 ΔG° and $E°_{cell}$ and the magnitude of K determine the direction of spontaneous reaction under standard conditions. (CC BY-NC-SA; Anonymous by request)

If ΔG is less than zero, E^o is greater than zero and K is greater than 1 then the direction of the reaction is spontaneous in forward direction. If ΔG is greater than zero, E^o is less than zero and K is less than one then the direction of reaction is spontaneous in reverse direction. If ΔG is zero, E is zero and K is one that there is no net reaction and the system is at equilibrium .

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 ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, $E°_{cell}$ and K are also related. Large equilibrium constants correspond to large positive values of E°.

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11.4: Dependence of Cell Potential on Concentration

Learning Objectives

- Relate cell potentials to Gibbs energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall that the actual free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{11.4.1}$$

We also know that $\Delta G = -nFE_{cell}$ (under non-standard conditions) and $\Delta G^o = -nFE^o_{cell}$ (under standard conditions). Substituting these expressions into Equation 11.4.1, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT \ln Q \tag{11.4.2}$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q \tag{11.4.3}$$

Equation 11.4.3 is called the **Nernst equation**, 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 ($\Delta G = 0$), then Equation 11.4.3 reduces to Equation 11.4.4 and 11.4.5 because $Q = K$, and there is no net transfer of electrons (i.e., E_{cell} = 0).

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln K = 0 \tag{11.4.4}$$

since

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{11.4.5}$$

Substituting the values of the constants into Equation 11.4.3 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):

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right) \log Q \tag{11.4.6}$$

The Power of the Nernst Equation

The Nernst Equation (11.4.3) 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 11.4.6 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 11.4.6 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 11.4.1

The following reaction proceeds spontaneously under standard conditions because E°$_{cell}$ > 0 (which means that ΔG° < 0):

$$2\,\mathrm{Ce^{4\,+}(aq)} + 2\,\mathrm{Cl^{-}(aq)} \longrightarrow 2\,\mathrm{Ce^{3\,+}(aq)} + \mathrm{Cl_2(g)} \qquad E^{\circ}_{cell} = 0.25\;V$$

Calculate E_{cell} 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, $P_{\mathrm{Cl_2}}$ = 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 11.4.6 instead of Equation 11.4.3. 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 11.4.6,

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log Q \\ &= 0.25\text{ V} - \left(\frac{0.0591\text{ V}}{2}\right)\log\left(\frac{[\text{Ce}^{3+}]^2 P_{\text{Cl}_2}}{[\text{Ce}^{4+}]^2[\text{Cl}^-]^2}\right) \\ &= 0.25\text{ V} - [(0.0296\text{ V})(8.37)] = 0.00\text{ V} \end{aligned}$$

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 11.4.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4\,\mathrm{MnO_2(s)} + 3\,\mathrm{O_2(g)} + 4\,\mathrm{OH^{-}(aq)} \longrightarrow 4\,\mathrm{MnO_4^{-}(aq)} + 2\,\mathrm{H_2O(l)} \quad E^{\circ}{}_{cell} = -0.20\;V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, $P_{\mathrm{O_2}}$ = 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 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:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E^{\circ}cell = 1.10V \tag{11.4.7}$$

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 11.4.6:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \tag{11.4.8}$$

$$= 1.10\text{ V} - \left(\frac{0.0591\text{ V}}{2}\right)\log\left(\frac{1.0\times10^{-6}}{1.0}\right) = 1.28\text{ V} \tag{11.4.9}$$

Thus the initial voltage is greater than E° because $Q < 1$. As the reaction proceeds, $[\text{Zn}^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[\text{Cu}^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$, so Q = 1 and $E_{\text{cell}} = E°_{\text{cell}}$. Beyond this point, $[\text{Zn}^{2+}]$ will continue to increase in the anode compartment, and $[\text{Cu}^{2+}]$ 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+}), $Q = 1.0 \times 10^{6}$, and the cell potential will be reduced to 0.92 V.

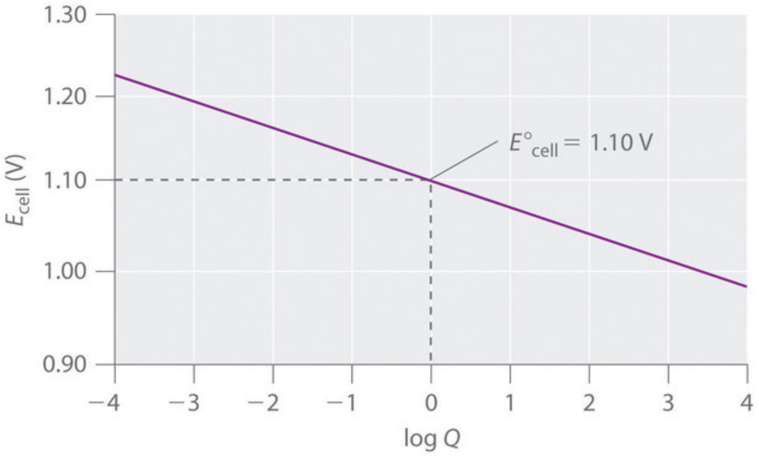

Figure 11.4.1: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than $E°_{\text{cell}}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$, log Q = 0 and $E_{\text{cell}} = E°_{\text{cell}}$ = 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.

The variation of E_{cell} with log Q over this range is linear with a slope of −0.0591/n, as illustrated in Figure 11.4.1. 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 $E_{\text{cell}} = 0$ is calculated as follows:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log Q = 0 \tag{11.4.10}$$

$$E^{\circ} = \left(\frac{0.0591\text{ V}}{n}\right)\log Q \tag{11.4.11}$$

$$\log Q = \frac{E^{\circ}n}{0.0591\text{ V}} = \frac{(1.10\text{ V})(2)}{0.0591\text{ V}} = 37.23 \tag{11.4.12}$$

$$Q = 10^{37.23} = 1.7\times10^{37} \tag{11.4.13}$$

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.

The Nernst Equation: The Nernst Equation (opens in new window) [youtu.be]

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$\mathrm{Ag(s)} \mid \mathrm{Ag}^+(aq, 0.010\ M) \,||\, \mathrm{Ag}^+(aq, 1.0\ M) \mid \mathrm{Ag(s)} \tag{11.4.14}$$

cathode:

$$\mathrm{Ag}^+(aq, 1.0\ M) + \mathrm{e}^- \rightarrow \mathrm{Ag(s)} \tag{11.4.15}$$

anode:

$$\mathrm{Ag(s)} \rightarrow \mathrm{Ag}^+(aq, 0.010\ M) + \mathrm{e}^- \tag{11.4.16}$$

Overall

$$\mathrm{Ag}^+(aq, 1.0\ M) \rightarrow \mathrm{Ag}^+(aq, 0.010\ M) \tag{11.4.17}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0 - \left(\frac{0.0591\ \text{V}}{1}\right)\log\left(\frac{0.010}{1.0}\right) \\ &= 0.12\ \text{V} \end{aligned}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell} = 0$).

✓ Example 11.4.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.
B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$\mathrm{Mn}^{2+}(aq, 2.0\,M) \rightarrow \mathrm{Mn}^{2+}(aq, 5.2 \times 10^{-2}\,M)$$

B For the reduction of Mn^{2+}(aq) to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 11.4.6:

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log Q \\ &= 0\text{ V} - \left(\frac{0.0591\text{ V}}{2}\right)\log\left(\frac{5.2\times10^{-2}}{2.0}\right) \\ &= 0.047\text{ V} \end{aligned}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

Exercise 11.4.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$\mathrm{O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)}$$

What will be the potential when the circuit is closed?

Answer

0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned previously, solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

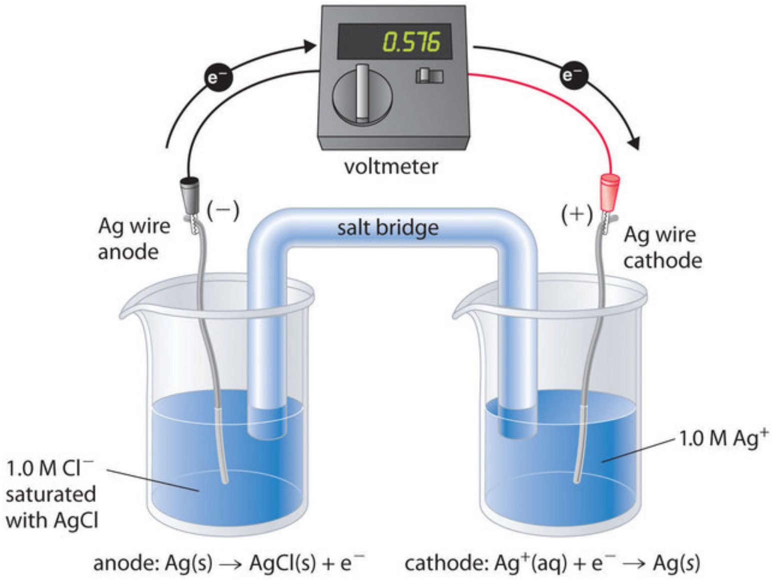

Figure 11.4.1: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M $Cl^−$ solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ between the two cells can be used to determine K_{sp}. (CC BY-NC-SA; Anonymous by request)

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 11.4.1, which is designed to measure the solubility product of silver chloride:

$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}].$$

In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M $Cl^−$ solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by $[Cl^−]$ and substituting:

$$\begin{aligned}[\mathrm{Ag^+}] &= \frac{K_{sp}}{[\mathrm{Cl^-}]} \\ &= \frac{K_{sp}}{1.0} = K_{sp}.\end{aligned}$$

The overall cell reaction is as follows:

$$\mathrm{Ag^+(aq, concentrated)} \rightarrow \mathrm{Ag^+(aq, dilute)}$$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$\begin{aligned}E_{\text{cell}} &= 0\text{ V} - \left(\frac{0.0591\text{ V}}{1}\right)\log\left(\frac{[\mathrm{Ag^+}]_{\text{dilute}}}{[\mathrm{Ag^+}]_{\text{concentrated}}}\right) \\ &= -0.0591\text{ V}\,\log\left(\frac{K_{\text{sp}}}{1.0}\right) \\ &= -0.0591\text{ V}\,\log K_{\text{sp}}\end{aligned} \tag{11.4.18}$$

By closing the circuit, we can measure the potential caused by the difference in [Ag+] in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 11.4.18for K_{sp},

$$\begin{aligned}\log K_{\text{sp}} &= \frac{-E_{\text{cell}}}{0.0591\text{ V}} = \frac{-0.580\text{ V}}{0.0591\text{ V}} = -9.81 \\ K_{\text{sp}} &= 1.5 \times 10^{-10}\end{aligned}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

✓ Example 11.4.3: Solubility of lead(II) sulfate

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure 11.4.1, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A. From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.
B. Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation ??? and solve for K_{sp}.

Solution

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of Pb^{2+} and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$\begin{aligned}[\mathrm{Pb}^{2+}][\mathrm{SO}_4^{2-}] &= K_{\mathrm{sp}} \\ [\mathrm{Pb}^{2+}] &= \frac{K_{\mathrm{sp}}}{[\mathrm{SO}_4^{2-}]} = \frac{K_{\mathrm{sp}}}{1.0\ \mathrm{M}} = K_{\mathrm{sp}}\end{aligned}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

$$Pb^{2+}(aq,\ concentrated) \rightarrow Pb^{2+}(aq,\ dilute)$$

so

$$\begin{aligned}E_{\mathrm{cell}} &= E^{\circ}_{\mathrm{cell}} - \left(\frac{0.0591}{n}\right)\log Q \\ 0.230\ \mathrm{V} &= 0\ \mathrm{V} - \left(\frac{0.0591\ \mathrm{V}}{2}\right)\log\left(\frac{[\mathrm{Pb}^{2+}]_{\mathrm{dilute}}}{[\mathrm{Pb}^{2+}]_{\mathrm{concentrated}}}\right) = -0.0296\ \mathrm{V}\log\left(\frac{K_{\mathrm{sp}}}{1.0}\right) \\ -7.77 &= \log K_{\mathrm{sp}} \\ 1.7\times10^{-8} &= K_{\mathrm{sp}}\end{aligned}$$

? Exercise 11.4.3

A concentration cell similar to the one described in Example 11.4.3 contains a 1.0 M solution of lanthanum nitrate $[La(NO_3)_3]$ in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer

5.7×10^{-17}

Using Cell Potentials to Measure Concentrations

Another 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 11.4.3, 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 below.

Example 11.4.4: Measuring pH

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. The pressure of hydrogen gas is 1.0 atm, but [H$^+$] in the second compartment is unknown. The cell diagram is as follows:

$$\text{Zn(s)}|\text{Zn}^{2+}(aq, 1.0\,M)||\text{H}^+(aq, ?\,M)|\text{H}_2(g, 1.0\,atm)|Pt(s)$$

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 P2):

$$\text{Zn(s)} + 2\text{H}^{2+}\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + \text{H}_2\text{(g)} \quad E°=0.76 \text{ V}$$

B By substituting the given values into the simplified Nernst equation (Equation 11.4.6), we can calculate [H$^+$] under nonstandard conditions:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591 \text{ V}}{n}\right)\log\left(\frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2}\right) \\ 0.26 \text{ V} &= 0.76 \text{ V} - \left(\frac{0.0591 \text{ V}}{2}\right)\log\left(\frac{(1.0)(1.0)}{[\text{H}^+]^2}\right) \\ 16.9 &= \log\left(\frac{1}{[\text{H}^+]^2}\right) = \log[\text{H}^+]^{-2} = (-2)\log[\text{H}^+] \\ 8.46 &= -\log[\text{H}^+] \\ 8.5 &= \text{pH} \end{aligned}$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise 11.4.4

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 ($E°_{\text{cathode}}$ = 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:

$$Pb_{(s)} \mid Pb^{2+}(aq, ?M) \parallel H^+(aq), 1.0M \mid O_2(g, 1.0atm) \mid Pt_{(s)}$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table P2 to determine the concentration of Pb^{2+} in the groundwater.

Answer

$$1.2 \times 10^{-9}\ M$$

Summary

The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution. 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 ΔG = 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.

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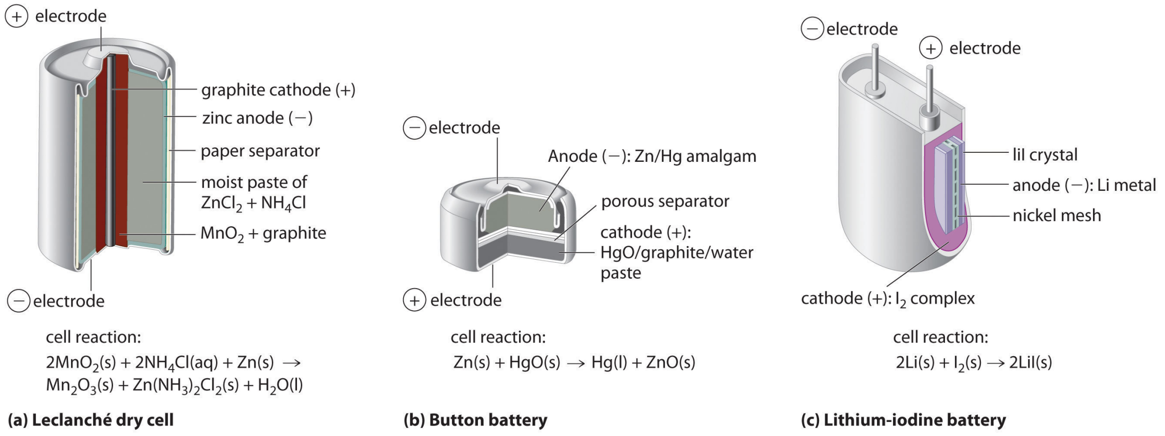
11.5: Batteries

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure 11.5.1). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.



(a) Leclanché dry cell **(b) Button battery** **(c) Lithium-iodine battery**

Figure 11.5.1: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a “wet cell,” in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

> The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a “wet cell”: the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure 11.5.1). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2\,MnO_2(s) + 2\,NH_4^+(aq) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l)$$

- anode (oxidation):

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$$

The $\mathrm{Zn^{2+}}$ ions formed by the oxidation of $\mathrm{Zn(s)}$ at the anode react with $\mathrm{NH_3}$ formed at the cathode and $\mathrm{Cl^-}$ ions present in solution, so the overall cell reaction is as follows:

- overall reaction:

$$\mathrm{2\,MnO_2(s) + 2\,NH_4Cl(aq) + Zn(s) \longrightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l)} \tag{11.5.1}$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the $\mathrm{MnO_2}$ that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with $\mathrm{NH_4Cl}$ in the electrolyte, causing the case to corrode and allowing the contents to leak out.

Close up of a hand holding one double <span class=
AA
battery" style="width: 287px; height: 215px;" width="287px" height="215px" data-cke-saved-src="/@api/deki/files/16647/battery.jpg" src="/@api/deki/files/16647/battery.jpg" data-quail-id="34">

Source: Photo courtesy of Mitchclanky2008, www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$\mathrm{2\,MnO_2(s) + H_2O(l) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,OH^-(aq)}$$

- anode (oxidation):

$$\mathrm{Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-}$$

- overall reaction:

$$\mathrm{Zn(s) + 2\,MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)}$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or $\mathrm{Ag_2O}$ as the oxidant rather than $\mathrm{MnO_2}$ in Figure $11.5.1b$).

Button batteries. (Gerhard H Wrodnigg via Wikipedia)

The cathode, anode and overall reactions and cell output for these two types of button batteries are as follows (two half-reactions occur at the anode, but the overall oxidation half-reaction is shown):

- cathode (mercury battery):

$$\mathrm{HgO(s) + H_2O(l) + 2\,e^- \longrightarrow Hg(l) + 2\,OH^-(aq)}$$

- Anode (mercury battery):

$$\mathrm{Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-}$$

- overall reaction (mercury battery):

$$\mathrm{Zn(s) + 2\,HgO(s) \longrightarrow 2\,Hg(l) + ZnO(s)}$$

  with $E_{cell} = 1.35\,V$.
- cathode reaction (silver battery):

$$\mathrm{Ag_2O(s) + H_2O(l) + 2\,e^- \longrightarrow 2\,Ag(s) + 2\,OH^-(aq)}$$

- anode (silver battery):

$$\mathrm{Zn} + 2\,\mathrm{OH^-} \longrightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2\,\mathrm{e^-}$$

- Overall reaction (silver battery):

$$\mathrm{Zn(s)} + 2\,\mathrm{Ag_2O(s)} \longrightarrow 2\,\mathrm{Ag(s)} + \mathrm{ZnO(s)}$$

  with $E_{cell} = 1.6\,V$.

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually “dry.” They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of $\mathrm{Li^+}$ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-{}_{(LiI)} \tag{11.5.2}$$

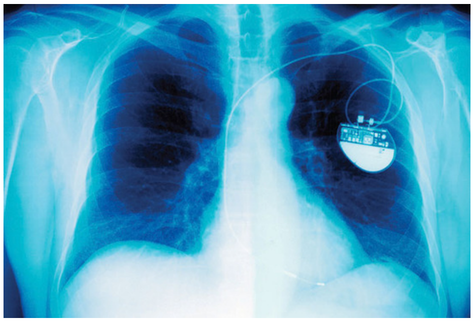
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{11.5.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{11.5.4}$$

with $E_{cell} = 3.5\,V$



Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure $11.5.1$, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure $11.5.2$, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

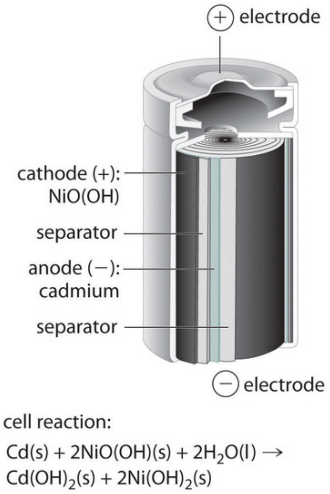


Figure 11.5.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a $NiCad$ battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{11.5.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{11.5.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{11.5.7}$$

$$E_{cell} = 1.4V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

\[NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \label{Eq16} \]

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

> Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells.

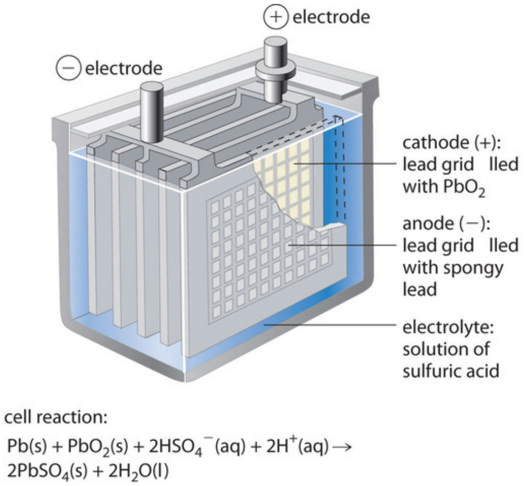


Figure 11.5.3: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As shown in Figure $11.5.3$, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):

\[PbO_{2(s)} + HSO^−_{4(aq)} + 3H^+_{(aq)} + 2e^− \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \label{Eq17} \]

with $E^\circ_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{11.5.8}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{11.5.9}$$

and $E^\circ_{cell} = 2.041\ V$

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.

A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{11.5.10}$$

This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

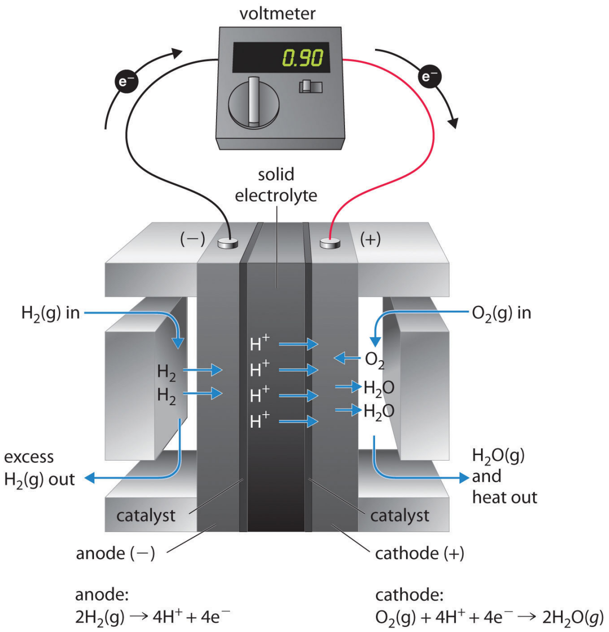


Figure 11.5.4: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of H_2(g) and O_2(g), as illustrated in Figure 11.5.4 The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{11.5.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{11.5.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{11.5.13}$$

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

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11.6: Corrosion

Learning Objectives

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

> *Corrosion is a REDOX process.*

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($\mathrm{Fe_2O_3 \cdot xH_2O}$), commonly known as rust, that does not provide a tight protective film (Figure $11.6.1$). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil will not rust because of the absence of water even if the solvent is saturated with oxygen.

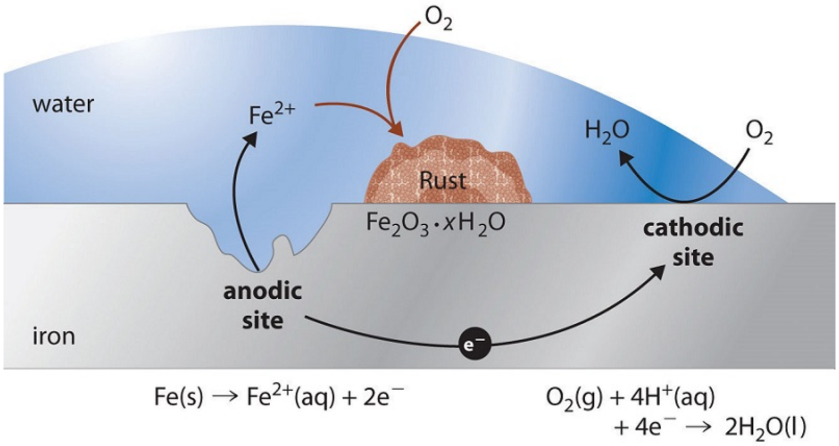

Figure 11.6.1: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to Fe^{2+}(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3 \cdot xH_2O$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen. (CC BY-NC-SA; anonymous)

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$\mathrm{O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)}$$

with $E^o_{SRP} = 1.23\ V$.

- at anode:

$$\mathrm{Fe(s)} \longrightarrow \mathrm{Fe^{2+}(aq)} + 2\,\mathrm{e^-}$$

  with $E^o_{SRP} = -0.45\ V$.
- overall:

$$2\,\mathrm{Fe(s)} + \mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} \longrightarrow 2\,\mathrm{Fe^{2+}(aq)} + 2\,\mathrm{H_2O(l)} \tag{11.6.1}$$

  with $E^o_{cell} = 1.68\ V$.

The $\mathrm{Fe^{2+}}$ ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing $\mathrm{Fe^{3+}}$, as represented in the following equation:

$$4\,\mathrm{Fe^{2+}(aq)} + \mathrm{O_2(g)} + (2 + 4\,x)\mathrm{H_2O} \rightarrow 2\,\mathrm{Fe_2O_3} \cdot x\mathrm{H_2O} + 4\,\mathrm{H^+(aq)} \tag{11.6.2}$$

The sign and magnitude of E^o_{cell} for the corrosion process (Equation 11.6.1) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car’s metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 11.6.2).

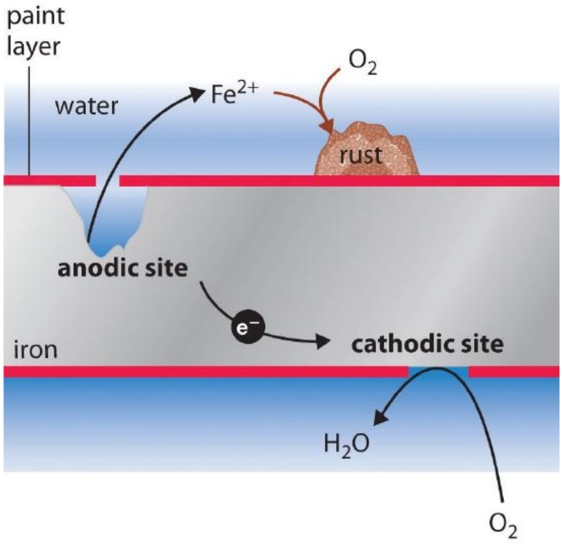

Figure 11.6.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the “tin cans” that hold soups and other foods are actually consist of steel container that is coated with a thin layer of tin. While neither chromium nor tin metals are intrinsically resistant to corrosion, they both form protective oxide coatings that hinder access of oxygen and water to the underlying steel (iron alloy).

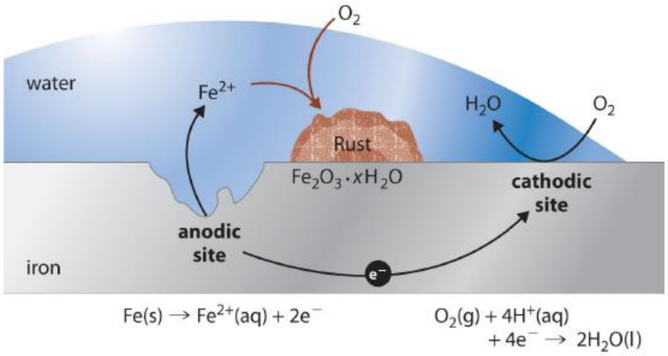

Figure 11.6.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for Sn^{2+} (E° = −0.14 V) and Fe^{2+} (E° = −0.45 V) in Table P2 show that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 11.6.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as Zn (E° = −0.76 V for $\mathrm{Zn}^{2+} + 2\,\mathrm{e}^- \longrightarrow \mathrm{Zn}$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{11.6.3}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{11.6.4}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{11.6.5}$$

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.

Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 11.6.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

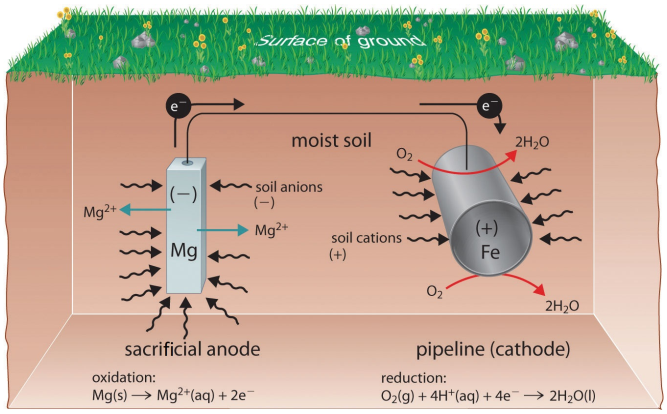

Figure 11.6.4: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium (E° = −2.37 V) is much more easily oxidized than iron (E° = −0.45 V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

✓ Example 11.6.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E^{o\circ}{}_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E^{o\circ}{}_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E^{o\circ}{}_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E^{o\circ}{}_{cell}$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

$$\begin{array}{lll} \text{cathode:} & O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) & E^\circ_{\text{cathode}} = 1.23\text{ V} \\ \text{anode:} & Fe(s) \rightarrow Fe^{2+} + 2e^- & E^\circ_{\text{anode}} = -0.45\text{ V} \\ \text{overall:} & 2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l) & E^\circ_{\text{overall}} = 1.68\text{ V} \end{array}$$

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 11.6.5).

Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

Exercise 11.6.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the Cu/Fe pipe joints will lead to rapid corrosion.

Answer b

Any existing Pb/Fe joints should be examined carefully for corrosion of the iron pipes due to the $Pb–Fe$ junction; the less active Pb will have served as the cathode for the reduction of O_2, promoting oxidation of the more active Fe nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

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11.7: 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 **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

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 (Figure $11.7.1a$).

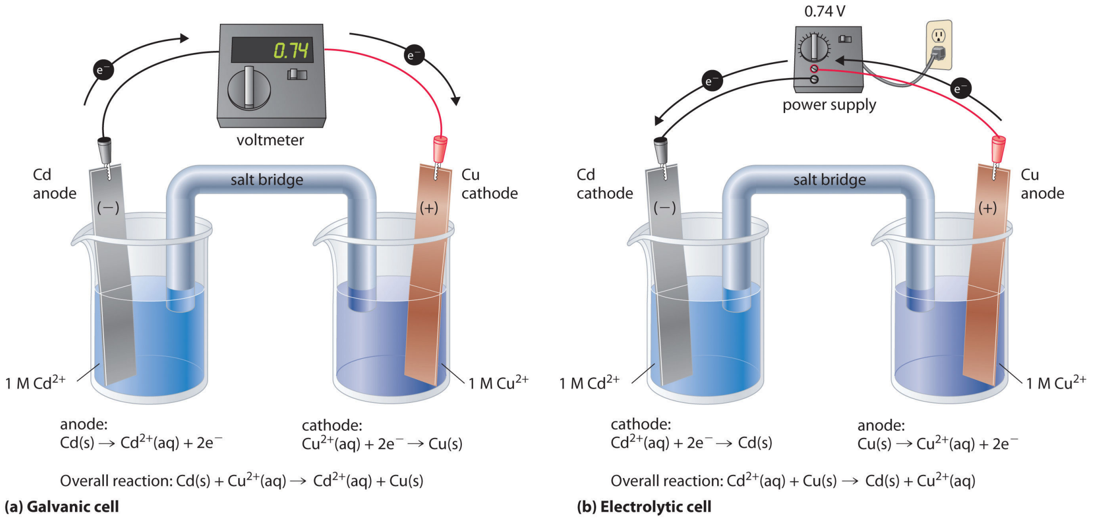

Figure 11.7.1: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) 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. (CC BY-SA-NC; anonymous)

The overall reaction is as follows:

$$\mathrm{Cd(s) + Cu^{2\,+}(aq) \rightarrow Cd^{2\,+}(aq) + Cu(s)}$$

with $E^\circ{}_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G^o < 0$):

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_\mathrm{cell} \\ &= -(2\ \mathrm{mol\ e^-})[96,485\ \mathrm{J/(V\cdot mol)}](0.74\ \mathrm{V}) \\ &= -140\ \mathrm{kJ\ (per\ mole\ Cd)} \end{aligned}$$

In this direction, the system is acting as a galvanic cell.

> *In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.*

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) (Figure $11.7.1b$). 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:

- half-reaction at the cathode:

$$\mathrm{Cd^{2+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{11.7.1}$$

with $E^\circ_{cathode} = -0.40\,V$

- half-reaction at the anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \tag{11.7.2}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall Reaction:

$$\mathrm{Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)} \tag{11.7.3}$$

with $E^\circ_{cell} = -0.74\,V$

Because $E^\circ_{cell} < 0$, 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 $11.7.1$.

Table 11.7.1: 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, $\mathrm{Cl^-}$ is oxidized at the anode, and $\mathrm{Na^+}$ is reduced at the cathode. The overall reaction is as follows:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{11.7.4}$$

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 $11.7.2$). In this specialized cell, $\mathrm{CaCl_2}$ (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.

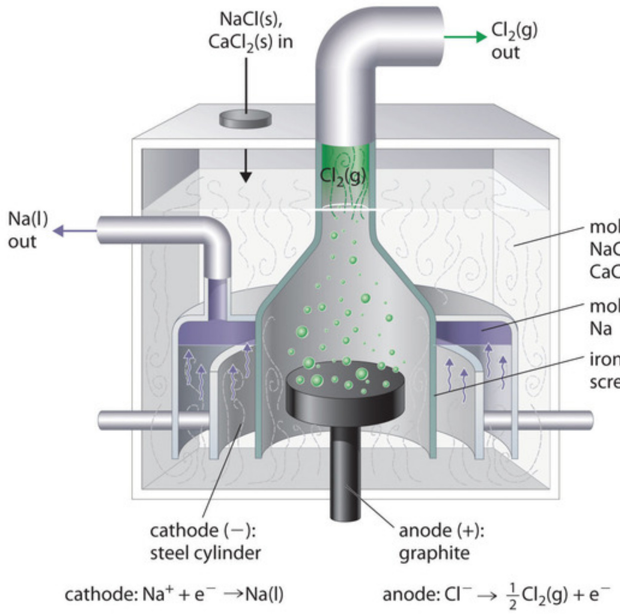

Figure 11.7.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the 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. (CC BY-SA-NC; anonymous)

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:

$$2\,\mathrm{Al_2O_3(l)} + 3\,\mathrm{C(s)} \longrightarrow 4\,\mathrm{Al(l)} + 3\,\mathrm{CO_2(g)} \tag{11.7.5}$$

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 P2, 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 11.7.1

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 7.5, 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 11.7.1

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 $11.7.3$).

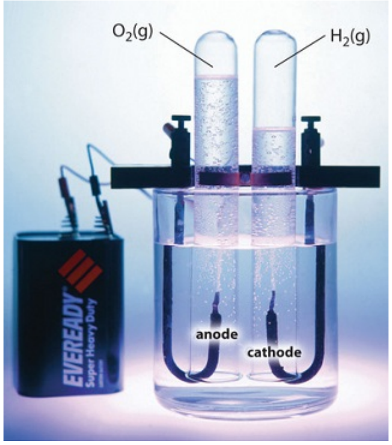

Figure 11.7.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{11.7.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{11.7.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{11.7.8}$$

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 to calculate E for the overall reaction:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log(P_{O_2}P^2_{H_2}) \tag{11.7.9}$$

$$= -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right)\log(1) = -1.23\ \text{V} \tag{11.7.10}$$

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 **overvoltage**, 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.

> *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 **electroplating**, 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 11.7.4

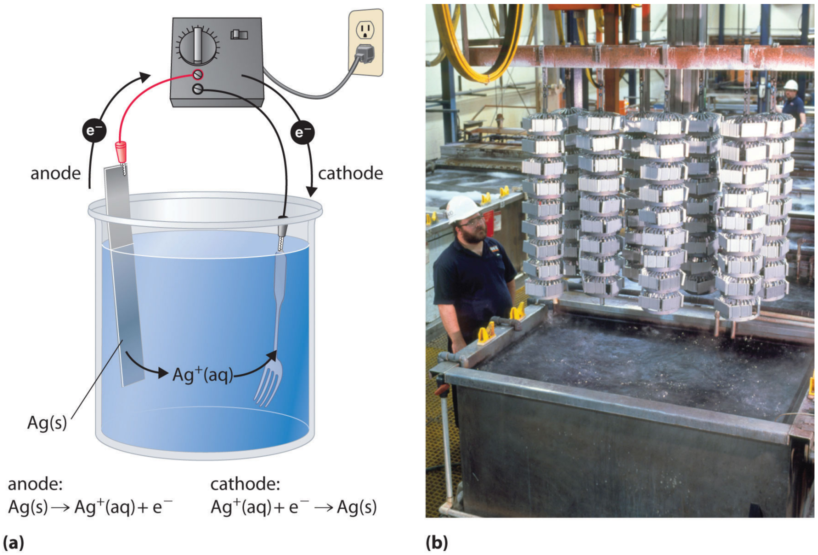

Figure 11.7.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually 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. (CC BY-SA-NC; anonymous)

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \qquad E^\circ{}_{cathode} = 0.80V$$

- anode (silver bar):

$$\mathrm{Ag(s) \longrightarrow Ag^+(aq) + e^-} \qquad E^\circ{}_{anode} = 0.80V$$

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 $E^o_{cell} = 0\,V$, 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

$$\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}$$

1 mol of electrons reduces 1 mol of $\mathrm{Ag^+}$ to Ag metal. In contrast, in the reaction

$$\mathrm{Cu^{2\,+}(aq) + 2\,e^- \rightarrow Cu(s)}$$

1 mol of electrons reduces only 0.5 mol of $\mathrm{Cu^{2\,+}}$ to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,485 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 (q in coulombs) transferred is the product of the current (I in amperes) and the time (t, in seconds):

$$q = I \times t \tag{11.7.11}$$

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 $\mathrm{CuSO_4}$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\begin{aligned} q &= (0.60\text{ A})(6.0\text{ min})(60\text{ s/min}) \\ &= 220\text{ A}\cdot\text{s} \\ &= 220\text{ C} \end{aligned}$$

The number of moles of electrons transferred to $\mathrm{Cu^{2\,+}}$ is therefore

$$\begin{aligned} \text{moles e}^- &= \frac{220\text{ C}}{96{,}485\text{ C/mol}} \\ &= 2.3 \times 10^{-3}\text{ mol e}^- \end{aligned}$$

Because two electrons are required to reduce a single $\mathrm{Cu^{2+}}$ 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 11.7.2

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:

$$\text{moles Ag} = \frac{2.00\ \text{g}}{107.868\ \text{g/mol}} = 1.85 \times 10^{-2}\ \text{mol Ag}$$

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,

$$\text{coulombs} = (1.85 \times 10^{-2} \text{mol e}^-)(96{,}485\ \text{C/mol e}^-) = 1.78 \times 10^3\ \text{C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\begin{aligned}\text{amperes} &= \frac{1.78 \times 10^3\ \text{C}}{(12.0\ \text{h})(60\ \text{min/h})(60\ \text{s/min})} \\ &= 4.12 \times 10^{-2}\ \text{C/s} = 4.12 \times 10^{-2}\ \text{A}\end{aligned}$$

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 11.7.2

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

Electroplating: Electroplating(opens in new window) [youtu.be]

Summary

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. Relationship of charge, current and time:

$$q = I \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. 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.

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11.8: Commercial Electrolytic Processes

Production of Aluminum

Electrorefining of Metals

Metal Plating

Electrolysis of Sodium Chloride

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CHAPTER OVERVIEW

Back Matter

Index

CHAPTER OVERVIEW

15: Chemical Kinetics

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Chemical kinetics is the study of rates of chemical processes and includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

Topic hierarchy

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15.1: Reaction Rates

Learning Objectives

- To determine the reaction rate of a reaction.

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

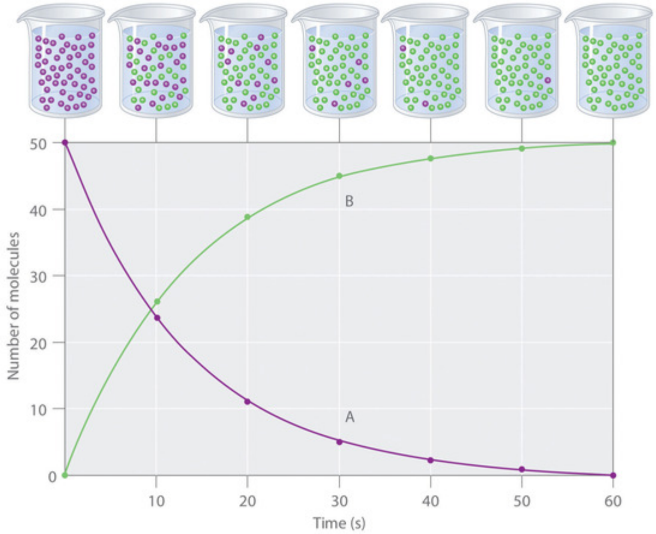

Figure 15.1.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure $15.1.1$; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure $15.1.1$. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{15.1.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 15.1.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*

A Video Discussing Average Reaction Rates. Video Link: Introduction to Chemical Reaction Kinetics(opens in new window) [youtu.be] (opens in new window)

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 15.1.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure 15.1.2.

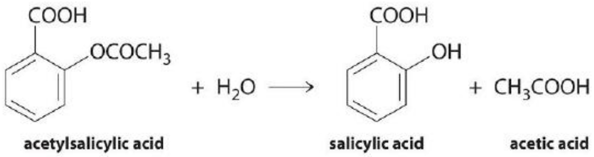

Figure 15.1.2: Hydrolysis of Aspirin reaction.

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 15.1.1 and are shown in the graph in Figure 15.1.3.

Table 15.1.1: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The data in Table 15.1.1 were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

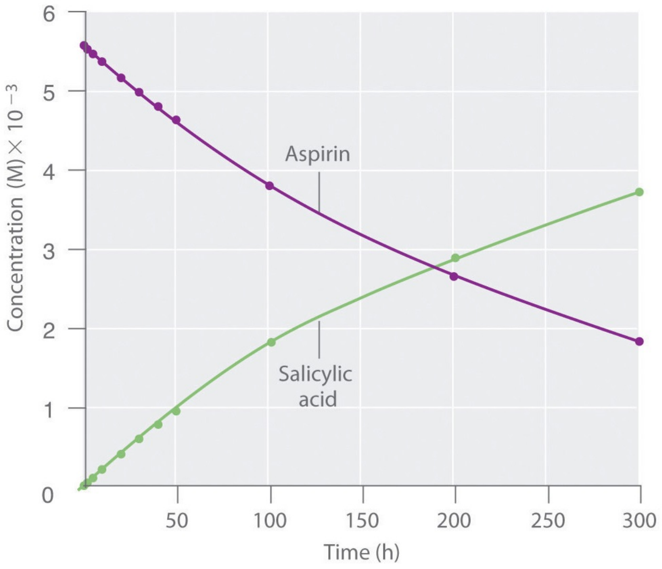

Figure 15.1.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

Graph of concentration against time in hours. The purple line is aspirin. The green line is salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= \frac{0.040\times10^{-3}\text{ M} - 0\text{ M}}{2.0\text{ h}} = 2.0\times10^{-5}\text{ M/h}\end{aligned}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= -\frac{(5.51\times10^{-3}\text{ M}) - (5.55\times10^{-3}\text{ M})}{2.0\text{ h}} \\ &= 2\times10^{-5}\text{ M/h}\end{aligned}$$

If the reaction rate is calculated during the last interval given in Table 15.1.1(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\begin{aligned}\text{rate}_{(t=200-300\text{h})} &= \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\text{ h} - 200\text{ h}} \\ &= -\frac{(3.73\times10^{-3}\text{ M}) - (2.91\times10^{-3}\text{ M})}{100\text{ h}} \\ &= 8.2\times10^{-6}\text{ M/h}\end{aligned}$$

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}}(aq) + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{15.1.2}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10, the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{15.1.3}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 15.1.3 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 15.1.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{15.1.4}$$

✓ Example 15.1.1: Decomposition Reaction I

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.
B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Exercise 15.1.1: Contact Process I

The contact process is used in the manufacture of sulfuric acid. A key step in this process is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer

$$\text{rate} = -\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{\Delta[\text{SO}_2]}{2\Delta t} = \frac{\Delta[\text{SO}_3]}{2\Delta t}$$

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> *Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, t = 0. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to t = 0.*

✓ Example 15.1.2: Decomposition Reaction II

Using the reaction shown in Example 15.1.1, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

calculate the reaction rate from the following data taken at 56°C:

Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example 15.1.1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.
B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example 15.1.1, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$\text{rate} = -\frac{\Delta[N_2O_5]}{2\Delta t} = -\frac{[N_2O_5]_{600} - [N_2O_5]_{240}}{2(600\text{ s} - 240\text{ s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197\text{ M} - 0.0388\text{ M}}{2(360\text{ s})} = 2.65 \times 10^{-5}\text{ M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{[NO_2]_{600} - [NO_2]_{240}}{4(600\text{ s} - 240\text{ s})} = \frac{0.0699\text{ M} - 0.0314\text{ M}}{4(360\text{ s})} = 2.67 \times 10^{-5}\text{ M/s}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{[O_2]_{600} - [O_2]_{240}}{600\text{ s} - 240\text{ s}} = \frac{0.0175\text{ M} - 0.00792\text{ M}}{360\text{ s}} = 2.66 \times 10^{-5}\text{ M/s}$$

Again, this is the same value obtained from the N_2O_5 and NO_2 data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

? Exercise 15.1.2: Contact Process II

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer:

9.0×10^{-6} M/s

Summary

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. Reaction rates can be determined over particular time intervals or at a given point in time.

- General definition of rate for A → B:

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t}$$

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15.2 Rate Laws: An Introduction

Learning Objectives

- To understand the meaning of the rate law.

The factors that affect the reaction rate of a chemical reaction, which may determine whether a desired product is formed. In this section, we will show you how to quantitatively determine the reaction rate.

Rate Laws

Typically, reaction rates decrease with time because reactant concentrations decrease as reactants are converted to products. Reaction rates generally increase when reactant concentrations are increased. This section examines mathematical expressions called **rate laws**, which describe the relationships between reactant rates and reactant concentrations. Rate laws are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A **differential rate law** expresses the reaction rate in terms of changes in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δt). In contrast, an **integrated rate law** describes the reaction rate in terms of the initial concentration ($[R]_0$) and the measured concentration of one or more reactants ([R]) after a given amount of time (t); integrated rate laws are discussed in more detail later. The integrated rate law is derived by using calculus to integrate the differential rate law. Whether using a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).

Reaction Orders

For a reaction with the general equation:

$$aA + bB \rightarrow cC + dD \tag{15.2 Rate Laws.1}$$

the experimentally determined rate law usually has the following form:

$$\text{rate} = k[A]^m[B]^n \tag{15.2 Rate Laws.2}$$

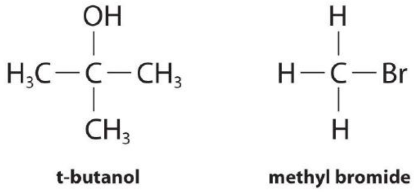
The proportionality constant (*k*) is called the **rate constant**, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular rate constant value under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of *k*, however, does not change as the reaction progresses under a given set of conditions.

> *Under a given set of conditions, the value of the rate constant does **not** change as the reaction progresses.*

The reaction rate thus depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers *m* and *n*, respectively. The values of *m* and *n* are derived from experimental measurements of the changes in reactant concentrations over time and indicate the **reaction order**, the degree to which the reaction rate depends on the concentration of each reactant; *m* and *n* need not be integers. For example, Equation 15.2 Rate Laws.2 tells us that Equation 15.2 Rate Laws.1 is m^{th} order in reactant A and n^{th} order in reactant B. It is important to remember that *n* and *m* are not related to the stoichiometric coefficients *a* and *b* in the balanced chemical equation and must be determined **experimentally**. The overall reaction order is the sum of all the exponents in the rate law: *m* + *n*.

> *The orders of the reactions (e.g. n and m) are **not** related to the stoichiometric coefficients in the balanced chemical (e.g., a and b).*

To illustrate how chemists interpret a differential rate law, consider the experimentally derived rate law for the hydrolysis of *t*-butyl bromide in 70% aqueous acetone.



This reaction produces *t*-butanol according to the following equation:

$$(CH_3)_3CBr_{(soln)} + H_2O_{(soln)} \rightarrow (CH_3)_3COH_{(soln)} + HBr_{(soln)} \tag{15.2 Rate Laws.3}$$

Combining the rate expression in Equation 15.2 Rate Laws.2with the definition of average reaction rate

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t}$$

gives a general expression for the differential rate law:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^m[\text{B}]^n \tag{15.2 Rate Laws.4}$$

Inserting the identities of the reactants into Equation 15.2 Rate Laws.4gives the following expression for the differential rate law for the reaction:

$$\text{rate} = -\frac{\Delta[(\text{CH}_3)_3\text{CBr}]}{\Delta t} = k[(\text{CH}_3)_3\text{CBr}]^m[\text{H}_2\text{O}]^n \tag{15.2 Rate Laws.5}$$

Experiments to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(CH_3)_3CBr$ but is independent of the concentration of water. Therefore, m and n in Equation 15.2 Rate Laws.4are 1 and 0, respectively, and,

$$\text{rate} = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr] \tag{15.2 Rate Laws.6}$$

Because the exponent for the reactant is 1, the reaction is first order in $(CH_3)_3CBr$. It is zeroth order in water because the exponent for $[H_2O]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus, the overall reaction order is 1 + 0 = 1. The reaction orders state in practical terms that doubling the concentration of $(CH_3)_3CBr$ doubles the reaction rate of the hydrolysis reaction, halving the concentration of $(CH_3)_3CBr$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has no effect on the reaction rate. (Again, when working with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of *k*, *m*, and *n* in the rate law must be determined experimentally.) Experimental data show that *k* has the value $5.15 \times 10^{-4}\ s^{-1}$ at 25°C. The rate constant has units of reciprocal seconds (s^{-1}) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH_3Br) is as follows:

$$\text{rate} = -\frac{\Delta[\text{CH}_3\text{Br}]}{\Delta t} = k'[\text{CH}_3\text{Br}] \tag{15.2 Rate Laws.7}$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 15.2 Rate Laws.7 is approximately 10^6 times smaller than that for *t*-butyl bromide. Thus, methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often alter reaction conditions to study the mechanics of a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH^- ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. In contrast, for methyl bromide, the differential rate law becomes

$$\text{rate} = k''[CH_3Br][OH^-]$$

with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, providing clues as to how the reactions differ on a molecular level.

✓ Example $15.2 RateLaws.1$: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

is second order in 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:

$$\text{rate} = k[NO_2]^m[CO]^n$$

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:

$$\text{rate} = k[NO_2]^2[CO]^0 = k[NO_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

? Exercise $15.2 RateLaws.1A$

The rate law for the reaction:

$$H_2(g) + 2\,NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

has been experimentally 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

- order in NO = 2
- order in H_2 = 1
- overall order = 3

? Exercise $15.2 RateLaws.1B$

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 ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$CH_3OH + CH_3CH_2OCOCH_3 \longrightarrow CH_3OCOCH_3 + CH_3CH_2OH$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[CH_3OH]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1
- order in $CH_3CH_2OCOCH_3$ = 0
- overall order = 1

✓ Example 15.2$RateLaws$.2: Differential Rate Laws

Below are three reactions and their experimentally determined differential rate laws. For each reaction, give the units of the rate constant, give the reaction order with respect to each reactant, give the overall reaction order, and predict what happens to the rate when the concentration of the first species in each chemical equation is doubled.

a.

$$2HI(g) \xrightarrow{Pt} H_2(g) + I_2(g)$$

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[HI]}{\Delta t}\right) = k[HI]^2$$

b.

$$2N_2O(g) \xrightarrow{\Delta} 2N_2(g) + O_2(g)$$

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = k$$

c.

$$\text{cyclopropane}(g) \rightarrow \text{propane}(g)$$

$$\text{rate} = -\frac{\Delta[\text{cyclopropane}]}{\Delta t} = k[\text{cyclopropane}]$$

Given: balanced chemical equations and differential rate laws

Asked for: units of rate constant, reaction orders, and effect of doubling reactant concentration

Strategy:

A. Express the reaction rate as moles per liter per second [mol/(L·s), or M/s]. Then determine the units of each chemical species in the rate law. Divide the units for the reaction rate by the units for all species in the rate law to obtain the units for the rate constant.
B. Identify the exponent of each species in the rate law to determine the reaction order with respect to that species. Add all exponents to obtain the overall reaction order.
C. Use the mathematical relationships as expressed in the rate law to determine the effect of doubling the concentration of a single species on the reaction rate.

Solution

1. **A** $[HI]^2$ will give units of (moles per liter)^2. For the reaction rate to have units of moles per liter per second, the rate constant must have reciprocal units [1/(M·s)]:

$$kM^2 = \frac{M}{s} k = \frac{M/s}{M^2} = \frac{1}{M \cdot s} = M^{-1} \cdot s^{-1}$$

   B The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second order overall.

   C If the concentration of HI is doubled, the reaction rate will increase from $k[HI]_0^2$ to $k(2[HI])_0^2 = 4k[HI]_0^2$. The reaction rate will therefore quadruple.

2. **A** Because no concentration term appears in the rate law, the rate constant must have M/s units for the reaction rate to have M/s units.

   B The rate law tells us that the reaction rate is constant and independent of the N_2O concentration. That is, the reaction is zeroth order in N_2O and zeroth order overall.

   C Because the reaction rate is independent of the N_2O concentration, doubling the concentration will have no effect on the reaction rate.

3. **A** The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds (s^{-1}) to have units of moles per liter per second for the reaction rate: $M \cdot s^{-1} = M/s$.

   B The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

C Doubling the initial cyclopropane concentration will increase the reaction rate from k[cyclopropane]$_0$ to 2k[cyclopropane]$_0$. This doubles the reaction rate.

? Exercise $15.2RateLaws.2$

Given the following two reactions and their experimentally determined differential rate laws: determine the units of the rate constant if time is in seconds, determine the reaction order with respect to each reactant, give the overall reaction order, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

a.

$$\mathrm{CH_3N{=}NCH_3(g) \rightarrow C_2H_6(g) + N_2(g)} \quad \text{rate} = -\frac{\Delta[\mathrm{CH_3N{=}NCH_3}]}{\Delta t} \tag{15.2 Rate Laws.8}$$

$$= k[\mathrm{CH_3N{=}NCH_3}] \tag{15.2 Rate Laws.9}$$

b.

$$\mathrm{2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)} \quad \text{rate} = -\frac{\Delta[\mathrm{F_2}]}{\Delta t} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{NO_2}]}{\Delta t}\right) \tag{15.2 Rate Laws.10}$$

$$= k[\mathrm{NO_2}][\mathrm{F_2}] \tag{15.2 Rate Laws.11}$$

Answer a

s^{-1}; first order in $CH_3N{=}NCH_3$; first order overall; doubling [$CH_3N{=}NCH_3$] will double the reaction rate.

Answer b

$M^{-1}{\cdot}s^{-1}$; first order in NO_2, first order in F_2; second order overall; doubling [NO_2] will double the reaction rate.

Determining the Rate Law of a Reaction

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding **reaction mechanisms** can simplify what might seem to be a confusing variety of chemical reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law. This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow products$, for example, we need to determine k and the exponents m and n in the following equation:

$$\text{rate} = k[A]^m[B]^n \tag{15.2 Rate Laws.12}$$

To do this, we might keep the initial concentration of B constant while varying the initial concentration of A and calculating the initial reaction rate. This information would permit us to deduce the reaction order with respect to A. Similarly, we could determine the reaction order with respect to B by studying the initial reaction rate when the initial concentration of A is kept constant while the initial concentration of B is varied. In earlier examples, we determined the reaction order with respect to a given reactant by comparing the different rates obtained when only the concentration of the reactant in question was changed. An alternative way of determining reaction orders is to set up a proportion using the rate laws for two different experiments. Rate data for a hypothetical reaction of the type $A + B \rightarrow products$ are given in Table $15.2RateLaws.1$.

Table $15.2RateLaws.1$: Rate Data for a Hypothetical Reaction of the Form $A + B \rightarrow products$

Experiment	[A] (M)	[B] (M)	Initial Rate (M/min)
1	0.50	0.50	8.5×10^{-3}
2	0.75	0.50	19×10^{-3}
3	1.00	0.50	34×10^{-3}
4	0.50	0.75	8.5×10^{-3}
5	0.50	1.00	8.5×10^{-3}

The general rate law for the reaction is given in Equation 15.2 Rate Laws.12 We can obtain m or n directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in Table $15.2RateLaws.3$.

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_3]^m[\text{B}_3]^n}$$

Inserting the appropriate values from Table $15.2 RateLaws.3$,

$$\frac{8.5\times 10^{-3}\ \text{M/min}}{34\times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[1.00\ \text{M}]^m[0.50\ \text{M}]^n}$$

Because 1.00 to any power is 1, $[1.00\ \text{M}]^m$ = 1.00 M. We can cancel like terms to give 0.25 = $[0.50]^m$, which can also be written as 1/4 = $[1/2]^m$. Thus we can conclude that *m* = 2 and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for *m*.

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for *n*.

$$\frac{\text{rate}_1}{\text{rate}_5} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_5]^m[\text{B}_5]^n}$$

Substituting the appropriate values from Table $15.2 RateLaws.3$,

$$\frac{8.5\times 10^{-3}\ \text{M/min}}{8.5\times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[0.50\ \text{M}]^m[1.00\ \text{M}]^n}$$

Canceling leaves 1.0 = $[0.50]^n$, which gives $n = 0$; that is, the reaction is zeroth order in B. The experimentally determined rate law is therefore

$$\text{rate} = k[\text{A}]^2[\text{B}]^0 = k[\text{A}]^2$$

We can now calculate the rate constant by inserting the data from any row of Table $15.2 RateLaws.3$ into the experimentally determined rate law and solving for k. Using Experiment 2, we obtain

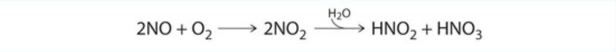
$$19 \times 10^{-3}\ \text{M/min} = k(0.75\ \text{M})^2$$

$$3.4 \times 10^{-2}\ \text{M}^{-1}\cdot\text{min}^{-1} = \text{k}$$

You should verify that using data from any other row of Table $15.2 RateLaws.1$ gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

✓ Example $15.2 RateLaws.3$

Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with O_2 to give NO_2, which then reacts rapidly with water to give nitrous acid and nitric acid:



These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with O_2 at 25°C:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Determine the rate law for the reaction and calculate the rate constant.

rate law for the reaction and calculate the rate constant.

Experiment	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial Rate (M/s)
1	0.0235	0.0125	7.98×10^{-3}
2	0.0235	0.0250	15.9×10^{-3}
3	0.0470	0.0125	32.0×10^{-3}
4	0.0470	0.0250	63.5×10^{-3}

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: rate law and rate constant

Strategy:

A. Compare the changes in initial concentrations with the corresponding changes in rates of reaction to determine the reaction order for each species. Write the rate law for the reaction.
B. Using data from any experiment, substitute appropriate values into the rate law. Solve the rate equation for *k*.

Solution

A Comparing Experiments 1 and 2 shows that as $[O_2]$ is doubled at a constant value of $[NO_2]$, the reaction rate approximately doubles. Thus the reaction rate is proportional to $[O_2]^1$, so the reaction is first order in O_2. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and $[O_2]$ is held constant. That is, the reaction rate is proportional to $[NO]^2$, which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

$$\text{rate} = k[NO]^2[O_2]$$

B The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k=\frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]}=\frac{7.98\times10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0125\ \text{M})}=1.16\times10^3\ \text{M}^{-2}\cdot\text{s}^{-1}$$

Alternatively, using Experiment 2 gives

$$k=\frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]}=\frac{15.9\times10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0250\ \text{M})}=1.15\times10^3\ \text{M}^{-2}\cdot\text{s}^{-1}$$

The difference is minor and associated with significant digits and likely experimental error in making the table.

The overall reaction order $(m+n)=3$, so this is a third-order reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

? Exercise 15.2$RateLaws$.3

The peroxydisulfate ion ($S_2O_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O^{2-}_{8(aq)}+3I^-_{(aq)}\rightarrow 2SO^{2-}_{4(aq)}+I^-_{3(aq)}$$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

kinetics data for this reaction at 25°C.

Experiment	$[S_2O_8^{2-}]_0$ (M)	$[I^-]_0$ (M)	Initial Rate (M/s)
1	0.27	0.38	2.05
2	0.40	0.38	3.06
3	0.40	0.22	1.76

Answer:

rate = $k[S_2O_8^{2-}][I^-]$; $k = 20\ M^{-1}\cdot s^{-1}$

A Video Discussing Initial Rates and Rate Law Expressions. Video Link: Initial Rates and Rate Law Expressions(opens in new window) [youtu.be]

Summary

The rate law for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a differential rate law, describing the change in reactant or product concentrations as a function of time, or as an integrated rate law, describing the actual concentrations of reactants or products as a function of time. The rate constant (k) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The exponent to which a concentration is raised in a rate law indicates the reaction order, the degree to which the reaction rate depends on the concentration of a particular reactant.

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SECTION OVERVIEW

15.3: Determining the Form of the Rate Law

In studying a chemical reaction, it is important to consider not only the chemical properties of the reactants, but also the conditions under which the reaction occurs, the mechanism by which it takes place, the rate at which it occurs, and the equilibrium toward which it proceeds. According to the law of mass action, the rate of a chemical reaction at a constant temperature depends only on the concentrations of the substances that influence the rate. The substances that influence the rate of reaction are usually one or more of the reactants, but can occasionally include products. Catalysts, which do not appear in the balanced overall chemical equation, can also influence reaction rate. The rate law is experimentally determined and can be used to predict the relationship between the rate of a reaction and the concentrations of reactants.

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15.4: The Integrated Rate Law

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The differential rate law describes how the rate of reaction varies with the concentrations of various species, usually reactants, in the system. The rate of reaction is proportional to the rates of change in concentrations of the reactants and products; that is, the rate is proportional to a derivative of a concentration. To illustrate this point, consider the reaction

A -> B

The rate of reaction, r, is given by

$$r = -\frac{d[A]}{dt}$$

Suppose this reaction obeys a first-order rate law:

$r = k[A]$

This rate law can also be written as

$$r = -\frac{d[A]}{dt} = k[A]$$

This equation is a differential equation that relates the rate of change in a concentration to the concentration itself. Integration of this equation produces the corresponding **integrated rate law**, which relates the concentration to time. When you viewed concentration-time curves in previous pages, you viewed the integrated rate laws.

$$\frac{d[A]}{[A]} = -k\,dt$$

At $t = 0$, the concentration of A is $[A]_0$. The integrated rate law is thus

$[A] = [A]_0 e^{-kt}$

Experimentally one almost always measures how the concentration of a reactant or product changes as the reaction progresses. In the previous page, you saw how the derivative of the concentration-time curve can be used to determine the differential rate law for a reaction. While this approach might work for simple systems with numerically exact data, this method for determining a rate law does not work well in practice. The experimental data suffers from random error and frequently one only collects points infrequently. Consequently it is difficult or impossible to determine the slope accurately.

A much better practical approach is to make characteristic kinetics plots. For each integrated rate law, there is a characteristic plot that can be created which will produce a straight line. These characteristic plots are presented in the table shown below; species A is a reactant in the chemical reaction.

Reaction Order	Differential Rate Law	Integrated Rate Law	Characteristic Kinetic Plot	Slope of Kinetic Plot	Units of Rate Constant
Zero	$-\frac{d[A]}{dt} = k$	$[A] = [A]_0 - kt$	$[A]$ vs t	$-k$	mole L^{-1} sec^{-1}

First	$-\frac{d[A]}{dt} = k[A]$	$[A] = [A]_0 e^{-kt}$	ln [A] vs *t*	- *k*	sec^{-1}
Second	$-\frac{d[A]}{dt} = k[A]^2$	$[A] = \frac{[A]}{1 + kt[A]_0}$	1/[A] vs *t*	*k*	$L\ mole^{-1}\ sec^{-1}$

The series of three graphs shown below illustrate the use of the characteristic kinetic plots. The graph on the left shows [A] vs *t* plots for a zero-order (red line), first-order (green line), and second-order (blue line) reaction. The graph in the middle shows ln [A] vs *t* plots for each reaction order, and the graph on the right shows 1/[A] vs *t* plots for each reaction order.

Notice that for each characteristic kinetic plot, a specific rate law shows a straight line. In the [A] vs *t* plot, only the zero-order reaction (red line) produces a straight line; the other lines curve. In the ln [A] vs *t* plot, only the first-order reaction (green line) produces a straight line, and in the 1/[A] vs *t* plot, only the second-order reaction (blue line) produces a straight line.

Experiment

Objectives

> - *Determine the rate law for a chemical reaction.*
> - *Determine the rate constant for a chemical reaction.*

Consider the following reaction between the persulfate ion and the iodide ion:

$S_2O_8^{2-}$ *(aq)* + 3 I^- *(aq)* --> 2 SO_4^{2-} *(aq)* + I_3^- *(aq)*

In this chemical system, the only species that absorbs visible light is the triiodide ion. Spectrophotometry can be employed to determine the concentration of triiodide ion, which with knowledge of the initial concentration of iodide ion permits the concentration of iodide ion to be determined at any point in time.

In this stopped-flow experiment, one syringe contains a 0.100 M solution of iodide ion and the other syringe contains a 0.100 M solution of persulfate ion. The two solutions are mixed in a 3:1 ratio, so that there is a stoichiometric amount of iodide and persulfate ions in the reaction solution. As the reaction is occurring, the concentration of iodide is plotted versus time in the left graph.

After the reaction is complete, prepare kinetic plots for the zero-, first-, and second-order reactions. In the kinetics plots, the data is plotted as red points and the line-of-best-fit is plotted in blue. Use the kinetics plots to determine the rate law for this reaction. The slope of the kinetic plot can be used to determine the rate constant for the reaction.

Start

Stop

Reset

Zero-Order Plot First-Order Plot Second-Order Plot slope =

intercept =

Contributors

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15.5: Rate Laws: A Summary

1.1 Chemistry in the Modern World

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15.6: Reaction Mechanisms

Learning Objectives

- To determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the mechanism of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the reaction mechanism.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

$$2\,\mathrm{C_8H_{18}(l)} + 25\,\mathrm{O_2(g)} \longrightarrow 16\,\mathrm{CO_2(g)} + 18\,\mathrm{H_2O(g)} \tag{15.6.1}$$

For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an **elementary reaction**, involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the **mechanism** of the reaction. The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.

> *The overall sequence of elementary reactions is the mechanism of the reaction.*

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

$$\mathrm{NO_2(g)} + \mathrm{CO(g)} \longrightarrow \mathrm{NO(g)} + \mathrm{CO_2(g)} \tag{15.6.2}$$

From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of $\mathrm{NO_2}$ with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$rate = k[\mathrm{NO_2}]^2 \tag{15.6.3}$$

The fact that the reaction is second order in $[\mathrm{NO_2}]$ and independent of $[\mathrm{CO}]$ tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be

$$rate = k[\mathrm{NO_2}][\mathrm{CO}].$$

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

two-step mechanism

step 1	$\mathrm{NO_2} + \mathrm{NO_2} \xrightarrow{\text{slow}} \mathrm{NO_3} + \mathrm{NO}$	elementary reaction
step 2	$\underline{\mathrm{NO_3} + \mathrm{CO} \rightarrow \mathrm{NO_2} + \mathrm{CO_2}}$	elementary reaction
sum	$\mathrm{NO_2} + \mathrm{CO} \rightarrow \mathrm{NO} + \mathrm{CO_2}$	overall reaction

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The $\mathrm{NO_3}$ molecule is an **intermediate** in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

> *The sum of the elementary reactions in a reaction mechanism **must** give the overall balanced chemical equation of the reaction.*

Using Molecularity to Describe a Rate Law

The **molecularity** of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as **unimolecular**; if there are two reactant molecules, it is **bimolecular**; and if there are three reactant molecules (a relatively rare situation), it is **termolecular**. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

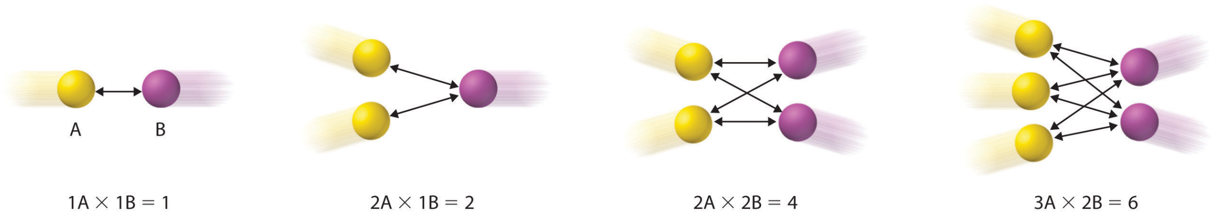

Figure 15.6.1: The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step. (CC BY-NC-SA; anonymous)

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order of the elementary reaction is the same as its molecularity (Table 15.6.1). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction (A → products) is

$$rate = k[A].$$

For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure 15.6.1. For a bimolecular elementary reaction of the form A + B → products, the general rate law is

$$rate = k[A][B].$$

Table 15.6.1: Common Types of Elementary Reactions and Their Rate Laws

Elementary Reaction	Molecularity	Rate Law	Reaction Order
A → products	unimolecular	rate = $k[A]$	first
2A → products	bimolecular	rate = $k[A]^2$	second
A + B → products	bimolecular	rate = $k[A][B]$	second
2A + B → products	termolecular	rate = $k[A]^2[B]$	third
A + B + C → products	termolecular	rate = $k[A][B][C]$	third

> *For elementary reactions, the order of the elementary reaction is the same as its molecularity. In contrast, the rate law* ***cannot*** *be determined from the balanced chemical equation for the overall reaction (unless it is a single step mechanism and is therefore also an elementary step).*

Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by which the reaction occurs, we cannot obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the slowest overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the **rate-determining step**, that must give the experimentally determined rate law for the overall reaction.This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.

Rate-determining step. The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow. (CC BY-NC-SA; anonymous)

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

rate laws for each elementary reaction in our example as well as for the overall reaction.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$	$\text{rate} = k_1[NO_2]^2$ (predicted)
step 2	$\underline{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}$	$\text{rate} = k_2[NO_3][CO]$ (predicted)
sum	$NO_2 + CO \xrightarrow{k} NO + CO_2$	$\text{rate} = k[NO_2]^2$ (observed)

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1. That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

✓ Example 15.6.1: A Reaction with an Intermediate

In an alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} N_2O_4$
step 2	$\underline{N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2}$
sum	$NO_2 + CO \rightarrow NO + CO_2$

Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:

A. Determine the rate law for each elementary reaction in the reaction.
B. Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

Solution

A The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4, directly.

? Exercise 15.6.1

Iodine monochloride (ICl) reacts with H_2 as follows:

$$2\,ICl(l) + H_2(g) \rightarrow 2\,HCl(g) + I_2(s)$$

The experimentally determined rate law is $rate = k[ICl][H_2]$. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Answer

Solutions to Exercise 14.6.1

step 1	$ICl + H_2 \xrightarrow{k_1} HCl + HI$	$rate = k_1[ICl][H_2]$ (slow)
step 2	$\underline{HI + ICl \xrightarrow{k_2} HCl + I_2}$	$rate = k_2[HI][ICl]$ (fast)
sum	$2ICl + H_2 \rightarrow 2HCl + I_2$	

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

✓ Example 15.6.2 : Nitrogen Oxide Reacting with Molecular Hydrogen

Assume the reaction between NO and H_2 occurs via a three-step process:

the reaction between NO and H_2 occurs via a three-step process

step 1	$NO + NO \xrightarrow{k_1} N_2O_2$	(fast)
step 2	$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$	(slow)
step 3	$N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$	(fast)

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction:

$$rate = k[NO]^2[H_2]? \qquad \text{(observed)}$$

Answer

- Step 1: $rate = k_1[NO]^2$
- Step 2: $rate = k_2[N_2O_2][H_2]$

- Step 3: $rate = k_3[N_2O][H_2]$

The overall reaction is then

$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

- Rate Determining Step : #2
- Yes, because the rate of formation of $[N_2O_2] = k_1[NO]^2$. Substituting $k_1[NO]^2$ for $[N_2O_2]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.

Reaction Mechanism (Slow step followed by fast step): Reaction Mechanism (Slow step Followed by Fast Step)(opens in new window) [youtu.be] (opens in new window)

Summary

A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law. A reaction mechanism is the microscopic path by which reactants are transformed into products. Each step is an elementary reaction. Species that are formed in one step and consumed in another are intermediates. Each elementary reaction can be described in terms of its *molecularity*, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the rate-determining step.

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15.7: The Steady-State Approximation

Learning Objectives

- Explain **steady state** and **steady-state approximation**.
- Derive a rate law when a mechanism is given but the rate determining step is not identified.
- Derive a general expression of the rate law using the steady-state approximation.
- Make appropriate assumptions so that the derived rate law agrees with the observed rate law.
- Give expressions for the producing *rate* of an intermediate.
- Give expressions for the consuming *rate* of an intermediate.
- Express concentration of intermediate in terms of concentration of reactants.
- Eliminate concentrations of intermediates using concentrations of reactants.
- Derive a **rate law** from the many elementary steps.
- Discuss the derived **rate law**.

The Steady-State Approximation

When a reaction mechanism has several steps of comparable rates, the rate-determining step is often not obvious. However, there is an intermediate in some of the steps. An **intermediate** is a species that is neither one of the reactants, nor one of the products. The **steady-state approximation** is a method used to derive a rate law. The method is based on the assumption that one intermediate in the reaction mechanism is consumed as quickly as it is generated. Its concentration remains the same in a duration of the reaction.

Definition: Intermediates

An **intermediate** is a species that is neither one of the reactants, nor one of the products. It transiently exists during the course of the reaction.

When a reaction involves one or more intermediates, the concentration of one of the intermediates remains constant at some stage of the reaction. Thus, the system has reached a **steady-state**. The concentration of one of the intermediates, $[Int]$, varies with *time* as shown in Figure $15.7.1$. At the start and end of the reaction, [Int] does vary with time.

$$\frac{d[Int]}{dt} = 0$$

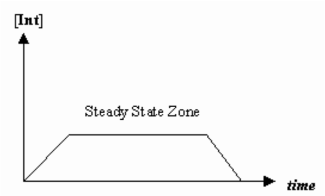

Figure 15.7.1: Example of the when an intermediate can be approximated as a steady-state.

When a reaction mechanism has several steps with comparable rates, the rate-determining step is not obvious. However, there is an intermediate in some of the steps. The steady-state approximation implies that you select an intermediate in the reaction mechanism, and calculate its concentration by assuming that it is consumed as quickly as it is generated. In the following, an example is given to show how the steady-state approximation method works.

Example 15.7.1

Use the steady-state approximation to derive the rate law for this reaction

$$2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$$

assuming it follows the following three-step mechanism:

$$N_2O_5 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NO_2 + NO_3 \tag{step 1}$$

$$NO_3 + NO_2 \xrightarrow{k_2} NO + NO_2 + O_2 \tag{step 2}$$

$$NO_3 + NO \xrightarrow{k_3} 2\,NO_2 \tag{step 3}$$

Solution

In these steps, NO and NO_3 are intermediates. You have

$$\begin{gathered} \text{production rate of NO} = k_2[NO_3][NO_2] \\ \text{consumption rate of NO} = k_3[NO_3][NO] \end{gathered}$$

A steady-state approach makes use of the assumption that the rate of production of an intermediate is equal to the rate of its consumption. Thus, we have

$$k_2[NO_3][NO_2] = k_3[NO_3][NO]$$

and solving for $[NO]$ gives the result,

$$[NO] = \frac{k_2[NO_3][NO_2]}{k_3[NO_3]} \tag{1}$$

For the other intermediate NO_3,

$$\begin{gathered} \text{production rate of } NO_3 = k_f[N_2O_5] \\ \text{consumption rate of } NO_3 = k_2[NO_3][NO_2] + k_3[NO_3][NO] + k_b[NO_3][NO_2] \end{gathered}$$

Applying the steady-state assumption gives:

$$k_f[N_2O_5] = k_2[NO_3][NO_2] + k_3[NO_3][NO] + k_b[NO_3][NO_2]$$

Thus,

$$[NO_3] = \frac{k_f[N_2O_5]}{k_2[NO_2] + k_3[NO] + k_b[NO_2]} \tag{2}$$

Let's review the three equations (steps) in the mechanism:
Step i. is at equilibrium and thus can not give a rate expression.
Step ii. leads to the production of some products, and the active species NO causes further reaction in step iii. This consideration led to a rate expression from step ii. as:

$$\frac{d[O_2]}{dt} = k_2[NO_3][NO_2] \tag{3}$$

Substituting (1) in (2) and then in (3) gives

$$\frac{d[O_2]}{dt} = \frac{k_f k_2[N_2O_5]}{k_b + 2k_2} = k[N_2O_5]$$

where $k = \dfrac{k_f k_2}{k_b + 2k_2}$.

This is the differential rate law, and it agrees with the experimental results. Carry out the above manipulation yourself on a piece of paper. Simply reading the above will not lead to solid learning yet.

This page gives another example to illustrate the technique of deriving rate laws using the steady-state approximation. The reaction considered here is between H_2 and I_2 gases.

✓ Example 15.7.1

For the reaction:

$$H_{2\,(g)} + I_{2\,(g)} \rightarrow 2\,HI_{(g)}$$

what mechanisms might be appropriate? Derive a rate law from the proposed mechanism.

Solution

Well, this question does not have a simple answer, and there is no way to prove one over another for its validity. Beginning chemistry students will not be asked to propose a mechanism, but you will be asked to derive the rate law from the proposed mechanism.

First of all, you should be able to express the rate of reaction in terms of the concentration changes,

$$rate = -\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$$

Look at the overall reaction equation again to see its relationship and the rate expressions.

Proposing a mechanism

In order to propose a mechanism, we apply the following reasoning. Since the bonding between $I-I$ is weak, we expect I_2 to dissociate into atoms or radicals. These radicals are active, and they react with H_2 to produce the products. Thus we propose the three-step mechanism:

i. $I_{2\,(g)} \xrightarrow{k_1} 2\,I_{(g)}$

ii. $2\,I_{(g)} \xrightarrow{k_2} I_{2\,(g)}$

iii. $H_{2\,(g)} + 2\,I_{(g)} \xrightarrow{k_3} 2\,HI_{(g)}$

Which step would you use to write the differential rate law?

Since only step iii. gives the real products, we expect you to recognize that step iii. hints the rate law to be:

$$rate = k_3[H_2][I]^2$$

However, this is not a proper rate law, because I is an intermediate, not a reactant. So, you have to express $[I]$ or $[I]^2$ in terms of the concentration of reactants. To do this, we use the steady-state approximation and write out the following relationships:

$$\begin{gathered}\text{rate of producing I} = 2k_1[I_2] \\ \text{rate of consuming I} = 2k_2[I]^2 + 2k_3[H_2][I]^2 \\ \text{producing rate of I} = \text{consuming rate of I}\end{gathered}$$

Thus,

$$[I]^2 = \frac{k_1[I_2]}{k_2 + k_3[H_2]}$$

Substituting this for $[I]^2$ into the *rate* expression, you have

$$\begin{aligned} rate &= k_3[H_2]\frac{k_1[I_2]}{k_2 + k_3[H_2]} \qquad (15.7.1) \\ &= \frac{k_1k_3[H_2][I_2]}{k_2 + k_3[H_2]} \qquad (15.7.2)\end{aligned}$$

Discussion

If step iii. is slow, then k_3 and $k_2 >> k_3[H_2]$. The rate law is reduced to

$$\text{rate} = \text{k}[H_2][I_2],$$

where $\text{k} = \frac{k_1k_3}{k_2}$. *(Work this out on paper yourself; reading the above derivation does not lead to learning.)*

Since the rate law is first order with respect to both reactants, one may argue that the rate law also supports a one-step mechanism,

$$H_{2\,(g)} + I_{2\,(g)} \rightarrow 2\,HI$$

This elementary step is the same as the overall reaction.

Suppose we use a large quantity of H_2 compared to I_2, then the change in $[H_2]$ is insignificant. For example, if $[H_2] = 10$, and $[I_2] = 0.1$ initially, $[H_2]$ remains essentially 10 (9.9 with only one significant figure). In other words, $[H_2]$ hardly changed when the reaction ended. Thus,

$$k_3[H_2] >> k_3$$

and the rate law becomes:

$$rate = k_1[I_2].$$

Thus, the reaction is a *pseudo first order reaction*, due to the large quantity of one reactant. The results suggest iii. a fast step (due to large quantity of H_2), and i. the rate determining step.

Contributors and Attributions

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15.8: A Model for Chemical Kinetics

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15.9: Catalysis

Learning Objectives

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Catalysts are substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it must appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a, but the net change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is not affected by the presence of a catalyst (Figure $15.9.1$). Nevertheless, because of its lower E_a, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of both the forward and the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, homogeneous catalysts, and enzymes.

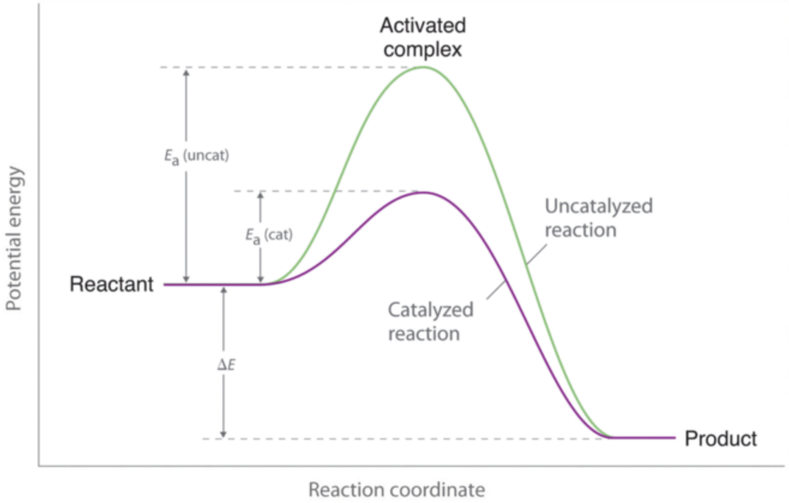


Figure $15.9.1$: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE). (CC BY-NC-SA; anonymous)

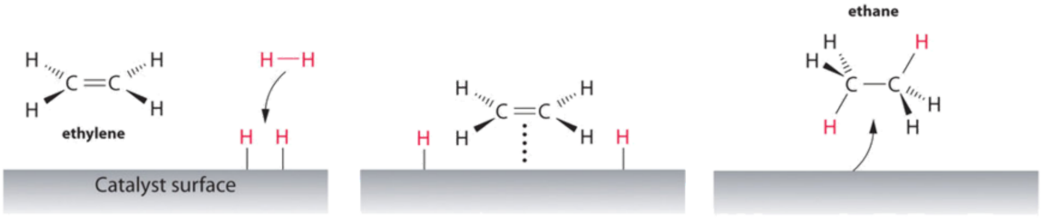
The green line represents the uncatalyzed reaction. The purple line represent the catalyzed reaction .

> *A catalyst affects E_a, not ΔE.*

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure $15.9.2$, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.



(a) Hydrogen (H_2) adsorbs to the catalyst surface (M) to form adsorbed H atoms.

(b) Ethylene (C_2H_4) adsorbs to the catalyst surface.

(c) Ethylene reacts with adsorbed H atoms to give the product ethane (C_2H_6).

Figure 15.9.2: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure 15.9.2 shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 15.9.1. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

Table 15.9.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

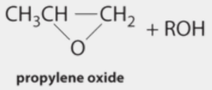
Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O$	$\underset{\text{acrylonitrile}}{CH_2{=}CHCN}$
catalytic hydrogenation	Ni, Pd, or Pt	RCH=CHR′ + H2 → RCH_2—CH_2R'	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In **homogeneous catalysis**, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table 15.9.2), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table 15.9.2: Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	$[Rh(CO)_2I_2]^-$	$CO + CH_3OH$	CH_3CO_2H
hydroperoxide process	Mo(VI) complexes	$CH_3CH{=}CH_2 + R{-}O{-}O{-}H$	
hydroformylation	Rh/PR_3 complexes	$RCH{=}CH_2 + CO + H_2$	RCH_2CH_2CHO
adiponitrile process	Ni/PR_3complexes	$2HCN + CH_2{=}CHCH{=}CH_2$	$NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon
olefin polymerization	$(RC_5H_5)_2ZrCl_2$	$CH_2{=}CH_2$	$–(CH_2CH_2–)_n$: high-density polyethylene

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a **substrate**.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37 °C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be proteases, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure 15.9.3).

Figure 15.9.3: A Catalytic Defense Mechanism. The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of H_2O_2.

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In heterogeneous catalysis, catalysts provide a surface to which reactants bind in a process of adsorption. In homogeneous catalysis, catalysts are in the same phase as the reactants. Enzymes are biological catalysts that produce large increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a substrate. Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

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CHAPTER OVERVIEW

16: Liquids and Solids

Chemical Principles (Zumdahl and Decoste)
Textmap Alternative

Topic hierarchy

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16.1: Intermolecular Forces

Learning Objectives

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

> *The properties of liquids are intermediate between those of gases and solids, but are more similar to solids.*

Intermolecular forces determine bulk properties, such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures.

In this section, we explicitly consider three kinds of intermolecular interactions. There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding, and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure $16.1.1a$.

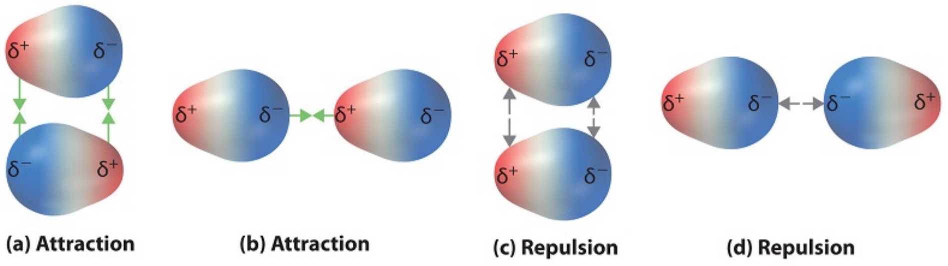


Figure 16.1.1: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions. (CC BY-SA-NC; anonymous)

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure $16.1.1c$). Hence dipole–dipole interactions, such as those in Figure $16.1.1b$, are *attractive intermolecular interactions*, whereas those in Figure $16.1.1d$ are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 16.1.2. On average, however, the attractive interactions dominate.

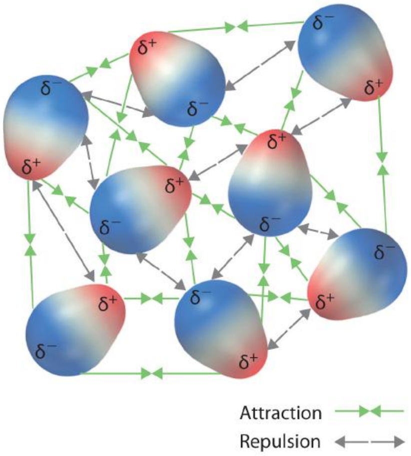


Figure 16.1.2: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules. (CC BY-SA-NC; anonymous)

The green arrows pointing towards each other represent attraction. The gray arrows pointing away from each other represent repulsion

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^3$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^3, or 8-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure. Conversely, NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 16.1.1.

Table 16.1.1: Relationships Between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

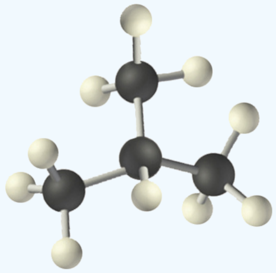
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

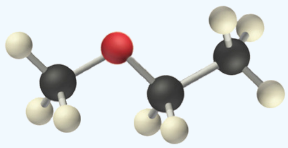
> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*

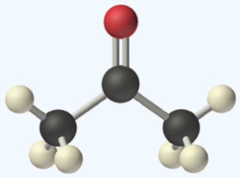
Video Discussing Dipole Intermolecular Forces. Source: Dipole Intermolecular Force, YouTube(opens in new window) [youtu.be]

✓ Example 16.1.1

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:


2-Methylpropane


Ethyl methyl ether


Acetone

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds.

The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point.

Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point.

Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.

Thus we predict the following order of boiling points:

2-methylpropane < ethyl methyl ether < acetone

This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

? Exercise 16.1.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far, we have considered only interactions between polar molecules. Other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature; why others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 16.1.2).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 16.1.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 16.1.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

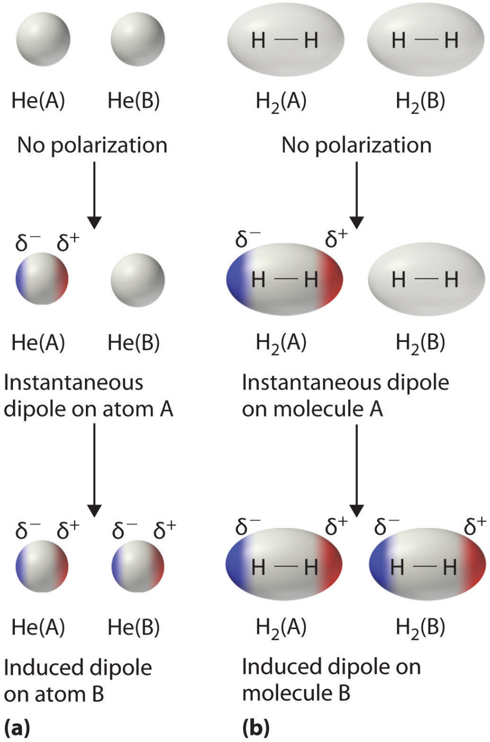
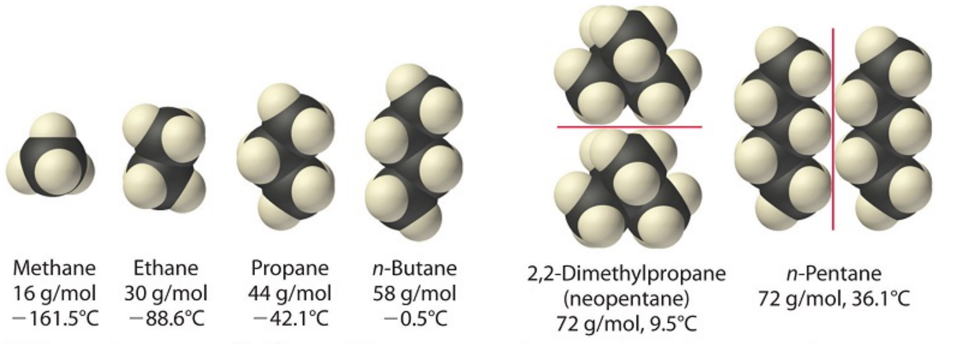


Figure 16.1.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 16.1.3, tends to become more pronounced as atomic and molecular masses increase (Table 16.1.2). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus, London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 16.1.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 16.1.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).



(a) Increasing mass and boiling point

(b) Increasing surface area and boiling point

Figure 16.1.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Video Discussing London/Dispersion Intermolecular Forces. Source: Dispersion Intermolecular Force, YouTube(opens in new window) [youtu.be]

✓ Example 16.1.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds, and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

? Exercise 16.1.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent, Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 16.1.5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

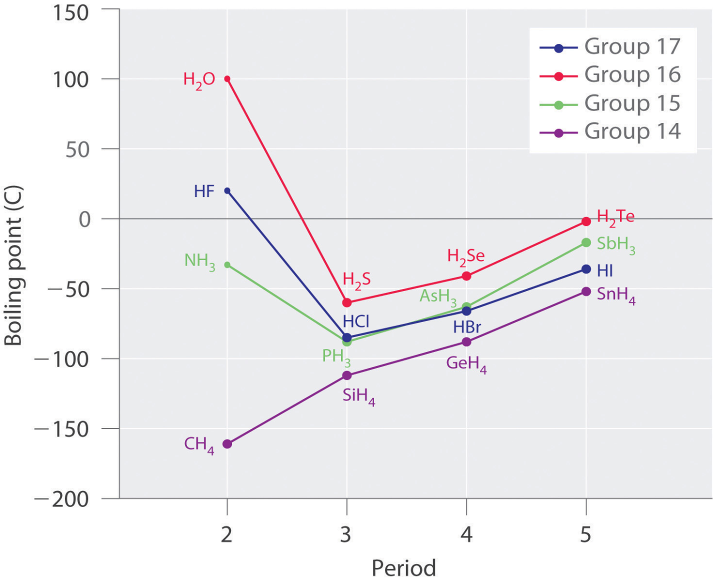


Figure 16.1.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Group 14 is in purple, group 15 is in green, group 16 is red, and group 17 is blue. Graph of boiling point against period.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 16.1.6. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O⋯H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water, rather than sinks.

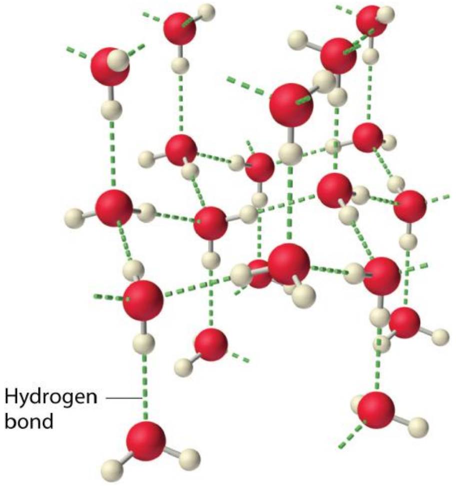


Figure 16.1.6: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cage like structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

> *Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.*

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Video Discussing Hydrogen Bonding Intermolecular Forces. Source: Hydrogen Bonding Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 16.1.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

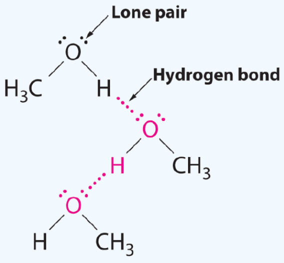
Strategy:

A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A. Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B. The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



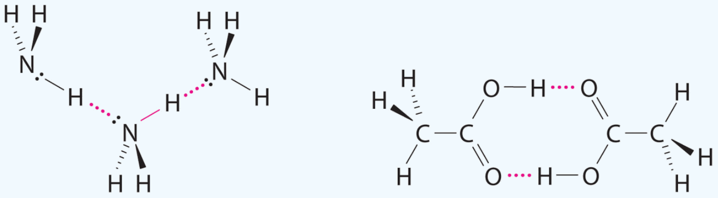
Hydrogen bonding in methanol

Exercise 16.1.3

Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia Hydrogen bonding in acetic acid

Hydrogen bonding in ammonia between nitrogen and hydrogen. hydrogen bonding in acetic acid is between oxygen and hydrogen.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

✓ Example 16.1.4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$\text{He } (-269°\text{C}) < \text{Ar } (-185.7°\text{C}) < N_2O\ (-88.5°\text{C}) < C_{60}\ (>280°\text{C}) < \text{NaCl } (1465°\text{C}).$$

? Exercise 16.1.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

✓ Example 16.1.5

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.
b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.
c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

? Exercise 16.1.6

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

dipole-dipole interactions

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid, or the liquid and gas phases, are due to changes in intermolecular interactions, but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^3$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules; their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones, because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O⋯H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cage like structure that is less dense than liquid water.

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16.2: The Liquid State

Learning Objectives

- To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions:

- surface tension,
- capillary action, and
- viscosity.

Surface Tension

If liquids tend to adopt the shapes of their containers, then why do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of 7.29 x 10^{-2} J/m^2 (at 20°C), while mercury with metallic bonds has as surface tension that is 15 times higher: 4.86 x 10^{-1} J/m^2 (at 20°C).

Figure $16.2.1$ presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

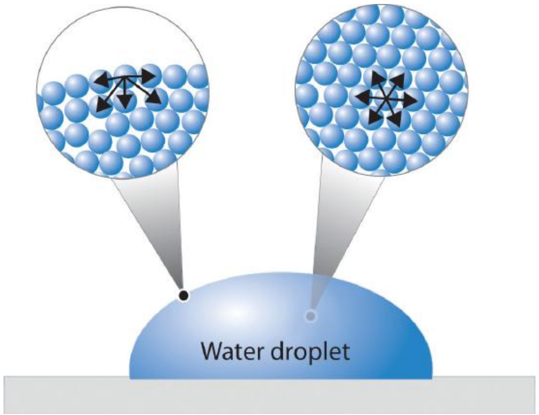


Figure 16.2.1: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it “floats,” even though steel is much denser than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is even observable in the zero gravity conditions of space as shown in Figure $16.2.2$ (and more so in the video link) where water wrung from a wet towel continues to float along the towel's surface!

Figure 16.2.2: The Effects of the High Surface Tension of Liquid Water. The full video can be found at www.youtube.com/watch?v=9jB7rOC5kG8.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2) or dyne per centimeter (dyn/cm), where 1 dyn = 1×10^{-5} N. The values of the surface tension of some representative liquids are listed in Table 16.2.1. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

Table 16.2.1: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension ($\times 10^{-3}$ J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure 16.2.3. When a glass capillary is is placed in liquid water, water rises up into the capillary. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

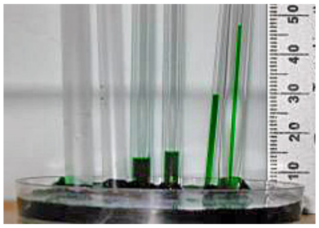


Figure 16.2.3: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.

> - Cohesive forces bind molecules of the same type together
> - Adhesive forces bind a substance to a surface

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (Figure 16.2.4). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure 16.2.4).

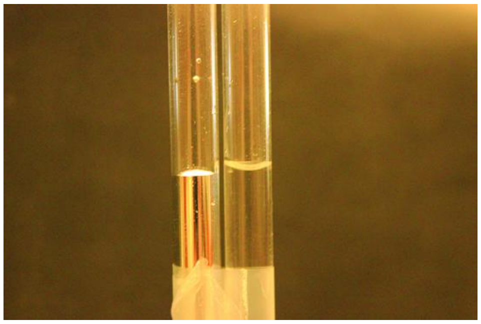


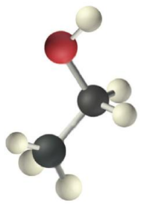
Figure 16.2.4: The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

> Polar substances are drawn up a glass capillary and generally have a concave meniscus.

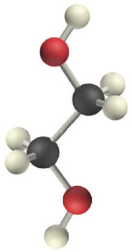
Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and “wick” the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 11.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



Ethanol



Ethylene glycol

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become "tangled" with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

> *Viscosity increases as intermolecular interactions or molecular size increases.*

Video Discussing Surface Tension and Viscosity. Video Link: Surface Tension, Viscosity, & Melting Point, YouTube(opens in new window) [youtu.be]

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures.

Figure 16.2.5: Oil being drained from a car

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity (Figure 16.2.5). So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives “for improved engine performance” are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

✓ Example 16.2.1

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A. Identify the cohesive forces in the motor oil.
B. Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains.

B Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

? Exercise 16.2.1

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer

Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Summary

Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. **Surface tension** is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

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- **11.3: Some Properties of Liquids** is licensed CC BY-NC-SA 3.0.

SECTION OVERVIEW

16.3: An Introduction to Structures and Types of Solids

Solid are characterized by structural rigidity and resistance to changes of shape or volume. Unlike a liquid, a solid object does not flow to take on the shape of its container, nor does expands to fill the entire volume available to it like a gas . The atoms in a solid are tightly bound to each other, either in a regular geometric lattice (crystalline solids, which include metals and ordinary water ice) or irregularly (an amorphous solid such as common window glass).

Topic hierarchy

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16.4: Structure and Bonding in Metals

In the early 1900's, Paul Drüde came up with the "sea of electrons" metallic bonding theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. Metallic bonds occur among metal atoms. Whereas ionic bonds join metals to non-metals, *metallic bonding joins a bulk of metal atoms*. A sheet of aluminum foil and a copper wire are both places where you can see metallic bonding in action.

Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a soft metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table. Sodium has the electronic structure $1s^2 2s^2 2p^6 3s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. Each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium. *All* of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals that extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons (Figure $16.4.1$).

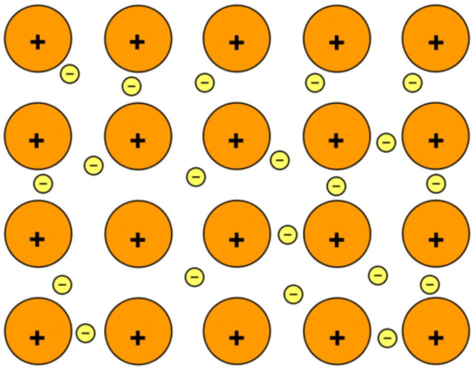

Figure 16.4.1: Metallic Bonding: The Electron Sea Model: Positive atomic nuclei (orange circles) surrounded by a sea of delocalized electrons (yellow circles).

This is sometimes described as "an array of positive ions in a sea of electrons". If you are going to use this view, beware! Is a metal made up of atoms or ions? It is made of atoms**.** Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron has not been lost - it may no longer have an attachment to a particular atom, but it's still there in the structure. Sodium metal is therefore written as Na, not Na^+.

✓ Example 16.4.1: Metallic bonding in magnesium

Use the sea of electrons model to explain why Magnesium has a higher melting point (650 °C) than sodium (97.79 °C).

Solution

If you work through the same argument above for sodium with magnesium, you end up with stronger bonds and hence a higher melting point.

Magnesium has the outer electronic structure $3s^2$. Both of these electrons become delocalized, so the "sea" has twice the electron density as it does in sodium. The remaining "ions" also have twice the charge (if you are going to use this particular view of the metal bond) and so there will be more attraction between "ions" and "sea".

More realistically, each magnesium atom has 12 protons in the nucleus compared with sodium's 11. In both cases, the nucleus is screened from the delocalized electrons by the same number of inner electrons - the 10 electrons in the $1s^2\ 2s^2\ 2p^6$ orbitals. That means that there will be a net pull from the magnesium nucleus of 2+, but only 1+ from the sodium nucleus.

So not only will there be a greater number of delocalized electrons in magnesium, but there will also be a greater attraction for them from the magnesium nuclei. Magnesium atoms also have a slightly smaller radius than sodium atoms, and so the delocalized electrons are closer to the nuclei. Each magnesium atom also has twelve near neighbors rather than sodium's eight. Both of these factors increase the strength of the bond still further.

Note: Transition metals tend to have particularly high melting points and boiling points. The reason is that they can involve the 3d electrons in the delocalization as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be.

Bulk properties of metals

Metals have several qualities that are unique, such as the ability to conduct electricity and heat, a low ionization energy, and a low electronegativity (so they will give up electrons easily to form cations). Their physical properties include a lustrous (shiny) appearance, and they are malleable and ductile. Metals have a crystal structure but can be easily deformed. In this model, the valence electrons are free, delocalized, mobile, and not associated with any particular atom. This model may account for:

- **Conductivity**: Since the electrons are free, if electrons from an outside source were pushed into a metal wire at one end (Figure $16.4.2$), the electrons would move through the wire and come out at the other end at the same rate (conductivity is the movement of charge).

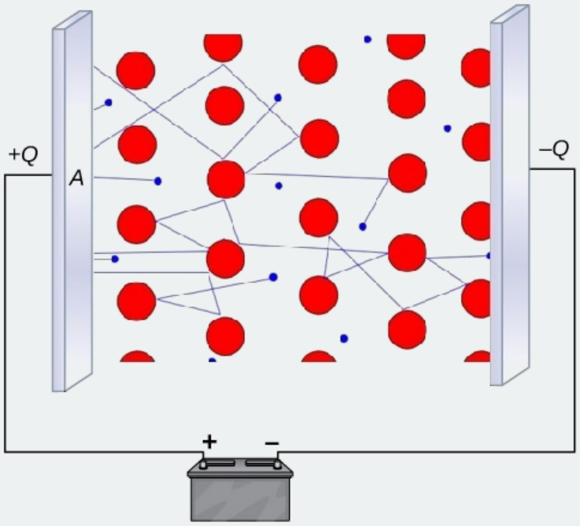

Figure 16.4.2: The "sea of electrons" is free to flow about the crystal of positive metal ions. These flowing electron can conduct electrical change when an electric field is applied (e.g., a battery). (CC-BY-SA; OpenStax and Rafaelgarcia).

- **Malleability** and **Ductility**: The electron-sea model of metals not only explains their electrical properties but their malleability and ductility as well. The sea of electrons surrounding the protons acts like a cushion, and so when the metal is hammered on, for instance, the overall composition of the structure of the metal is not harmed or changed. The protons may be rearranged but the sea of electrons with adjust to the new formation of protons and keep the metal intact. When one layer of ions in an electron sea moves along one space with respect to the layer below it, the crystal structure does not fracture but is only deformed (Figure $16.4.3$).

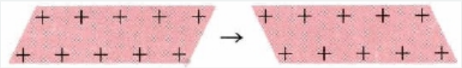

Figure 16.4.3: Malleability of metals originate from each of moving layer of atoms with respect to each other. The final situation is much the same as the initial. Thus if we hit a metal with a hammer, the crystals do not shatter, but merely change their shape, This is very different from the behavior of ionic crystals.

- **Heat capacity**: This is explained by the ability of free electrons to move about the solid.
- **Luster**: The free electrons can absorb photons in the "sea," so metals are opaque-looking. Electrons on the surface can bounce back light at the same frequency that the light hits the surface, therefore the metal appears to be shiny.

However, these observations are only qualitative, and not quantitative, so they cannot be tested. The "Sea of Electrons" theory stands today only as an oversimplified model of how metallic bonding works.

In a molten metal, the metallic bond is still present, although the ordered structure has been broken down. The metallic bond is not fully broken until the metal boils. That means that boiling point is actually a better guide to the strength of the metallic bond than melting point is. On melting, the bond is loosened, not broken. The strength of a metallic bond depends on three things:

1. The number of electrons that become delocalized from the metal
2. The charge of the cation (metal).
3. The size of the cation.

A **strong** metallic bond will be the result of more delocalized electrons, which causes the effective nuclear charge on electrons on the cation to increase, in effect making the size of the cation smaller. Metallic bonds are strong and require a great deal of energy to break, and therefore **metals have high melting and boiling points.** A metallic bonding theory must explain how so much bonding can occur with such few electrons (since metals are located on the left side of the periodic table and do not have many electrons in their valence shells). The theory must also account for all of a metal's unique chemical and physical properties.

Expanding the Range of Bonding Possible

Previously, we argued that bonding between atoms can classified as range of possible bonding between **ionic bonds** (fully charge transfer) and **covalent bonds** (fully shared electrons). When two atoms of slightly differing electronegativities come together to form a covalent bond, one atom attracts the electrons more than the other; this is called a polar covalent bond. However, simple “ionic” and “covalent” bonding are idealized concepts and most bonds exist on a two-dimensional continuum described by the van Arkel-Ketelaar Triangle (Figure 16.4.4).

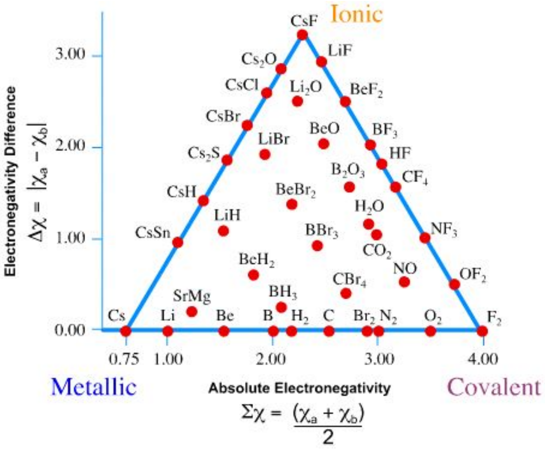

Figure 16.4.4: van Arkel-Ketelaar Triangle plots the difference in electronegativity ($\Delta\chi$) and the average electronegativity in a bond ($\sum\chi$). the top region is where bonds are mostly ionic, the lower left region is where bonding is metallic, and the lower right region is where the bonding is covalent.

Bond triangles or **van Arkel–Ketelaar** triangles (named after Anton Eduard van Arkel and J. A. A. Ketelaar) are triangles used for showing different compounds in varying degrees of ionic, metallic and covalent bonding. In 1941 van Arkel recognized three extreme materials and associated bonding types. Using 36 main group elements, such as metals, metalloids and non-metals, he placed ionic, metallic and covalent bonds on the corners of an equilateral triangle, as well as suggested intermediate species. The bond triangle shows that chemical bonds are not just particular bonds of a specific type. Rather, bond types are interconnected and different compounds have varying degrees of different bonding character (for example, polar covalent bonds).

Video 16.4.1: What is the van Arkel-Ketelaar Triangle of Bonding?

Using electronegativity - two compound average electronegativity on x-axis of Figure 16.4.4

$$\sum \chi = \frac{\chi_A + \chi_B}{2} \tag{16.4.1}$$

and electronegativity difference on y-axis,

$$\Delta \chi = |\chi_A - \chi_B| \tag{16.4.2}$$

we can rate the dominant bond between the compounds. On the right side of Figure 16.4.4 (from ionic to covalent) should be compounds with varying difference in electronegativity. The compounds with equal electronegativity, such as Cl_2 (chlorine) are placed in the covalent corner, while the ionic corner has compounds with large electronegativity difference, such as $NaCl$ (table salt). The bottom side (from metallic to covalent) contains compounds with varying degree of directionality in the bond. At one extreme is metallic bonds with delocalized bonding and at the other are covalent bonds in which the orbitals overlap in a particular direction. The left side (from ionic to metallic) is meant for delocalized bonds with varying electronegativity difference.

The Three Extremes in bonding

In general:

- Metallic bonds have low $\Delta\chi$ **and** low average $\sum\chi$.
- Ionic bonds have moderate-to-high $\Delta\chi$ and moderate values of average $\sum\chi$.
- Covalent bonds have moderate to high average $\sum\chi$ and can exist with moderately low $\Delta\chi$.

Example 16.4.2

Use the tables of electronegativities (Table A2) and Figure 16.4.4 to estimate the following values

- difference in electronegativity ($\Delta\chi$)
- average electronegativity in a bond ($\sum\chi$)
- percent ionic character
- likely bond type

for the selected compounds:

a. AsH (e.g., in arsine AsH)
b. SrLi
c. KF.

Solution

a: AsH

- The electronegativity of As is 2.18
- The electronegativity of H is 2.22

Using Equations 16.4.1 and 16.4.2:

$$\begin{aligned}\sum \chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{2.18 + 2.22}{2} \\ &= 2.2\end{aligned}$$

$$\begin{aligned}\Delta \chi &= \chi_A - \chi_B \\ &= 2.18 - 2.22 \\ &= 0.04\end{aligned}$$

- From Figure 16.4.4, the bond is fairly nonpolar and has a low ionic character (10% or less)
- The bonding is in the middle of a covalent bond and a metallic bond

b: SrLi

- The electronegativity of Sr is 0.95
- The electronegativity of Li is 0.98

Using Equations 16.4.1 and 16.4.2:

$$\begin{aligned}\sum \chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{0.95 + 0.98}{2} \\ &= 0.965\end{aligned}$$

$$\begin{aligned}\Delta \chi &= \chi_A - \chi_B \\ &= 0.98 - 0.95 \\ &= 0.025\end{aligned}$$

- From Figure 16.4.4, the bond is fairly nonpolar and has a low ionic character (~3% or less)
- The bonding is likely metallic.

c: KF

- The electronegativity of K is 0.82
- The electronegativity of F is 3.98

Using Equations 16.4.1 and 16.4.2:

$$\begin{aligned}\sum \chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{0.82 + 3.98}{2} \\ &= 2.4\end{aligned}$$

$$\begin{aligned}\Delta \chi &= \chi_A - \chi_B \\ &= |0.82 - 3.98| \\ &= 3.16\end{aligned}$$

- From Figure 16.4.4, the bond is fairly polar and has a high ionic character (~75%)
- The bonding is likely ionic.

? Exercise 16.4.2

Contrast the bonding of NaCl and silicon tetrafluoride.

Answer

NaCl is an ionic crystal structure, and an electrolyte when dissolved in water; $\Delta\chi = 1.58$, average $\sum\chi = 1.79$, while silicon tetrafluoride is covalent (molecular, non-polar gas; $\Delta\chi = 2.08$, average $\sum\chi = 2.94$.

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16.5: Carbon and Silicon: Network Atomic Solids

Learning Objectives

- To understand the correlation between bonding and the properties of solids.
- To classify solids as ionic, molecular, covalent (network), or metallic, where the general order of increasing strength of interactions.

Crystalline solids fall into one of four categories. All four categories involve packing discrete molecules or atoms into a lattice or repeating array, though *network solids* are a special case. The categories are distinguished by the nature of the interactions holding the discrete molecules or atoms together. Based on the nature of the forces that hold the component atoms, molecules, or ions together, solids may be formally classified as ionic, molecular, covalent (network), or metallic. The variation in the relative strengths of these four types of interactions correlates nicely with their wide variation in properties.

Table 16.5.1: Solids may be formally classified as ionic, molecular, covalent (network), or metallic

Type of Solid	Interaction	Properties	Examples
Ionic	Ionic	High Melting Point, Brittle, Hard	NaCl, MgO
Molecular	Hydrogen Bonding, Dipole-Dipole, London Dispersion	Low Melting Point, Nonconducting	H_2, CO_2
Metallic	Metallic Bonding	Variable Hardness and Melting Point (depending upon strength of metallic bonding), Conducting	Fe, Mg
Network	Covalent Bonding	High Melting Point, Hard, Nonconducting	C (diamond), SiO_2 (quartz)

In ionic and molecular solids, there are no chemical bonds between the molecules, atoms, or ions. The solid consists of discrete chemical species held together by intermolecular forces that are **electrostatic** or **Coulombic** in nature. This behavior is most obvious for an ionic solid such as $NaCl$, where the positively charged Na^+ ions are attracted to the negatively charged Cl^- ions. Even in the absence of ions, however, electrostatic forces are operational. For polar molecules such as CH_2Cl_2, the positively charged region of one molecular is attracted to the negatively charged region of another molecule (dipole-dipole interactions). For a nonpolar molecule such as CO_2, which has no permanent dipole moment, the random motion of electrons gives rise to temporary polarity (a temporary dipole moment). Electrostatic attractions between two temporarily polarized molecules are called London Dispersion Forces.

Hydrogen bonding is a term describing an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. (See the IUPAC Provisional Recommendation on the definition of a hydrogen bond.) Dots are employed to indicate the presence of a hydrogen bond: X–H•••Y. The attractive interaction in a hydrogen bond typically has a strong electrostatic contribution, but dispersion forces and weak covalent bonding are also present.

In metallic solids and network solids, however, chemical bonds hold the individual chemical subunits together. The crystal is essential a single, macroscopic molecule with continuous chemical bonding throughout the entire structure. In metallic solids, the valence electrons are no longer exclusively associated with a single atom. Instead these electrons exist in molecular orbitals that are delocalized over many atoms, producing an electronic band structure. The metallic crystal essentially consists of a set of metal cations in a sea of electrons. This type of chemical bonding is called metallic bonding.

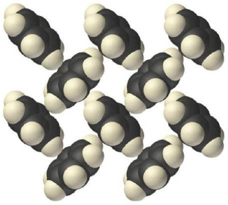
Ionic Solids

You learned previously that an ionic solid consists of positively and negatively charged ions held together by electrostatic forces. The strength of the attractive forces depends on the charge and size of the ions that compose the lattice and determines many of the physical properties of the crystal.

The **lattice energy** (i.e., the energy required to separate 1 mol of a crystalline ionic solid into its component ions in the gas phase) is directly proportional to the product of the ionic charges and inversely proportional to the sum of the radii of the ions. For example, NaF and CaO both crystallize in the face-centered cubic (fcc) sodium chloride structure, and the sizes of their component ions are about the same: Na^+ (102 pm) versus Ca^{2+} (100 pm), and $F^−$ (133 pm) versus $O^{2−}$ (140 pm). Because of the higher charge on the ions in CaO, however, the lattice energy of CaO is almost four times greater than that of NaF (3401 kJ/mol versus 923 kJ/mol). The forces that hold Ca and O together in CaO are much stronger than those that hold Na and F together in NaF, so the heat of fusion of CaO is almost twice that of NaF (59 kJ/mol versus 33.4 kJ/mol), and the melting point of CaO is 2927°C versus 996°C for NaF. In both cases, however, the values are large; that is, simple ionic compounds have high melting points and are relatively hard (and brittle) solids.

Molecular Solids

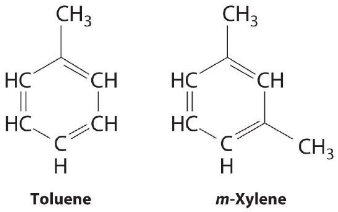
Molecular solids consist of atoms or molecules held to each other by dipole–dipole interactions, London dispersion forces, or hydrogen bonds, or any combination of these. The arrangement of the molecules in solid benzene is as follows:



The structure of solid benzene. In solid benzene, the molecules are not arranged with their planes parallel to one another but at 90° angles. (CC BY-NC-SA; Anonymous by request).

Because the intermolecular interactions in a molecular solid are relatively weak compared with ionic and covalent bonds, molecular solids tend to be soft, low melting, and easily vaporized (ΔH_{fus} and ΔH_{vap} are low). For similar substances, the strength of the London dispersion forces increases smoothly with increasing molecular mass. For example, the melting points of benzene (C_6H_6), naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$), with one, two, and three fused aromatic rings, are 5.5°C, 80.2°C, and 215°C, respectively. The enthalpies of fusion also increase smoothly within the series: benzene (9.95 kJ/mol) < naphthalene (19.1 kJ/mol) < anthracene (28.8 kJ/mol). If the molecules have shapes that cannot pack together efficiently in the crystal, however, then the melting points and the enthalpies of fusion tend to be unexpectedly low because the molecules are unable to arrange themselves to optimize intermolecular interactions. Thus toluene ($C_6H_5CH_3$) and m-xylene [m-$C_6H_4(CH_3)_2$] have melting points of −95°C and −48°C, respectively, which are significantly lower than the melting point of the lighter but more symmetrical analog, benzene.

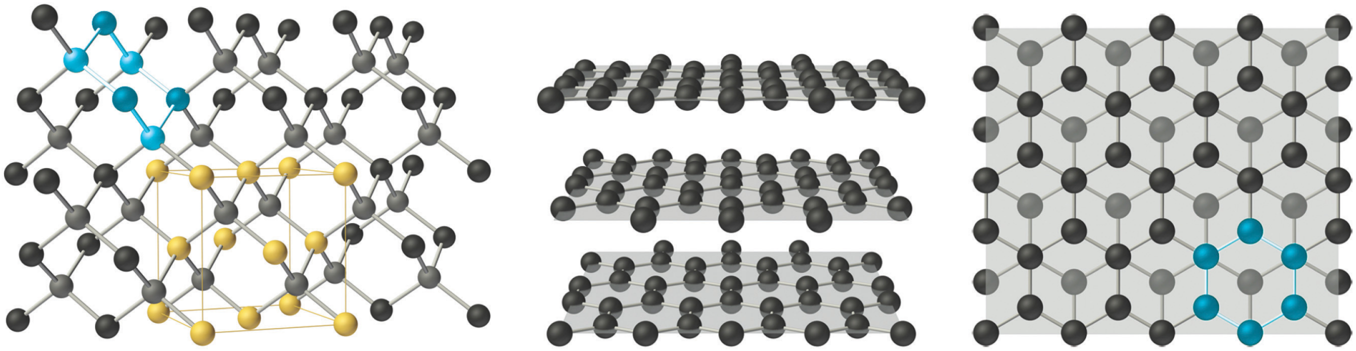
Self-healing rubber is an example of a molecular solid with the potential for significant commercial applications. The material can stretch, but when snapped into pieces it can bond back together again through reestablishment of its hydrogen-bonding network without showing any sign of weakness. Among other applications, it is being studied for its use in adhesives and bicycle tires that will self-heal.



Toluene and m-xylene. The methyl groups attached to the phenyl ring in toluene and m-xylene prevent the rings from packing together as in solid benzene. (CC BY-NC-SA; Anonymous by request).

Covalent Network Solids

Covalent solids are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure 16.5.1, consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.



(a) Diamond

(b) Graphite

Figure 16.5.1: The Structures of Diamond and Graphite. (a) Diamond consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. This is easier to see in the rotating cube shown in Figure 16.5.2 below. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer. (CC BY-NC-SA; Anonymous by request).

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in Section 12.3, except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (SiO_2), shown in Section 12.1, can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in Figure 16.5.1. It contains planar networks of six-membered rings of sp2 hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized 2pz orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in Chapter 9. In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimes at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the "lead" in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other hand, is colorless when pure because it has no delocalized electrons. Table 16.5.2 compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table 16.5.2: A Comparison of Intermolecular (ΔH_{sub}) and Intramolecular Interactions

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
phosphorus (s)	58.98	201

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
sulfur (s)	64.22	226
iodine (s)	62.42	149

Carbon: An example of an Covalent Network Solid

In network solids, conventional chemical bonds hold the chemical subunits together. The bonding between chemical subunits, however, is identical to that within the subunits, resulting in a continuous network of chemical bonds. One common examples of network solids are diamond (a form of pure carbon) Carbon exists as a pure element at room temperature in three different forms: graphite (the most stable form), diamond, and fullerene.

Diamonds

The structure of diamond is shown at the right in a "ball-and-stick" format. The balls represent the carbon atoms and the sticks represent a covalent bond. Be aware that in the "ball-and-stick" representation the size of the balls do not accurately represent the size of carbon atoms. In addition, a single stick is drawn to represent a covalent bond irrespective of whether the bond is a single, double, or triple bond or requires resonance structures to represent. In the diamond structure, all bonds are single covalent bonds (σ bonds). The "space-filling" format is an alternate representation that displays atoms as spheres with a radius equal to the van der Waals radius, thus providing a better sense of the size of the atoms.

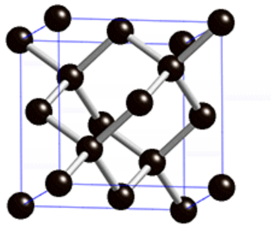


Figure 16.5.2: Rotating model of diamond cubic. (CC0; H.K.D.H. Bhadeshia via Wikipedia)

Notice that diamond is a network solid. The entire solid is an "endless" repetition of carbon atoms bonded to each other by covalent bonds. (In the display at the right, the structure is truncated to fit in the display area.)

Questions to consider

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in diamond?
- The diamond structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- Diamond are renowned for its hardness. Explain why this property is expected on the basis of the structure of diamond.

Graphite

The most stable form of carbon is graphite. Graphite consists of sheets of carbon atoms covalently bonded together. These sheets are then stacked to form graphite. Figure $16.5.3$ shows a ball-and-stick representation of graphite with sheets that extended "indefinitely" in the xy plane, but the structure has been truncated for display purposed. Graphite may also be regarded as a network solid, even though there is no bonding in the z direction. Each layer, however, is an "endless" bonded network of carbon atoms.

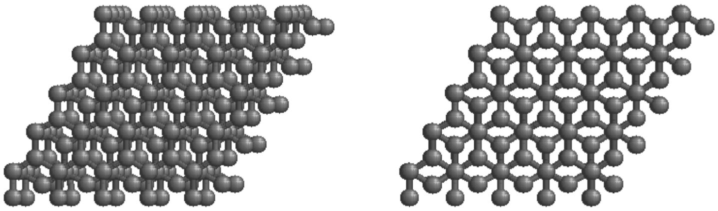


Figure 16.5.3: Animation of a rotating graphite structure. This is a stereogram and can be viewed in 3D if a viewer's eyes are crossed slightly to overlap the two panels. Images used with permission from Wikipedia.

Questions to consider

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in graphite?
- The a layer of the graphite structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- What force holds the carbon sheets together in graphite?
- Graphite is very slippery and is often used in lubricants. Explain why this property is expected on the basis of the structure of graphite.
- The slipperiness of graphite is enhanced by the introduction of impurities. Where would such impurities be located and why would they make graphite a better lubricant?

Fullerenes

Until the mid 1980's, pure carbon was thought to exist in two forms: graphite and diamond. The discovery of C_{60} molecules in interstellar dust in 1985 added a third form to this list. The existence of C_{60}, which resembles a soccer ball, had been hypothesized by theoreticians for many years. In the late 1980's synthetic methods were developed for the synthesis of C_{60}, and the ready availability of this form of carbon led to extensive research into its properties.

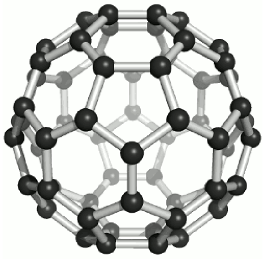


Figure 16.5.4: Example of fullerenes: a buckyball (C_{60} on left and an extended bucktube. Images used with permission from Wikipedia.

The C_{60} molecule (Figure $16.5.4$; left), is called buckminsterfullerene, though the shorter name fullerene is often used. The name is a tribute to the American architect R. Buckminster Fuller, who is famous for designing and constructing geodesic domes which bear a close similarity to the structure of C_{60}. As is evident from the display, C_{60} is a sphere composed of six-member and five-member carbon rings. These balls are sometimes fondly referred to as "Bucky balls". It should be noted that fullerenes are an entire class of pure carbon compounds rather than a single compound. A distorted sphere containing more than 60 carbon atoms have also been found, and it is also possible to create long tubes (Figure $16.5.4$; right). All of these substances are pure carbon.

Questions to Consider

- What is the bonding geometry around each carbon? (Note that this geometry is distorted in C_{60}.)
- What is the hybridization of carbon in fullerene?
- A single crystal of C60 falls into which class of crystalline solids?
- It has been hypothesized that C60 would make a good lubricant. Why might C60 make a good lubricant?

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 16.5.5. 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.

Metals are characterized by their ability to reflect light, called luster, their high electrical and thermal conductivity, their high heat capacity, and their malleability and ductility. Every lattice point in a pure metallic element is occupied by an atom of the same metal. The packing efficiency in metallic crystals tends to be high, so the resulting metallic solids are dense, with each atom having as many as 12 nearest neighbors.

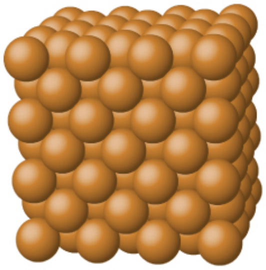


Figure 16.5.5: Copper is a metallic solid. (CC BY 4.0; OpenStax).

Bonding in metallic solids is quite different from the bonding in the other kinds of solids we have discussed. Because all the atoms are the same, there can be no ionic bonding, yet metals always contain too few electrons or valence orbitals to form covalent bonds with each of their neighbors. Instead, the valence electrons are delocalized throughout the crystal, providing a strong cohesive force that holds the metal atoms together.

> *Valence electrons in a metallic solid are delocalized, providing a strong cohesive force that holds the atoms together.*

The strength of metallic bonds varies dramatically. For example, cesium melts at 28.4°C, and mercury is a liquid at room temperature, whereas tungsten melts at 3680°C. Metallic bonds tend to be weakest for elements that have nearly empty (as in Cs) or nearly full (Hg) valence subshells, and strongest for elements with approximately half-filled valence shells (as in W). As a result, the melting points of the metals increase to a maximum around group 6 and then decrease again from left to right across the d block. Other properties related to the strength of metallic bonds, such as enthalpies of fusion, boiling points, and hardness, have similar periodic trends.

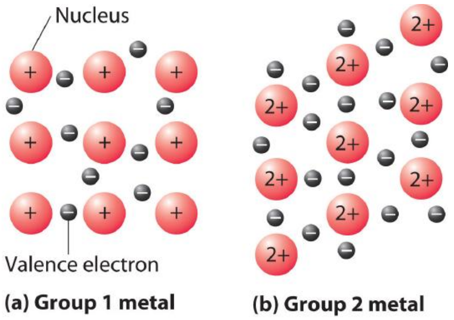


Figure 16.5.6: The Electron-Sea Model of Bonding in Metals. Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a "sea" of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting point.

A somewhat oversimplified way to describe the bonding in a metallic crystal is to depict the crystal as consisting of positively charged nuclei in an electron sea (Figure 16.5.6). In this model, the valence electrons are not tightly bound to any one atom but are distributed uniformly throughout the structure. Very little energy is needed to remove electrons from a solid metal because they are not bound to a single nucleus. When an electrical potential is applied, the electrons can migrate through the solid toward the positive electrode, thus producing high electrical conductivity. The ease with which metals can be deformed under pressure is attributed to the ability of the metal ions to change positions within the electron sea without breaking any specific bonds. The transfer of energy through the solid by successive collisions between the metal ions also explains the high thermal conductivity of metals. This model does not, however, explain many of the other properties of metals, such as their metallic luster and the observed trends in bond strength as reflected in melting points or enthalpies of fusion. Some general properties of the four major classes of solids are summarized in Table $16.5.2$

Table $16.5.2$: Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous

*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.

The general order of increasing strength of interactions in a solid is:

$$\textit{molecular solids} < \textit{ionic solids} \approx \textit{metallic solids} < \textit{covalent solids}$$

Example $16.5.1$

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

A. Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.
B. Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

A Germanium lies in the p block just under Si, along the diagonal line of semimetallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a covalent solid. RbI contains a metal from group 1 and a nonmetal from group 17, so it is an ionic solid containing Rb^+ and I^- ions. The compound C6(CH3)6 is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form a molecular solid with no covalent bonds between them. Zn is a d-block element, so it is a metallic solid.

B Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is $C_6(CH_3)_6$ < Zn ~ RbI < Ge. The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

? Exercise 16.5.1

Classify C_{60}, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer

> C_{60} (molecular) < AgZn (metallic) ~ $BaBr_2$ (ionic) < GaAs (covalent). The actual melting points are C60, about 300°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

Summary

The major types of solids are ionic, molecular, covalent, and metallic. Ionic solids consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to have high melting points and are rather hard. Molecular solids are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. As a result, they tend to be rather soft and have low melting points, which depend on their molecular structure. Covalent solids consist of two- or three-dimensional networks of atoms held together by covalent bonds; they tend to be very hard and have high melting points. Metallic solids have unusual properties: in addition to having high thermal and electrical conductivity and being malleable and ductile, they exhibit luster, a shiny surface that reflects light. An alloy is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (substitutional alloys), by inserting smaller atoms into holes in the metal lattice (interstitial alloys), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form intermetallic compounds with unique properties.

Contributors and Attributions

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16.7: Ionic Solids

, they become free to move about in the water allowing the solution to conduct electrical current.

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16.10: Vapor Pressure and Changes of State

Learning Objectives

- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- To understand that the relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressure of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (KE) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure 16.10.1), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

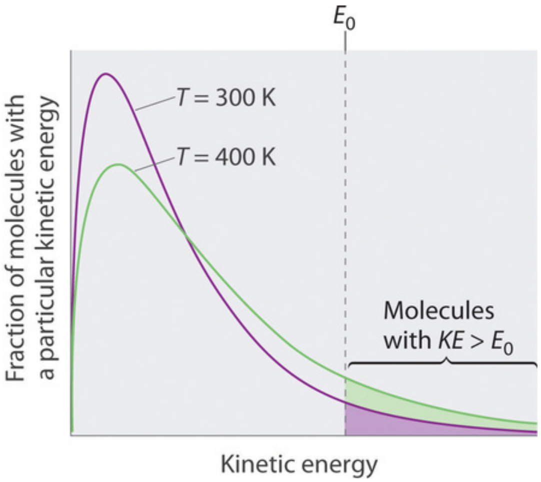

Figure 16.10.1: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature. (CC BY-SA-NC; Anonymous by request)

Graph of fraction of molecules with a particular kinetic energy against kinetic energy. Green line is temperature at 400 kelvin, purple line is temperature at 300 kelvin.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 16.10.2 When a liquid is introduced into an evacuated chamber (part (a) in Figure 16.10.2), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

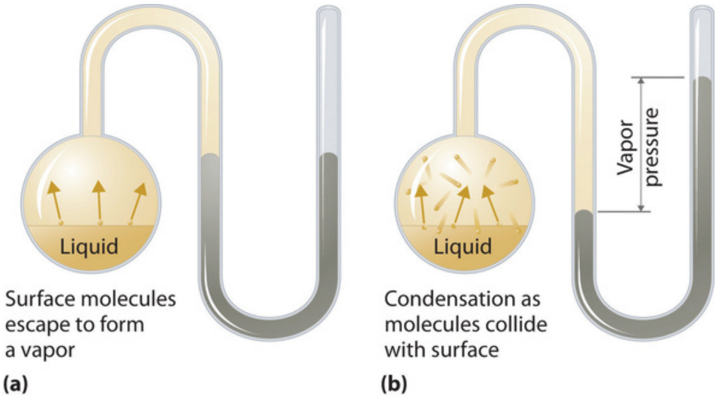

Figure 16.10.2: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant. (CC BY-SA-NC; Anonymous by request)

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure 16.10.2). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure 16.10.3

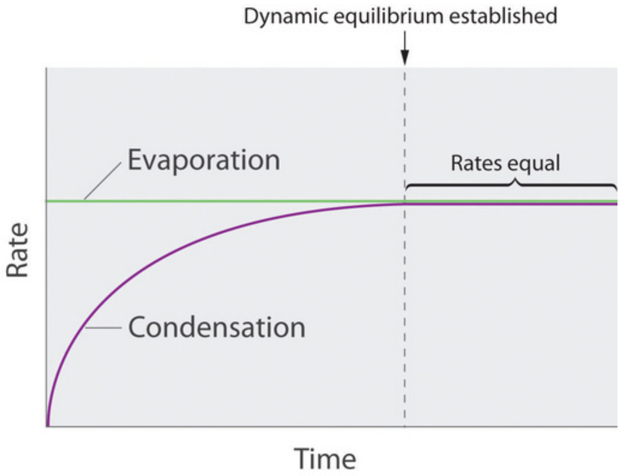

Figure 16.10.3: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation. (CC BY-SA-NC; Anonymous by request)

Graph of rate against time. The green line is evaporation while the pruple line is condensation. Dynamic equilibrium is established when the evaporation and condensation rates are equal.

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has “disappeared.” The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Figure 16.10.4) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

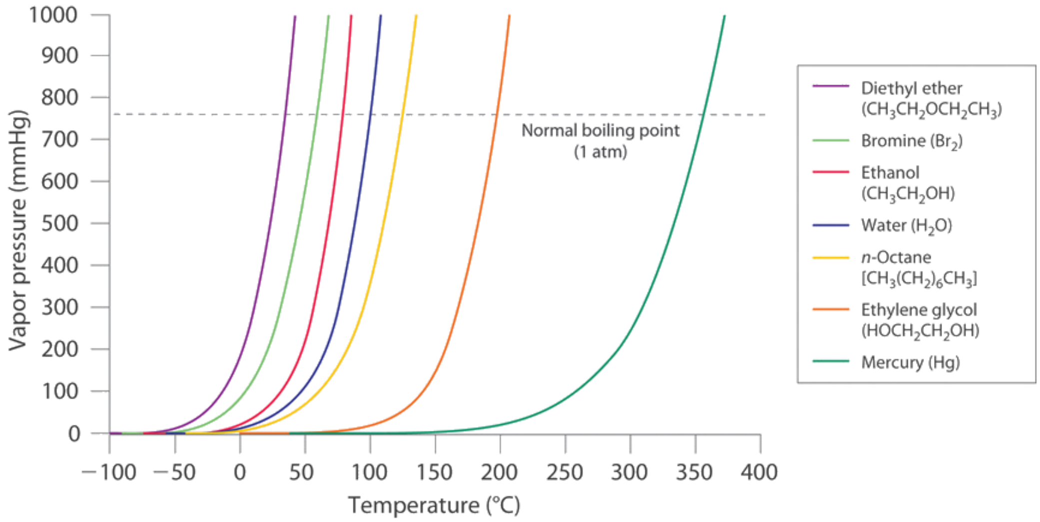

Figure 16.10.4: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; Anonymous by request)

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 16.10.4 Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won’t explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

> *Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.*

A Video Discussing Vapor Pressure and Boiling Points. Video Source: Vapor Pressure & Boiling Point(opens in new window) [youtu.be]

The exponential rise in vapor pressure with increasing temperature in Figure 16.10.4allows us to use natural logarithms to express the nonlinear relationship as a linear one.

$$\boxed{\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C} \tag{16.10.1}$$

where

- $\ln P$ is the natural logarithm of the vapor pressure,
- ΔH_{vap} is the enthalpy of vaporization,
- R is the universal gas constant [8.314 J/(mol•K)],
- T is the temperature in kelvins, and
- C is the y-intercept, which is a constant for any given line.

Plotting $\ln P$ versus the inverse of the absolute temperature ($1/T$) is a straight line with a slope of $-\Delta H_{vap}/R$. Equation 16.10.1, called the Clausius–Clapeyron Equation, can be used to calculate the ΔH_{vap} of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine ΔH_{vap} is to measure the vapor pressure of a liquid at **two** temperatures and insert the values of P and T for these points into Equation 16.10.2, which is derived from the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{16.10.2}$$

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation 16.10.2 to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example 16.10.1.

A Video Discussing the Clausius-Clapeyron Equation. Video Link: The Clausius-Clapeyron Equation(opens in new window) [youtu.be]

Example 16.10.1: Vapor Pressure of Mercury

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

experimentally measured vapor pressures of liquid Hg at four temperatures

T (°C)	80.0	100	120	140
P (torr)	0.0888	0.2729	0.7457	1.845

From these data, calculate the enthalpy of vaporization (ΔH_{vap}) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

Given: vapor pressures at four temperatures

Asked for: ΔH_{vap} of mercury and vapor pressure at 160°C

Strategy:

A. Use Equation 16.10.2to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.
B. Substitute the calculated value of ΔH_{vap} into Equation 16.10.2to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 16.10.1and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 16.10.2to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvin because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 16.10.2gives

$$\begin{aligned} \ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) &= \frac{-\Delta H_{vap}}{8.314\ J/mol\cdot K}\left(\frac{1}{(120+273)\,K}-\frac{1}{(80.0+273)\,K}\right) \\ \ln(8.398) &= \frac{-\Delta H_{vap}}{8.314\ J/mol\cdot\ \cancel{K}}\left(-2.88\times 10^{-4}\ \ \cancel{K^{-1}}\right) \\ 2.13 &= -\Delta H_{vap}\left(-3.46\times 10^{-4}\right) J^{-1}\cdot mol \\ \Delta H_{vap} &= 61,400\ J/mol = 61.4\ kJ/mol \end{aligned}$$

B We can now use this value of ΔH_{vap} to calculate the vapor pressure of the liquid (P_2) at 160.0°C (T_2):

$$\ln\left(\frac{P_2}{0.0888\ torr}\right) = \frac{-61,400\ \ J/\cancel{mol}}{8.314\ \ J/\cancel{mol}\ K^{-1}}\left(\frac{1}{(160+273)\,K}-\frac{1}{(80.0+273)\,K}\right)$$

Using the relationship $e^{\ln x} = x$, we have

$$\begin{aligned} \ln\left(\frac{P_2}{0.0888\ Torr}\right) &= 3.86 \\ \frac{P_2}{0.0888\ Torr} &= e^{3.86} = 47.5 \\ P_2 &= 4.21 Torr \end{aligned}$$

At 160°C, liquid Hg has a vapor pressure of 4.21 torr, substantially greater than the pressure at 80.0°C, as we would expect.

? Exercise 16.10.1: Vapor Pressure of Nickel

The vapor pressure of liquid nickel at 1606°C is 0.100 torr, whereas at 1805°C, its vapor pressure is 1.000 torr. At what temperature does the liquid have a vapor pressure of 2.500 torr?

Answer

1896°C

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure $16.10.4$ are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table 16.10.1: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table $16.10.1$lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a “three-minute egg” may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

✓ Example 16.10.2: Boiling Mercury

Use Figure $16.10.4$to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C

Mercury boils at 356 °C at room pressure. To see video go to www.youtube.com/watch?v=0iizsbXWYoo

Given: Data in Figure 16.10.4, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure 16.10.4and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.
B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.
b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

? Exercise 16.10.2: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure 16.10.4to estimate the following.

a. the normal boiling point of ethylene glycol
b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

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16.11: Phase Diagrams

Learning Objectives

- To understand the basics of a one-component phase diagram as a function of temperature and pressure in a closed system.
- To be able to identify the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical fluid.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure 16.11.1). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure 16.11.1) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

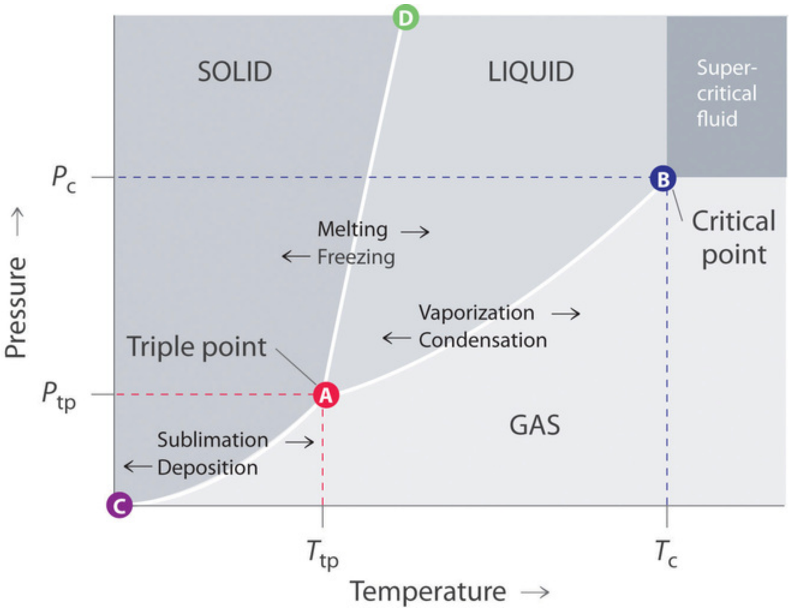

Figure 16.11.1: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

> The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure 16.11.1, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure 16.11.1, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure 16.11.2 shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

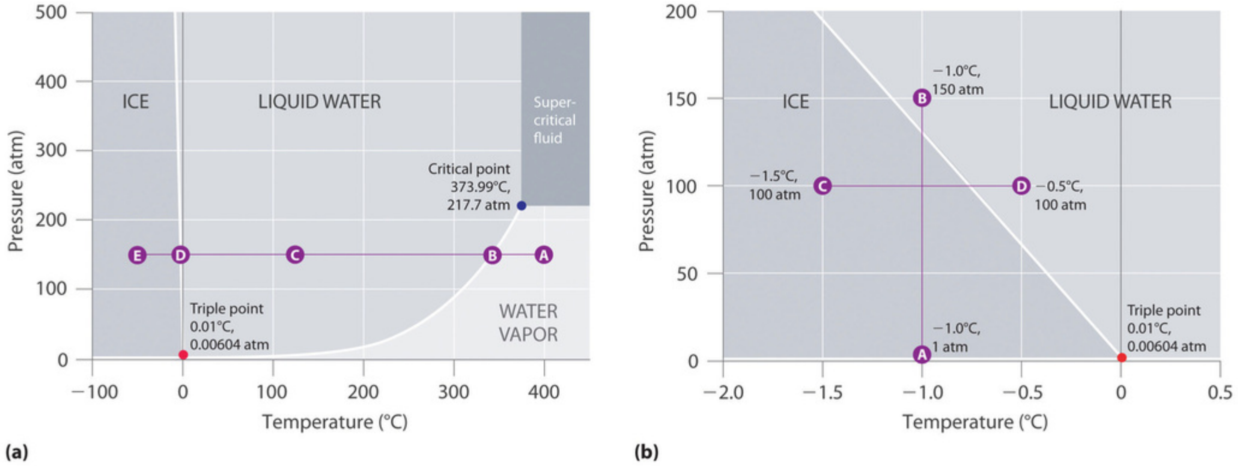

Figure 16.11.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 16.11.1).

The phase diagram for water illustrated in Figure 16.11.2b shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure 16.11.1; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure 16.11.2b point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Ice Skating: An Incorrect Hypothesis of Phase Transitions

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater's blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively satisfying, it is incorrect, as we can show by a simple calculation.

Pressure from ice skates on ice. from wikihow.com.

Recall that pressure (*P*) is the force (*F*) applied per unit area (*A*):

$$P=\frac{F}{A}$$

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

$$F=mg$$

where *m* is the mass and *g* is the acceleration due to Earth’s gravity (9.81 m/s^2). Thus the force is

$$F=(75.0\ kg)(9.81\ m/s^2)=736\ (kg\bullet m)/s^2=736N$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

$$A=(2.0\times 10^{-3}\ m)(25\times 10^{-2}\ m)=5.0\times 10^{-4}m^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

$$P=\frac{736\ N}{5.0\times 10^{-4}\ m^2}=1.5\times 10^6\ N/m^2=1.5\times 10^6\ Pa=15\ atm$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C, and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water. These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about −7°C, when the number of lubricating surface water layers decreases.

✓ Example 16.11.1: Water

Referring to the phase diagram of water in Figure $16.11.2$

a. predict the physical form of a sample of water at 400°C and 150 atm.
b. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A. Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.
B. Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

a. **A** Locate the starting point on the phase diagram in part (a) in Figure $16.11.2$ The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at *T* = 400°C and *P* = 150 atm is a gas.

b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure 16.11.2. At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At $P = 150$ atm and $T = -50$°C, therefore, the sample is solid ice.

? Exercise 16.11.2

Referring to the phase diagram of water in Figure 16.11.2, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer

The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure 16.11.3) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.

Dry ice ($CO_2(s)$) sublimed in air under room temperature and pressure. from Wikipedia.

Also notice the critical point at 30.98°C and 72.79 atm. Supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

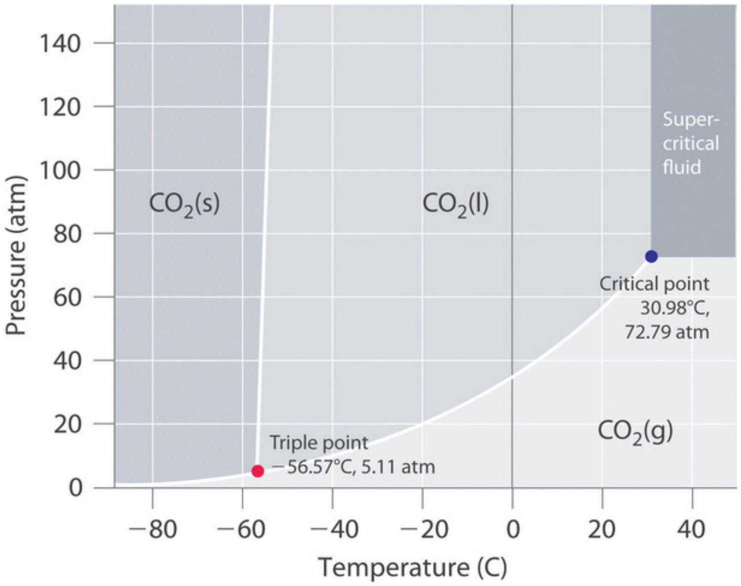

Figure 16.11.3: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

The triple point is at -57.57 degrees C and 5.11 atm. The critical point is at 30.98 degree C and 72.79 atm.

The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure 16.11.1.

Figure 16.11.1: Critical Temperatures and Pressures of Some Simple Substances

Substance	**T_c (°C)**	**P_c (atm)**
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

> High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.

Supercritical Fluids

A Video Discussing Phase Diagrams. Video Source: Phase Diagrams(opens in new window) [youtu.be]

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16.12: Nanotechnology

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16.E: Exercises

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

1. For each of the following pairs of substances, specify the type of interparticle bonding in each, and indicate which one has the higher boiling point:

a. NH_3 or PH_3
b. C_4H_{10} or C_6H_{14}
c. CO_2 or H_2O
d. HCl or LiCl
e. Na or NaCl

2. For each of the following types of solids, describe its structure and the nature of the forces holding it together, and give the formula of at least one example:

a. ionic
b. covalent (molecular)
c. metallic
d. network covalent

3. List the substance types in (3) in order of increasing melting point.

4. Which of the types of substances in (3) conduct electricity as solids? as liquids?

5. Of the following substances: NaCl, diamond, Fe, F_2, C_3H_7OH, which one

a. has the lowest boiling point?
b. is held together by ionic bonds?

6. Define boiling point, critical temperature, critical pressure, and triple point.

7. Explain how each of the following affects the vapor pressure of a liquid:

a. surface area
b. temperature
c. intermolecular attractive forces
d. volume of liquid

8. What are the three types of intermolecular attractive forces and list them in order of increasing strength?

9. The normal (1 atm) melting and boiling points of O_2 are -218°C and -183°C, respectively. Its triple point is at -219°C and 1.14 x 10^{-3} atm, and its critical point is at -119°C and 49.8 atm.

a. Sketch the phase diagram for O_2, showing the 4 points given above and indicating the area in which each phase is stable.
b. Which is denser, $O_2(s)$ or $O_2(l)$? Explain.
c. As it is heated, will solid O_2 sublime or melt at a pressure of 1 atm?

10. The vapor pressure of solid iodine (I_2) at 30°C is 0.466 mm Hg. How many milligrams of iodine will sublime into an evacuated 1.00-liter flask?

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CHAPTER OVERVIEW

17: Solutions

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Solutions are all around us. Air, for example, is a solution. If you live near a lake, a river, or an ocean, that body of water is not pure H_2O but most probably a solution. Much of what we drink—for example, soda, coffee, tea, and milk—is at least in part a solution. Solutions are a large part of everyday life. A lot of the chemistry occurring around us happens in solution. In fact, much of the chemistry that occurs in our own bodies takes place in solution, and many solutions—such as the Ringer’s lactate IV solution—are important for our health. In our understanding of chemistry, we need to understand a little bit about solutions. In this chapter, you will learn about the special characteristics of solutions, how solutions are characterized, and some of their properties.

Topic hierarchy

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SECTION OVERVIEW

17.1: Solution Composition

The concept of an ideal solution is fundamental to chemical thermodynamics and its applications, such as the use of colligative properties. An **ideal solution** or ideal mixture is a solution in which the enthalpy of solution ($\Delta H_{solution} = 0$) is zero; with the closer to zero the enthalpy of solution, the more "ideal" the behavior of the solution becomes. Since the enthalpy of mixing (solution) is zero, the change in Gibbs energy on mixing is determined solely by the entropy of mixing ($\Delta S_{solution}$).

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17.2: The Energies of Solution Formation

Some forces that interact within pure liquids are also present during mixtures and solutions. Forces such as Cohesive as well as Adhesive forces still apply to mixtures; however, more importantly we focus on the interaction between different molecules. Why is oil only soluble in benzene and not water? Why do only "like" molecules dissolve in "like" molecules?

The process of Mixing

Before we go on to the more specific mechanisms of mixing, let's discuss its process. Mixing is a spontaneous process that increases the entropy of the solution. In order to form a mixture of homogenous solutions by distributing the solute molecules evenly within the solvent molecules, heat transfers are inevitable. This heat transfer is denoted ΔH_{soln} for our general comprehension. ΔH is the change in heat energy found by subtracting the enthalpy of the reactant from that of the product:

$$H_{products} - H_{reactants} = \Delta H_{soln}. \tag{17.2.1}$$

Enthalpy of Solution

What then is the significance of ΔH_{soln}? It presents a clear indication of the magnitude as well as direction of the heat transfer so that when:

- $\Delta H>0$: Endothermic Reaction (positive), because the products encompass more energy than the reactants
- $\Delta H<0$: Exothermic Reaction (negative), because the reactants consist of more energy than the products.

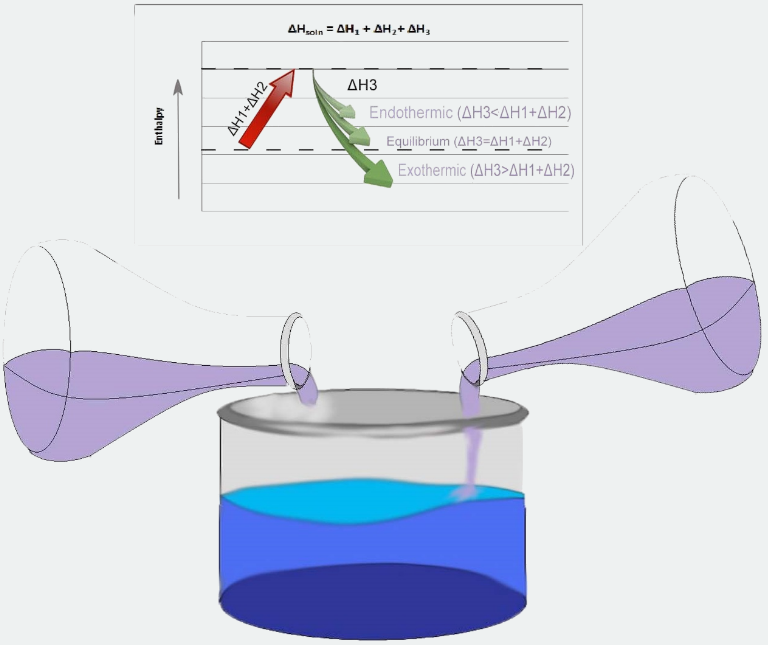
What we have to supply for our understanding for this equation is that the extra energy is seized either from or give to the surrounding. And to ascertain the enthalpy of solution, we take the three step approach in enthalpy when a solute is mixed with the solvent.

Three Step Approach to Finding the Enthalpy of Solution: $\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$

1. Each molecule of solute is Separated from each other (**expand the solute**), **endothermic reaction.** (ΔH_1)
2. Each molecule of solvent is separated from each other (**expand solvent**), **endothermic reaction.** (ΔH_2) *Now the molecules of solute and molecules of solvent can be permitted to attract one another in solution.*
3. The molecules of solute and solvent react with each other and a solution will result. **exothermic reaction** (ΔH_3)

Note

note that usually ΔH_1 and ΔH_2 are opposite in sign as ΔH_3. Separating the solute and the solvent solutions alone are usually endothermic reactions in that their cohesive forces are broken while letting the molecules to react freely is an exothermic reaction. The figure below explains pictorially how positive and negative ΔH can be obtained through the three step process of mixing solution.

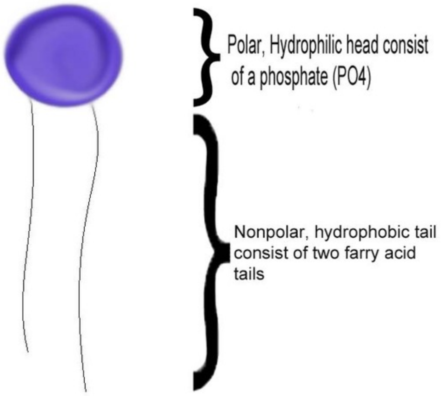


ΔH's Relationship to the Behavior of the Solution

Ideal solution is the mixture that has little to no net intermolecular interactions that differentiates it from its ideal behavior. Thus if the intermolecular forces of attraction are the same and have the same strength, both the solvent and solute will mix at random. This solution is called an **ideal solution**, which means that $\Delta H_{soln} = 0$. If the intermolecular forces of attraction of different molecules are greater than the forces of attraction of like molecules, then it is called a nonideal solution. This will result in an exothermic process ($\Delta H_{soln} < 0$). If the intermolecular forces of attraction of different molecules are a bit weaker than the forces of attraction of like molecules. This solution is a nonideal solution, has bigger enthalpy value than pure components, and it goes through an endothermic process. Lastly, if the intermolecular forces of attraction of different molecules is a lot weaker than the forces of attraction of like molecules, the solution becomes a heterogeneous mixture (e.g., water and olive oil).

The Effects of Intermolecular Forces in Solution.

The epitome of intermolecular forces in solution is the miracle of solubility, because when a matter precipitates it no longer interacts with the solvent. So what is the attraction between "like" molecules that makes them attract to each other? Let's take a phospholipid, the building block of a cell's membrane, as an example. This molecule is amphipathic, meaning that it is both hydrophilic and hydrophobic. Beginning with the structure of a phospholipid, it has a polar head which is hydrophilic and a nonpolar tail which is hydrophobic as the picture below.



How can a single molecule be both polar molecule loving and polar molecule disliking at the same time? This is because at the polar head, the phosphate has a net negative charge thus attracting the partial positive charge of the hydrogen molecules of water. Its nonpolar tails on the other hand, is a very organized form of hydrocarbon, consisting of no net charges. The tail is then repelled by water as it struggles to fit between the partial positive and partial negative of the water molecule.

Another side effect of the interactions of molecules is reflected by the use of the activity coefficient during thermodynamic equilibrium constant calculations. This constant differentiates ideal and nonideal solutions so that interactions for solution equilibrium can be more accurately estimated. Most versions of the equilibrium constant K utilizes activity instead of concentration so that the units would disappear more fluently. For an ideal solution, the activity coefficient is 1 [x]/ ^{o}Celcius, thus when the concentration is dived by it to yield activity, it is unaltered.

✓ Example 17.2.1

Based on the concept of intermolecular interactions, ascertain the reason behind freezing-point depression and boiling-point elevation.

Solution

When an ion is added into solution, it exerts an intermolecular force which binds loosely to the water molecules in solution. This weak force then increases the energy necessary to break each molecule loose, thus increasing temperature in relationship to vapor pressure. It now takes more energy input to obtain the same vapor pressure, thus elevating the boiling point. For freezing-point depression, the same force that is holding the water molecules from evaporating is holding them against being placed into an organized solid form. It now takes more energy to form the weak bonds between each water molecule because the intermolecular forces between water and the ions first have to be overcome, hence reducing the freezing point.

✓ Example 17.2.2

Give examples that present the involvement of intermolecular forces thus differentiating ideal from nonideal solutions.

Solution

Gibbs free energy (relating ΔG with ΔG^{o}), calculating thermodynamic equilibrium constants, boiling-point elevation, and freezing-point depression

References

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17.3: Factors Affecting Solubility

Learning Objectives

- To understand how Temperature, Pressure, and the presence of other solutes affect the solubility of solutes in solvents.

Solubility is defined as the upper limit of solute that can be dissolved in a given amount of solvent at equilibrium. In such an equilibrium, Le Chatelier's principle can be used to explain most of the main factors that affect solubility. Le Châtelier's principle dictates that the effect of a stress upon a system in chemical equilibrium can be predicted in that the system tends to shift in such a way as to alleviate that stress.

Solute-Solvent Interactions Affect Solubility

The relation between the solute and solvent is very important in determining **solubility**. Strong solute-solvent attractions equate to greater solubility while weak solute-solvent attractions equate to lesser **solubility**. In turn, polar solutes tend to dissolve best in polar solvents while non-polar solutes tend to dissolve best in non-polar solvents. In the case of a polar solute and non-polar solvent (or vice versa), it tends to be insoluble or only soluble to a miniscule degree. A general rule to remember is, "Like dissolves like."

Common-Ion Effect

The common-ion effect is a term that describes the decrease in **solubility** of an ionic compound when a salt that contains an ion that already exists in the chemical equilibrium is added to the mixture. This effect best be explained by Le Chatelier's principle. Imagine if the slightly soluble ionic compound calcium sulfate, $CaSO_4$, is added to water. The net ionic equation for the resulting chemical equilibrium is the following:

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)} \tag{17.3.1}$$

Calcium sulfate is slightly soluble; at equilibrium, most of the calcium and sulfate exists in the solid form of calcium sulfate.

Suppose the soluble ionic compound copper sulfate ($CuSO_4$) were added to the solution. Copper sulfate is soluble; therefore, its only important effect on the net ionic equation is the addition of more sulfate (SO_4^{2-}) ions.

$$CuSO_{4(s)} \rightleftharpoons Cu^{2+}_{(aq)} + SO^{2-}_{4(aq)} \tag{17.3.2}$$

The sulfate ions dissociated from copper sulfate are already present (common to) in the mixture from the slight dissociation of calcium sulfate. Thus, this addition of sulfate ions places stress on the previously established equilibrium. Le Chatelier's principle dictates that the additional stress on this product side of the equilibrium results in the shift of equilibrium towards the reactants side in order to alleviate this new stress. Because of the shift toward the reactant side, the solubility of the slightly soluble calcium sulfate is reduced even further.

Temperature Affects Solubility

Temperature changes affect the solubility of solids, liquids and gases differently. However, those effects are finitely determined only for solids and gases.

Solids

The effects of temperature on the solubility of solids differ depending on whether the reaction is endothermic or exothermic. Using Le Chatelier's principle, the effects of temperature in both scenarios can be determined.

1. First, consider an **endothermic** reaction ($\Delta H_{solvation} > 0$): Increasing the temperature results in a stress on the reactants side from the additional heat. Le Chatelier's principle predicts that the **system shifts toward the product side** in order to alleviate this stress. By shifting towards the product side, more of the solid is dissociated when equilibrium is again established, resulting in **increased** solubility.
2. Second, consider an **exothermic** reaction (($\Delta H_{solvation} < 0$): Increasing the temperature results in a stress on the products side from the additional heat. Le Chatelier's principle predicts that the **system shifts toward the reactant side** in order to alleviate this stress. By shifting towards the reactant's side, less of the solid is dissociated when equilibrium is again established, resulting in **decreased** solubility.

Liquids

In the case of liquids, there is no defined trends for the effects of temperature on the solubility of liquids.

Gases

In understanding the effects of temperature on the solubility of gases, it is first important to remember that temperature is a measure of the average kinetic energy. As temperature increases, kinetic energy increases. The greater kinetic energy results in greater molecular motion of the gas particles. As a result, the gas particles dissolved in the liquid are more likely to escape to the gas phase and the existing gas particles are less likely to be dissolved. The converse is true as well. The trend is thus as follows: increased temperatures mean lesser solubility and decreased temperatures mean higher solubility.

Le Chatelier's principle allows better conceptualization of these trends. First, note that the process of dissolving gas in liquid is usually **exothermic**. As such, **increasing** temperatures result in stress on the product side (because heat is on the product side). In turn, Le Chatelier's principle predicts that the system shifts towards the reactant side in order to alleviate this new stress. Consequently, the equilibrium concentration of the gas particles in gaseous phase increases, resulting in **lowered** solubility.

Conversely, **decreasing** temperatures result in stress on the reactant side (because heat is on the product side). In turn, Le Chatelier's principle predicts that the system shifts toward the product side in order to compensate for this new stress. Consequently, the equilibrium concentration of the gas particles in gaseous phase would decrease, resulting in **greater** solubility.

Pressure Affects Solubility of Gases

The effects of pressure are only significant in affecting the solubility of gases in liquids.

- **Solids & Liquids:** The effects of pressure changes on the solubility of solids and liquids are negligible.
- **Gases**: The effects of pressure on the solubility of gases in liquids can best be described through a combination of Henry's law and Le Chatelier principle. Henry's law dictates that when temperature is constant, the solubility of the gas corresponds to it's partial pressure. Consider the following formula of Henry's law:

$$p = k_h \; c \tag{17.3.3}$$

where:

- p is the partial pressure of the gas above the liquid,
- k_h is Henry's law constant, and
- c is the concentrate of the gas in the liquid.

This formula indicates that (at a constant temperature) when the partial pressure decreases, the concentration of gas in the liquid decreases as well, and consequently the solubility also decreases. Conversely, when the partial pressure increases in such a situation, the concentration of gas in the liquid will increase as well; the solubility also increases. Extending the implications from Henry's law, the usefulness of Le Chatelier's principle is enhanced in predicting the effects of pressure on the solubility of gases.

Consider a system consisting of a gas that is partially dissolved in liquid. An increase in pressure would result in greater partial pressure (because the gas is being further compressed). This increased partial pressure means that more gas particles will enter the liquid (there is therefore less gas above the liquid, so the partial pressure decreases) in order to alleviate the stress created by the increase in pressure, resulting in greater solubility.

The converse case in such a system is also true, as a decrease in pressure equates to more gas particles escaping the liquid to compensate.

✓ Example 1

Consider the following exothermic reaction that is in equilibrium

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \tag{17.3.4}$$

What will happen to the solubility of the carbon dioxide if:

a. Temperature is increased?
b. Pressure and temperature are increased?
c. Pressure is increased but temperature is decreased?
d. Pressure is increased?

Solution

a. The reaction is exothermic, so an increase in temperature means that solubility would decrease.
b. The change in solubility cannot be determined from the given information. Increasing pressure increased solubility, but increasing temperature decreases solubility
c. An increase in pressure and an increase in temperature in this reaction results in greater solubility.
d. An increase in pressure results in more gas particles entering the liquid in order to decrease the partial pressure. Therefore, the solubility would increase.

✓ Example 2: The Common Ion Effect

Bob is in the business of purifying silver compounds to extract the actual silver. He is extremely frugal. One day, he finds a barrel containing a saturated solution of silver chloride. Bob has a bottle of water, a jar of table salt (NaCl(s)), and a bottle of vinegar (CH_3COOH). Which of the three should Bob add to the solution to maximize the amount of solid silver chloride (minimizing the solubility of the silver chloride)?

Solution

Bob should add table salt to the solution. According to the common-ion effect, the additional Cl^- ions would reduce the solubility of the silver chloride, which maximizes the amount of solid silver chloride.

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Allison has always wanted to start her own carbonated drink company. Recently, she opened a factory to produce her drinks. She wants her drink to "out-fizz" all the competitors. That is, she wants to maximize the solubility of the gas in her drink. What conditions (high/low temperature, high/low pressure) would best allow her to achieve this goal?

Solution

She would be able to maximize the solubility of the gas, (CO_2 in this case, in her drink (maximize fizz) when the pressure is high and temperature is low.

✓ Example 4

Butters is trying to increase the solubility of a solid in some water. He begins to frantically stir the mixture. Should he continue stirring? Why or why not?

Solution

He stop stop stirring. Stirring only affects how fast the system will reach equilibrium and does not affect the solubility of the solid at all.

✓ Example 5: Outgassing Soda

With respect to Henry's law, why is it a poor ideal to open a can of soda in a low pressure environment?

Solution

The fizziness of soda originates from dissolved CO_2, partially in the form of carbonic acid. The concentration of CO_2 dissolved in the soda depends on the amount of ambient pressure pressing down on the liquid. Hence, the soda can will be under pressure to maintain the desired CO_2 concentration. When the can is opened to a lower pressure environment (e.g., the ambient atmosphere), the soda will quickly "outgas" (CO_2 will come out of solution) at a rate depending on the surrounding atmospheric pressure. If a can of soda were opened under a lower pressure environment, this outgassing will be faster and hence more explosive (and dangerous) than under a high pressure environment.

Terms

- The **solubility** of a solute is the concentration of the saturated solution.
- A **saturated solution** a solution in which the maximum amount of solute has dissolved in the solvent at a given temperature.
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17.4: The Vapor Pressures of Solutions

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17.5: Boiling-Point Elevation and Freezing-Point Depression

Freezing point depression is a colligative property observed in solutions that results from the introduction of solute molecules to a solvent. The freezing points of solutions are all lower than that of the pure solvent and is directly proportional to the *molality* of the solute.

$$\begin{aligned}\Delta T_f &= T_f(solvent) - T_f(solution) \\ &= K_f \times m\end{aligned}$$

where ΔT_f is the freezing point depression, T_f (solution) is the freezing point of the solution, T_f (solvent) is the freezing point of the solvent, K_f is the freezing point depression constant, and *m* is the molality.

Introduction

Nonelectrolytes are substances with no ions, only molecules. Strong electrolytes, on the other hand, are composed mostly of ionic compounds, and essentially all soluble ionic compounds form electrolytes. Therefore, if we can establish that the substance that we are working with is uniform and is not ionic, it is safe to assume that we are working with a nonelectrolyte, and we may attempt to solve this problem using our formulas. This will most likely be the case for all problems you encounter related to freezing point depression and boiling point elevation in this course, but it is a good idea to keep an eye out for ions. It is worth mentioning that these equations work for both volatile and nonvolatile solutions. This means that for the sake of determining freezing point depression or boiling point elevation, the vapor pressure does not effect the change in temperature. Also, remember that a pure solvent is a solution that has had nothing extra added to it or dissolved in it. We will be comparing the properties of that pure solvent with its new properties when added to a solution.

Adding solutes to an ideal solution results in a positive ΔS, an increase in entropy. Because of this, the newly altered solution's chemical and physical properties will also change. The properties that undergo changes due to the addition of solutes to a solvent are known as colligative properties. These properties are dependent on the number of solutes added, not on their identity. Two examples of colligative properties are boiling point and freezing point: due to the addition of solutes, the boiling point tends to increase, and freezing point tends to decrease.

The freezing point and boiling point of a pure solvent can be changed when added to a solution. When this occurs, the freezing point of the pure solvent may become lower, and the boiling point may become higher. The extent to which these changes occur can be found using the formulas:

$$\Delta T_f = -K_f \times m \tag{17.5.1}$$

$$\Delta T_b = K_b \times m \tag{17.5.2}$$

where m is the solute *molality* and K values are proportionality constants; (K_f and K_b for freezing and boiling, respectively).

Molality

Molality is defined as the number of moles of solute per kilogram **solvent**. Be careful not to use the mass of the entire solution. Often, the problem will give you the change in temperature and the proportionality constant, and you must find the molality first in order to get your final answer.

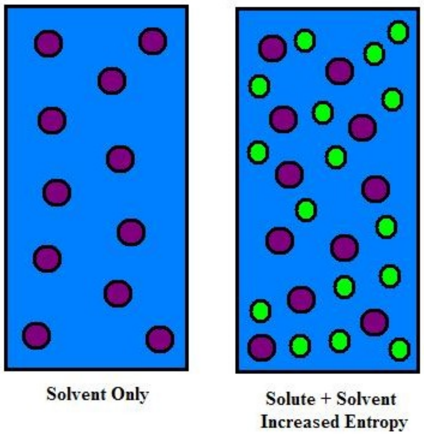
If solving for the proportionality constant is not the ultimate goal of the problem, these values will most likely be given. Some common values for K_f and K_b respectively, are in Table $17.5.1$:

Table 17.5.1: Ebullioscopic and cryoscopic constants for select solvents. Note that the nature of the solute does not affect colligative property relations.

Solvent	K_f	K_b
Water	1.86	.512
Acetic acid	3.90	3.07
Benzene	5.12	2.53

Solvent	K_f	K_b
Phenol	7.27	3.56

The solute, in order for it to exert any change on colligative properties, must fulfill two conditions. First, it must not contribute to the vapor pressure of the solution, and second, it must remain suspended in the solution even during phase changes. Because the solvent is no longer pure with the addition of solutes, we can say that the **chemical potential** of the solvent is lower. Chemical potential is the molar Gibb's energy that one mole of solvent is able to contribute to a mixture. The higher the chemical potential of a solvent is, the more it is able to drive the reaction forward. Consequently, solvents with higher chemical potentials will also have higher vapor pressures.

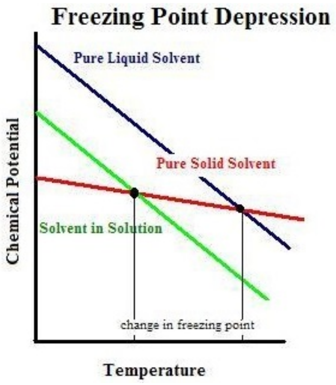


The boiling point is reached when the chemical potential of the pure solvent, a liquid, reaches that of the chemical potential of pure vapor. Because of the decrease in the chemical potential of mixed solvents and solutes, we observe this intersection at higher temperatures. In other words, the boiling point of the impure solvent will be at a higher temperature than that of the pure liquid solvent. Thus, **boiling point elevation** occurs with a temperature increase that is quantified using

$$\Delta T_b = K_b m \tag{17.5.3}$$

where K_b is known as the *ebullioscopic constant* and m is the molality of the solute.

Freezing point is reached when the chemical potential of the pure liquid solvent reaches that of the pure solid solvent. Again, since we are dealing with mixtures with decreased chemical potential, we expect the freezing point to change. Unlike the boiling point, the chemical potential of the impure solvent requires a colder temperature for it to reach the chemical potential of the pure solid solvent. Therefore, a **freezing point depression** is observed.



Example 17.5.1

2.00 g of some unknown compound reduces the freezing point of 75.00 g of benzene from 5.53 to 4.90 $^\circ C$. What is the molar mass of the compound?

Solution

First we must compute the molality of the benzene solution, which will allow us to find the number of moles of solute dissolved.

$$\begin{aligned} m &= \frac{\Delta T_f}{-K_f} \\ &= \frac{(4.90 - 5.53)^\circ C}{-5.12^\circ C/m} \\ &= 0.123 m \end{aligned}$$

$$\begin{aligned} \text{Amount Solute } &= 0.07500 \; kg \; benzene \times \frac{0.123 \; m}{1 \; kg \; benzene} \\ &= 0.00923 \; m \; solute \end{aligned}$$

We can now find the molecular weight of the unknown compound:

$$\begin{aligned} \text{Molecular Weight} &= \frac{2.00 \; g \; unknown}{0.00923 \; mol} \\ &= 216.80 \; g/mol \end{aligned}$$

The freezing point depression is especially vital to aquatic life. Since saltwater will freeze at colder temperatures, organisms can survive in these bodies of water.

Exercise 17.5.1

Benzophenone has a freezing point of 49.00°C. A 0.450 molal solution of urea in this solvent has a freezing point of 44.59°C. Find the freezing point depression constant for the solvent.

Answer

$9.80 \, ^oC/m$

Applications

Road salting takes advantage of this effect to lower the freezing point of the ice it is placed on. Lowering the freezing point allows the street ice to melt at lower temperatures. The maximum depression of the freezing point is about −18 °C (0 °F), so if the ambient temperature is lower, NaCl will be ineffective. Under these conditions, CaCl_2 can be used since it dissolves to make three ions instead of two for NaCl.

Figure 17.5.1: Workers manually spreading salt from a salt truck in Milwaukee, Wisconsin. (CC BY-SA 2.0 Generic; Michael Pereckas via Wikipedia)

References

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17.7: Colligative Properties of Electrolyte Solutions

Using the rule "like dissolves like" with the formation of ionic solutions, we must assess first assess two things: 1) the strength of the ion-dipole forces of attraction between water and the ionic compound and 2) the strength of the interionic bond of the ionic compound.

For an ionic compound to form a solution, the ion-dipole forces between water and ionic compound must be greater than the interionic bonds. Therefore, to form a compound: ion-dipole forces > interionic bonds

When the ionic compound is surrounded by water, the water dipoles surround the crystal's clustered structure. The water's negative ends of the dipole will be attracted to the positive dipoles of the ion and the positive ends of the water's dipole will be attracted to the negative dipoles of the ion. If the force of this attraction is stronger than the interionic bonds, the crystal's interionic bonds will be broken, then surrounded by the water molecules or hydrated .

There is a 3-step process that we can use to approach the energy involved in ionic solution formation. 1) Breaking apart the ionic compound is endothermic and requires energy. 2) Hydrating cation is exothermic and therefore releases energy. 3) Hydrating the anion is exothermic and also releases energy. The sum of these 3 steps will then give us the enthalpy of the solution.

✓ Example 17.7.1: CaCl2

1) $CaCl_2$ (s) -> Ca^{2+} (g) + Cl_2(g) energy > 0

2) Ca^{2+}(g) ~~H_2O-~~> Ca^{2+}(aq) energy < 0

3) Cl_2(g) ~~H_2O-~~> Cl_2(aq) energy < 0

$CaCl_2$ (s) ~~H_2O~~> Ca^{2+}(aq) + Cl_2 (aq) energy > 0 The dissolution is endothermic because in the formation of ionic solutions, you must take into account entropy in addition to the enthalpy of the solution to determine whether it will occur spontaneously.

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17.7: Osmotic Pressure

Introduction

Semipermiable membranes do not let the solute pass through (Think of the sugar example). A solvent will move to the side that is more concentrated to try to make each side more similar! Since there is a flow of solvents, the height of each side changes, which is *osmotic pressure*. When we work with aqueous solutions, we use mm of H_2O to describe the difference.

Osmosis is the diffusion of a fluid through a semipermeable membrane. When a semipermeable membrane (animal bladders, skins of fruits and vegetables) separates a solution from a solvent, then only solvent molecules are able to pass through the membrane. The osmotic pressure of a solution is the pressure difference needed to stop the flow of solvent across a semipermeable membrane. The osmotic pressure of a solution is proportional to the *molar concentration* of the solute particles in solution.

$$\Pi = i\frac{n}{V}RT = iMRT \tag{17.7.1}$$

where

- Π is the osmotic pressure,
- R is the ideal gas constant (0.0821 L atm / mol K),
- T is the temperature in Kelvin,
- i is the van 't Hoff factor
- n is the number of moles of solute present,
- V is the volume of the solution, and
- M is the molar concentration of added solute (the i factor accounts for how many species in solution are generated)

? Exercise 17.7.1

Calculate molarity of a sugar solution in water (300 K) has osmotic pressure of 3.00 atm.

Answer

Since it is sugar, we know it doesn't dissociate in water, so i is 1. Then we use Equation 17.7.1directly

$$M = \frac{\Pi}{RT} = \frac{3.00\,atm}{(0.0821\,atm.\,L/mol.\,K)(300\,K)} = 0.122\,M$$

? Exercise 17.7.2

Calculate osmotic pressure for 0.10 M Na_3PO_4 aqueous solution at 20°C.

Answer

Since Na_3PO_4 ionizes into four particles (3 Na+1 + PO_4^{-3}), then $i = 4$. We can then calculate the osmotic pressure via Equation 17.7.1

$$\Pi = iMRT = (0.40)(0.0821)(293) = 9.6\,atm$$

? Exercise 17.7.3

Hemoglobin is a large molecule that carries oxygen in human blood. A water solution that contains 0.263 g of hemoglobin (Hb) in 10.0 mL of solution has an osmotic pressure of 7.51 torr at 25^oC. What is the molar mass of the hemoglobin?

Answer

$6.51 \times 10^4\ g/mol$

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17.8: Colloids

A colloid is one of the three primary types of mixtures, with the other two being a solution and suspension. A colloid is a mixture that has particles ranging between 1 and 1000 nanometers in diameter, yet are still able to remain evenly distributed throughout the solution. These are also known as colloidal dispersions because the substances remain dispersed and do not settle to the bottom of the container. In colloids, one substance is evenly dispersed in another. The substance being dispersed is referred to as being in the dispersed phase, while the substance in which it is dispersed is in the continuous phase.

To be classified as a colloid, the substance in the dispersed phase must be larger than the size of a molecule but smaller than what can be seen with the naked eye. This can be more precisely quantified as one or more of the substance's dimensions must be between 1 and 1000 nanometers. If the dimensions are smaller than this the substance is considered a solution and if they are larger than the substance is a suspension.

Classifying Colloids

A common method of classifying colloids is based on the phase of the dispersed substance and what phase it is dispersed in. The types of colloids includes sol, emulsion, foam, and aerosol.

1. **Sol** is a colloidal suspension with solid particles in a liquid.
2. **Emulsion** is between two liquids.
3. **Foam** is formed when many gas particles are trapped in a liquid or solid.
4. **Aerosol** contains small particles of liquid or solid dispersed in a gas.

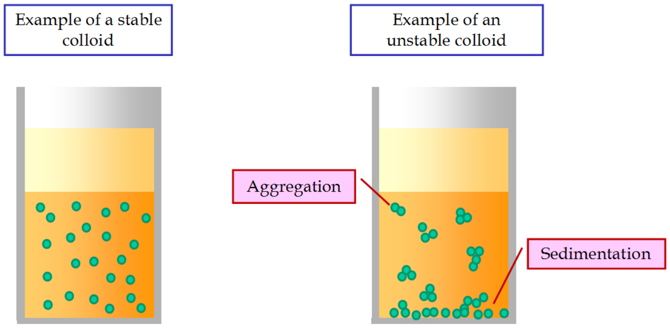

Figure 1: Examples of a stable and of an unstable colloidal dispersion.from Wikipedia.

When the dispersion medium is water, the collodial system is often referred to as a **hydrocolloid**. The particles in the dispersed phase can take place in different phases depending on how much water is available. For example, Jello powder mixed in with water creates a hydrocolloid. A common use of hydrocolloids is in the creation of medical dressings.

Table 1: Examples of Colloids

Dispersion Medium	Dispersed Phase	Type of Colloid	Example
Solid	Solid	Solid sol	Ruby glass
Solid	Liquid	Solid emulsion/gel	Pearl, cheese
Solid	Gas	Solid foam	Lava, pumice
Liquid	Solid	Sol	Paints, cell fluids
Liquid	Liquid	Emulsion	Milk, oil in water
Liquid	Gas	Foam	Soap suds, whipped cream
Gas	Solid	Aerosol	Smoke
Gas	Liquid	Aerosol	Fog, mist

An easy way of determining whether a mixture is colloidal or not is through use of the Tyndall Effect. When light is shined through a true solution, the light passes cleanly through the solution, however when light is passed through a colloidal solution, the substance in the dispersed phases scatters the light in all directions, making it readily seen. An example of this is shining a flashlight into fog. The beam of light can be easily seen because the fog is a colloid.

Figure 2: Light being shined through water and milk. The light is not reflected when passing through the water because it is not a colloid. It is however reflected in all directions when it passes through the milk, which is colloidal.

Another method of determining whether a mixture is a colloid is by passing it through a semipermeable membrane. The larger dispersed particles in a colloid would be unable to pass through the membrane, while the surrounding liquid molecules can. Dialysis takes advantage of the fact that colloids cannot diffuse through semipermeable membranes to filter them out of a medium.

Problems

1. Is dust a colloid? If so, what type is it?
2. Is whipped cream a colloid? if so, what type is it?
3. What does Sol mean?
4. When hit by light what happens to a colloidal mixture?
5. What is the mixture considered if the particles are larger than the particles of a colloidal substance

Answers

1. Dust is a colloid if suspended in air. It consists of a solid in a gas, so it is a aerosol.
2. Whipped cream is a colloid. It consists of a gas in a liquid, so it is a foam.
3. Sol is a colloidal suspension with solid particles in a liquid.
4. The light is reflected off the large particles and spread out.
5. It's considered a suspension if the particles are larger than 1000 nanometers.

References

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CHAPTER OVERVIEW

18: The Representative Elements

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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18.1: A Survey of the Representative Elements

Learning Objectives

- To know important periodic trends in several atomic properties.

As we begin our summary of periodic trends, recall that the single most important unifying principle in understanding the chemistry of the elements is the systematic increase in atomic number, accompanied by the orderly filling of atomic orbitals by electrons, which leads to periodicity in such properties as atomic and ionic size, ionization energy, electronegativity, and electron affinity. The same factors also lead to periodicity in valence electron configurations, which for each group results in similarities in oxidation states and the formation of compounds with common stoichiometries.

The most important periodic trends in atomic properties are summarized in Figure $18.1.1$. Recall that these trends are based on periodic variations in a single fundamental property, the **effective nuclear charge** (Z_{eff}), which increases from left to right and from top to bottom in the periodic table.

The diagonal line in Figure $18.1.1$ separates the metals (to the left of the line) from the nonmetals (to the right of the line). Because metals have relatively low electronegativities, they tend to lose electrons in chemical reactions to elements that have relatively high electronegativities, forming compounds in which they have positive oxidation states. Conversely, nonmetals have high electronegativities, and they therefore tend to gain electrons in chemical reactions to form compounds in which they have negative oxidation states. The semimetals lie along the diagonal line dividing metals and nonmetals. It is not surprising that they tend to exhibit properties and reactivities intermediate between those of metals and nonmetals. Because the elements of groups 13, 14, and 15 span the diagonal line separating metals and nonmetals, their chemistry is more complex than predicted based solely on their valence electron configurations.

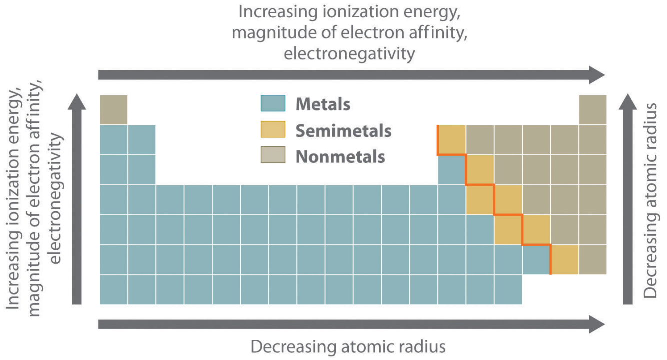

Figure 18.1.1: Summary of Periodic Trends in Atomic Properties. *Ionization energies, the magnitude of electron affinities, and electronegativities generally increase from left to right and from bottom to top. In contrast, atomic size decreases from left to right and from bottom to top. Consequently, the elements in the upper right of the periodic table are the smallest and most electronegative; the elements in the bottom left are the largest and least electronegative. The semimetals lie along the diagonal line separating the metals from the nonmetals and exhibit intermediate properties.*

Unique Chemistry of the Lightest Elements

The chemistry of the second-period element of each group (n = 2: Li, Be, B, C, N, O, and F) differs in many important respects from that of the heavier members, or congeners, of the group. Consequently, the elements of the third period (n = 3: Na, Mg, Al, Si, P, S, and Cl) are generally more representative of the group to which they belong. The anomalous chemistry of second-period elements results from three important characteristics: small radii, energetically unavailable d orbitals, and a tendency to form pi (π) bonds with other atoms.

Note

In contrast to the chemistry of the second-period elements, the chemistry of the third-period elements is more representative of the chemistry of the respective group.

Due to their small radii, second-period elements have electron affinities that are less negative than would be predicted from general periodic trends. When an electron is added to such a small atom, increased electron–electron repulsions tend to destabilize the anion. Moreover, the small sizes of these elements prevent them from forming compounds in which they have more than four nearest neighbors. Thus BF_3 forms only the four-coordinate, tetrahedral BF_4^- ion, whereas under the same conditions AlF_3 forms the six-coordinate, octahedral AlF_6^{3-} ion. Because of the smaller atomic size, simple binary ionic compounds of second-period elements also have more covalent character than the corresponding compounds formed from their heavier congeners. The very small cations derived from second-period elements have a high charge-to-radius ratio and can therefore polarize the filled valence shell of an anion. As such, the bonding in such compounds has a significant covalent component, giving the compounds properties that can differ significantly from those expected for simple ionic compounds. As an example, LiCl, which is partially covalent in character, is much more soluble than NaCl in solvents with a relatively low dielectric constant, such as ethanol ($\varepsilon = 25.3$ versus 80.1 for H_2O).

Because d orbitals are never occupied for principal quantum numbers less than 3, the valence electrons of second-period elements occupy 2s and 2p orbitals only. The energy of the 3d orbitals far exceeds the energy of the 2s and 2p orbitals, so using them in bonding is energetically prohibitive. Consequently, electron configurations with more than four electron pairs around a central, second-period element are simply not observed. You may recall that the role of d orbitals in bonding in main group compounds with coordination numbers of 5 or higher remains somewhat controversial. In fact, theoretical descriptions of the bonding in molecules such as SF_6 have been published without mentioning the participation of d orbitals on sulfur. Arguments based on d-orbital availability and on the small size of the central atom, however, predict that coordination numbers greater than 4 are unusual for the elements of the second period, which is in agreement with experimental results.

One of the most dramatic differences between the lightest main group elements and their heavier congeners is the tendency of the second-period elements to form species that contain multiple bonds. For example, N is just above P in group 15: N_2 contains an N≡N bond, but each phosphorus atom in tetrahedral P_4 forms three P–P bonds. This difference in behavior reflects the fact that within the same group of the periodic table, the relative energies of the π bond and the sigma (σ) bond differ. A C=C bond, for example, is approximately 80% stronger than a C–C bond. In contrast, an Si=Si bond, with less p-orbital overlap between the valence orbitals of the bonded atoms because of the larger atomic size, is only about 40% stronger than an Si–Si bond. Consequently, compounds that contain both multiple and single C to C bonds are common for carbon, but compounds that contain only sigma Si–Si bonds are more energetically favorable for silicon and the other third-period elements.

The Inert-Pair Effect

The **inert-pair effect** refers to the empirical observation that the heavier elements of groups 13–17 often have oxidation states that are lower by 2 than the maximum predicted for their group. For example, although an oxidation state of +3 is common for group 13 elements, the heaviest element in group 13, thallium (Tl), is more likely to form compounds in which it has a +1 oxidation state. There appear to be two major reasons for the inert-pair effect: increasing ionization energies and decreasing bond strengths.

> **Note**
>
> In moving down a group in the p-block, increasing ionization energies and decreasing bond strengths result in an inert-pair effect.

The ionization energies increase because filled (n − 1)d or (n − 2)f subshells are relatively poor at shielding electrons in ns orbitals. Thus the two electrons in the ns subshell experience an unusually high effective nuclear charge, so they are strongly attracted to the nucleus, reducing their participation in bonding. It is therefore substantially more difficult than expected to remove these ns^2electrons, as shown in Table 18.1.1 by the difference between the first ionization energies of thallium and aluminum. Because Tl is less likely than Al to lose its two ns^2 electrons, its most common oxidation state is +1 rather than +3.

Table 18.1.1: Ionization Energies (I) and Average M–Cl Bond Energies for the Group 13 Elements

Element	Electron Configuration	I_1 (kJ/mol)	$I_1 + I_2 + I_3$ (kJ/mol)	Average M–Cl Bond Energy (kJ/mol)
B	[He] $2s^22p^1$	801	6828	536
Al	[Ne] $3s^23p^1$	578	5139	494
Ga	[Ar] $3d^{10}4s^24p^1$	579	5521	481
In	[Kr] $4d^{10}5s^2p^1$	558	5083	439

Element	Electron Configuration	I_1 (kJ/mol)	$I_1 + I_2 + I_3$ (kJ/mol)	Average M–Cl Bond Energy (kJ/mol)
Tl	[Xe] $4f^{14}5d^{10}6s^2p^1$	589	5439	373

Source of data: John A. Dean, Lange's Handbook of Chemistry, 15th ed. (New York: McGraw-Hill, 1999).

Going down a group, the atoms generally became larger, and the overlap between the valence orbitals of the bonded atoms decreases. Consequently, bond strengths tend to decrease down a column. As shown by the M–Cl bond energies listed in Table 18.1.1, the strength of the bond between a group 13 atom and a chlorine atom decreases by more than 30% from B to Tl. Similar decreases are observed for the atoms of groups 14 and 15.

The net effect of these two factors—increasing ionization energies and decreasing bond strengths—is that in going down a group in the p-block, the additional energy released by forming two additional bonds eventually is not great enough to compensate for the additional energy required to remove the two ns^2 electrons.

✓ Example 18.1.1

Based on the positions of the group 13 elements in the periodic table and the general trends outlined in this section,

a. classify these elements as metals, semimetals, or nonmetals.
b. predict which element forms the most stable compounds in the +1 oxidation state.
c. predict which element differs the most from the others in its chemistry.
d. predict which element of another group will exhibit chemistry most similar to that of Al.

Given: positions of elements in the periodic table

Asked for: classification, oxidation-state stability, and chemical reactivity

Strategy:

From the position of the diagonal line in the periodic table separating metals and nonmetals, classify the group 13 elements. Then use the trends discussed in this section to compare their relative stabilities and chemical reactivities.

Solution

a. Group 13 spans the diagonal line separating the metals from the nonmetals. Although Al and B both lie on the diagonal line, only B is a semimetal; the heavier elements are metals.
b. All five elements in group 13 have an ns^2np^1 valence electron configuration, so they are expected to form ions with a +3 charge from the loss of all valence electrons. The inert-pair effect should be most important for the heaviest element (Tl), so it is most likely to form compounds in an oxidation state that is lower by 2. Thus the +1 oxidation state is predicted to be most important for thallium.
c. Among the main group elements, the lightest member of each group exhibits unique chemistry because of its small size resulting in a high concentration of charge, energetically unavailable d orbitals, and a tendency to form multiple bonds. In group 13, we predict that the chemistry of boron will be quite different from that of its heavier congeners.
d. Within the s and p blocks, similarities between elements in different groups are most marked between the lightest member of one group and the element of the next group immediately below and to the right of it. These elements exhibit similar electronegativities and charge-to-radius ratios. Because Al is the second member of group 13, we predict that its chemistry will be most similar to that of Be, the lightest member of group 2.

? Exercise 18.1.1

Based on the positions of the group 14 elements C, Si, Ge, Sn, and Pb in the periodic table and the general trends outlined in this section,

a. classify these elements as metals, semimetals, or nonmetals.
b. predict which element forms the most stable compounds in the +2 oxidation state.
c. predict which element differs the most from the others in its chemistry.
d. predict which element of group 14 will be chemically most similar to a group 15 element.

Answer

a. nonmetal: C; semimetals: Si and Ge; metals: Sn and Pb
b. Pb is most stable as M^{2+}.
c. C is most different.
d. C and P are most similar in chemistry.

Summary

The most important unifying principle in describing the chemistry of the elements is that the systematic increase in atomic number and the orderly filling of atomic orbitals lead to periodic trends in atomic properties. The most fundamental property leading to periodic variations is the effective nuclear charge (Z_{eff}). Because of the position of the diagonal line separating metals and nonmetals in the periodic table, the chemistry of groups 13, 14, and 15 is relatively complex. The second-period elements (n = 2) in each group exhibit unique chemistry compared with their heavier congeners because of their smaller radii, energetically unavailable d orbitals, and greater ability to form π bonds with other atoms. Increasing ionization energies and decreasing bond strengths lead to the inert-pair effect, which causes the heaviest elements of groups 13–17 to have a stable oxidation state that is lower by 2 than the maximum predicted for their respective groups.

Key Takeaway

- The chemistry of the third-period element in a group is most representative of the chemistry of the group because the chemistry of the second-period elements is dominated by their small radii, energetically unavailable d orbitals, and tendency to form π bonds with other atoms.

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18.2: Group 1A Metals

Li, Na, K, Rb, and Cs are all group IA elements, also known as the alkali metals. The seventh member of the group, francium (Fr) is radioactive and so rare that only 20 atoms of Fr may exist on Earth at any given moment[1]. The term *alkali* is derived from an Arabic word meaning "ashes." Compounds of potassium as well as other alkali metals were obtained from wood ashes by early chemists. All the alkali metals are soft and, except for Cs which is yellow, are silvery-gray in color.

Lithium, sodium, potassium, rubidium, and cesium have a great many other properties in common. All are solids at 0°C and melt below 200°C. Each has metallic properties such as good conduction of heat and electricity, malleability (the ability to be hammered into sheets), and ductility (the ability to be drawn into wires). The high thermal (heat) conductivity and the relatively low melting point (for a metal) of sodium make it an ideal heat-transfer fluid. It is used to cool certain types of nuclear reactors (liquid-metal fast breeder reactors, LMFBRs) and to cool the valves of high-powered automobile engines for this reason.

Some general properties of the alkali metals are summarized in the table below. All these metal atoms contain a singles electron outside a noble-gas configuration, and so the valence electron is-well shielded from nuclear charge and the atomic radii are relatively large. The large volume of each atom results in a low density—small enough that Li, Na, and K float on water as they react with it.

Table 18.2.1 Properties of the Group IA Alkali Metals

Element	Symbol	Electron Configuration	Usual Oxidation State	Atomic Radius/pm	Ionic (M^+) Radius/pm
Lithium	Li	$[He]2s^1$	+1	122	60
Sodium	Na	$[Ne]3s^1$	+1	157	95
Potassium	K	$[Ar]4s^1$	+1	202	133
Rubidium	Rb	$[Kr]5s^1$	+1	216	148
Cesium	Cs	$[Xe]6s^1$	+1	235	169

Symbol	Ionization Energy/MJ mol^{-1}		Density/ g cm^{-3}	Electronegativity	Melting Point (in °C)
	First	Second			
Li	0.526	7.305	0.534	1.0	179
Na	0.502	4.569	0.97	0.9	98
K	0.425	3.058	0.86	0.8	64
Rb	0.409	2.638	1.52	0.8	39
Cs	0.382	2.430	1.87	0.7	28

The atoms do not have a strong attraction for the single valence electron, and so it is easily lost (small first ionization energy) to from a +1 ion. Because they readily donate electrons in this way, all the alkali metals are strong reducing agents. They are quite reactive, even reducing water.

Weak attraction for the valence electron also results in weak metallic bonding, because it is attraction among nuclei and numerous valence electrons that holds metal atoms together. Weak metallic bonding results in low melting points, especially for the larger atoms toward the bottom of the group. Cs, for example, melts just above room temperature. Weak metallic bonding also accounts for the fact that all these metals are rather soft.

That the chemistry of alkali metals is confined to the +1 oxidation state is confirmed by the large second-ionization energies. Removing the first electron from the large, diffuses orbital is easy, but removing a second electron from an octet in an M^+ ion is much too difficult for any oxidizing agent to do.

Two other elements are found in group IA. Hydrogen, although many of its compounds have formulas similar to the alkali metals, is a nonmetal and is almost unique in its chemical behavior. Therefore it is not usually included in this group. Francium (Fr) is quite radioactive, and only small quantities are available for study; so it too is usually omitted. Its properties, however, appear to be similar to those of Cs and the other alkali metals.

Chemical Reactions and Compounds

The element lithium combines violently and spectacularly with water. Hydrogen gas is given off, which propels the the lithium metal across the water as it reacts. If the excess water is evaporated, the compound lithium hydroxide (LiOH) remains behind. LiOH is visualized by phenolphthalein indicator, which turns pink as LiOH, a base, is produced. Thus the equation for this reaction is

$$2\mathrm{Li}(s)+2\mathrm{H}_2\mathrm{O}(l)\rightarrow 2\mathrm{LiOH}(aq)+\mathrm{H}_2(g)$$

The elements sodium, potassium, rubidium, and cesium also combine violently with water to form hydroxides. The equations for their reactions are

$$2\mathrm{Na}(s)+2\mathrm{H}_2\mathrm{O}(l)\rightarrow 2\mathrm{NaOH}(aq)+\mathrm{H}_2(g)$$

$$2\mathrm{K}(s)+2\mathrm{H}_2\mathrm{O}(l)\rightarrow 2\mathrm{KOH}(aq)+\mathrm{H}_2(g)$$

$$2\mathrm{Rb}(s)+2\mathrm{H}_2\mathrm{O}(l)\rightarrow 2\mathrm{RbOH}(aq)+\mathrm{H}_2(g)$$

$$2\mathrm{Cs}(s)+2\mathrm{H}_2\mathrm{O}(l)\rightarrow 2\mathrm{CsOH}(aq)+\mathrm{H}_2(g)$$

Since the alkali metals all react with water in the same way, a *general equation* may be written:

$$2\mathrm{M}(s)+2\mathrm{H}_2\mathrm{O}(l)\rightarrow 2\mathrm{MOH}(aq)+\mathrm{H}_2(g)$$

with M = K, Li, Na, Rb, or Cs.

The symbol M represents any one of the five elements.

In addition to their behavior when added to water, the alkali metals react directly with many elements. All combine swiftly with oxygen in air to form white oxide:

$$4\mathrm{M}(s)+\mathrm{O}_2(g)\rightarrow 2\mathrm{M}_2\mathrm{O}(s)$$

with M = Li, Na, K, Rb, or Cs

(Li_2O is lithium oxide, Na_2O is sodium oxide, etc.)

All except lithium react further to form yellow peroxides, M_2O_2:

$$2\mathrm{M}_2\mathrm{O}(s)+\mathrm{O}_2(g)\rightarrow 2\mathrm{M}_2\mathrm{O}_2(s)$$

M = Na, K, Rb, or Cs

(Na_2O_2 is sodium peroxide, etc.)

Potassium, rubidium, and cesium are sufficiently reactive that yellow superoxides (whose general formula is MO_2) can be formed:

$$2\mathrm{M}_2\mathrm{O}_2(s)+\mathrm{O}_2(g)\rightarrow 2\mathrm{MO}_2(s)$$

with M = K, Rb, or Cs

Unless the surface of a sample of an alkali metal is scraped clean, it will appear white or gray instead of having a silvery metallic luster. This is due to the oxide, peroxide, or superoxide coating that forms after a few seconds of exposure to air. The following movie shows how a freshly cut piece of lithium is shiny, but dulls to gray when exposed to oxygen in the air. The video also focuses on another important property of alkali metals: they are soft, and easy to cut, compared to other metals.

A dull gray oxidized cylinder of lithium metal is cut, revealing a shiny silvery surface. After 1 minute, the surface has dulled, and after 10 minutes, the cut surface has returned to the dull gray of the rest of the lithium metal. Since the alkali metal is lithium, the only reaction with oxygen that occurs is:

$$4\mathrm{Li}(s)+\mathrm{O}_2(g)\rightarrow 2\mathrm{Li}_2\mathrm{O}(s)$$

The alkali also combine directly with hydrogen gas to form compounds known as hydrides, MH:

$$2\mathrm{M}(s)+\mathrm{H}_2(g)\rightarrow 2\mathrm{MH}(s)$$

with M = Li, Na, K, Rb, or Cs

They react with sulfur to form sulfides, M_2S:

$$2\mathrm{M}(s)+\mathrm{S}(g)\rightarrow \mathrm{M}_2\mathrm{S}(s)$$

with M = Li, Na, K, Rb, or Cs

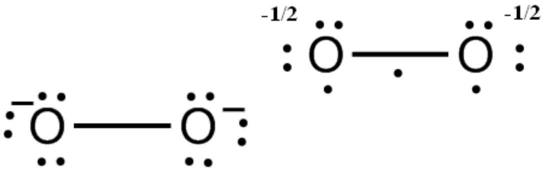
These oxides, hydrides, hydroxides, and sulfides all dissolve in water to give basic solutions, and these compounds are among the strong bases.

The peroxides and superoxides formed when the heavier alkali metals react with O_2 also dissolve to give basic solutions:

$$2\mathrm{NaO}_2(s)+2\mathrm{H}_2\mathrm{O}(l)\rightarrow 4\mathrm{Na}^+(aq)+4\mathrm{OH}^-(aq)+\mathrm{O}_2(g)$$

$$4\mathrm{K}_2\mathrm{O}(s)+2\mathrm{H}_2\mathrm{O}(l)\rightarrow 4\mathrm{K}^+ +4\mathrm{OH}^- +3\mathrm{O}_2(g)$$

Both of the latter equations describe redox as well as acid-base processes, as you can confirm by assigning oxidation numbers. The peroxide and superoxide ions contain O atoms in the unusual (for O) –1 and –½ oxidation states:



Therefore **disproportionation** (simultaneous oxidation and reduction) of O_2^{2-} or O_2^- to the more common oxidation states of 0 (in O_2) and –2 (in OH^-) is possible.

The alkali metals also react directly with the halogens, for instance with chlorine, forming chlorides,

$$2\mathrm{M}(s)+\mathrm{Cl}_2(g)\rightarrow 2\mathrm{MCl}(s)$$

M = Li, Na, K, Rb, or Cs

Below is an example of the reaction of Na with Cl_2

A piece of sodium metal is added to a flask containing chlorine gas. Initially no reaction takes place, but when a drop of water is added, sodium and chlorine react, violently flaring up and producing so much heat that sand is needed in the bottom of the flask to absorb the heat and prevent the glass from cracking. This equation for this reaction is:

$$2\mathrm{Na}(s)+\mathrm{Cl}_2(g)\rightarrow 2\mathrm{NaCl}(s)$$

with fluorine to form fluorides, MF:

$$2\mathrm{M}(s)+\mathrm{F}_2(g)\rightarrow 2\mathrm{MF}(s)$$

M = Li, Na, K, Rb, or Cs

and with bromine to form bromides, MBr:

$$2\mathrm{M}(s)+\mathrm{Br}_2(g)\rightarrow 2\mathrm{MBr}(s)$$

M = Li, Na, K, Rb, or Cs

Below is an example of K reacting with Br_2

In this video, potassium, which is stored in inert mineral oil due to its high reactivity, is placed in a beaker of liquid bromine after the protective layer of mineral oil has been removed. The potassium reacts explosively with the bromine. The container is covered during the whole process to prevent reactants and products from entering the environment. The chemical equation for this reaction is:

$$2\mathrm{K}(s)+\mathrm{Br}_2(g)\rightarrow 2\mathrm{KBr}(s)$$

Sodium and potassium are quite abundant, ranking sixth and seventh among all elements in the earth’s crust, but the other alkali metals are rare. Sodium and potassium ions are components of numerous silicate crystal lattices seen in the Earth's crust, but since most of their compounds are water soluble, they are also important constituents of seawater and underground deposits of brine. Sodium chloride obtained from such brines is the chief commercial source of sodium, while potassium can be obtained from the ores sylvite (KCl) or carnallite ($KCl•MgCl_2•6H_2O$).

Both sodium (Na^+) and potassium (K^+) ions are essential to living systems. Na^+ is the main cation in fluids surrounding the cells, while $K^+$is most important inside the cells. Na^+ plays a role in muscle contraction, and both K^+ and Na^+ play a role in transmitting nerve impulses. K is more important than Na in plants, and it is one of three elements (K, P, N) which must be supplied in fertilizer to maintain high crop yields. K is especially abundant in trees—wood ashes from kitchen fires (potash) were the major source of this element as recently as a century ago, and they still make good fertilizer for your garden. Wood ashes contain a mixture of potassium oxide and potassium carbonate, the latter formed by combination of K_2O with CO_2 produced when C in the wood combines with O_2:

$$\mathrm{K_2O}+\mathrm{CO_2}\rightarrow \mathrm{K_2CO_3}$$

Na compounds are obtained commercially from brine or from seawater. When an electrical current is passed through an NaCl solution (a process called **electrolysis**), Cl_2(g), H_2(g), and a concentrated solution of NaOH (caustic soda or lye) are obtained:

$$\mathrm{Na}^+(aq)+2\mathrm{Cl}^-(aq)+2\mathrm{H_2O}(l)\xrightarrow{\text{electrolysis}}\mathrm{Cl_2}(g)+\mathrm{H_2}(g)+\mathrm{Na}^+(aq)+2\mathrm{OH}^-(aq)$$

This process is described in more detail in the section on electrochemical cells, but you can see from the equation that the electrical current oxidizes $Cl^–$ to Cl_2 and reduces H_2O to H_2. NaOH(*aq*) is used as a strong base in numerous industrial processes to make soap, rayon, cellophane, paper, dyes, and many other products. Lye is also used in home drain cleaners. It must be handled with care because it is strongly basic, highly caustic, and can severely burn the skin. A second important industrial use of brine is the **Solvay process**:

$$\mathrm{CO_2}(g)+\mathrm{NH_3}(aq)+\mathrm{Na}^+(aq)+\mathrm{Cl}^-(aq)+\mathrm{H_2O}(l)\rightarrow \mathrm{NaHCO_3}(s)+\mathrm{NH_4^+}(aq)+\mathrm{Cl}^-(aq)$$

The Solvay process is an acid-base reaction combined with a precipitation. The acid anhydride, CO_2, reacts with H_2O to produce H_2CO_3. This weak acid donates a proton to NH_3, yielding NH_4^+ and $HCO_3^–$, and the latter ion precipitates with Na^+. The weakly basic sodium hydrogen carbonate produced by the Solvay process can be purified for use as an antacid (bicarbonate of soda), but most of it is converted to sodium carbonate (soda ash) by heating:

$$2\mathrm{NaHCO_3}(s)\xrightarrow{\Delta}\mathrm{Na_2CO_3}(s)+\mathrm{H_2O}(g)+\mathrm{CO_2}(g)$$

(The Δ in this equation indicates heating of the reactant.) Sodium carbonate (Na_2CO_3) is used in manufacturing glass and paper, and in some detergents. The carbonate ion is a rather strong base, however, and detergents containing Na_2CO_3 (washing soda) have resulted in severe chemical burns to some small children who, out of curiosity, have eaten them.

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18.3: The Chemistry of Hydrogen

Learning Objectives

- To describe the physical and chemical properties of hydrogen and predict its reactivity.

We now turn from an overview of periodic trends to a discussion of the s-block elements, first by focusing on hydrogen, whose chemistry is sufficiently distinct and important to be discussed in a category of its own. Most versions of the periodic table place hydrogen in the upper left corner immediately above lithium, implying that hydrogen, with a $1s^1$ electron configuration, is a member of group 1. In fact, the chemistry of hydrogen does not greatly resemble that of the metals of Group 1. Indeed, some versions of the periodic table place hydrogen above fluorine in Group 17 because the addition of a single electron to a hydrogen atom completes its valence shell.

> *Although hydrogen has an ns^1 electron configuration, its chemistry does not resemble that of the Group 1 metals.*

Isotopes of Hydrogen

Hydrogen, the most abundant element in the universe, is the ultimate source of all other elements by the process of nuclear fusion. Table 18.3.1 "The Isotopes of Hydrogen" compares the three isotopes of hydrogen, all of which contain one proton and one electron per atom. The most common isotope is **protium** (^1H or H), followed by **deuterium** (^2H or D), which has an additional neutron. The rarest isotope of hydrogen is **tritium** (^3H or T), which is produced in the upper atmosphere by a nuclear reaction when cosmic rays strike nitrogen and other atoms; it is then washed into the oceans by rainfall. Tritium is radioactive, decaying to ^3He with a half-life of only 12.32 years. Consequently, the atmosphere and oceans contain only a very low, steady-state level of tritium. The term hydrogen and the symbol H normally refer to the naturally occurring mixture of the three isotopes.

Table 18.3.1: The Isotopes of Hydrogen

	Protium	Deuterium	Tritium
symbol	${}^{1}_{1}H$	${}^{2}_{1}H$	${}^{3}_{1}H$
neutrons	0	1	2
mass (amu)	1.00783	2.0140	3.01605
abundance (%)	99.9885	0.0115	$\sim 10^{-17}$
half-life (years)	—	—	12.32
boiling point of X_2 (K)	20.28	23.67	25
melting point/boiling point of X_2O (°C)	0.0/100.0	3.8/101.4	4.5/?

The different masses of the three isotopes of hydrogen cause them to have different physical properties. Thus H_2, D_2, and T_2 differ in their melting points, boiling points, densities, and heats of fusion and vaporization. In 1931, Harold Urey and coworkers discovered deuterium by slowly evaporating several liters of liquid hydrogen until a volume of about 1 mL remained. When that remaining liquid was vaporized and its emission spectrum examined, they observed new absorption lines in addition to those previously identified as originating from hydrogen. The natural abundance of tritium, in contrast, is so low that it could not be detected by similar experiments; it was first prepared in 1934 by a nuclear reaction.

Harold Urey (1893–1981)

Urey won the Nobel Prize in Chemistry in 1934 for his discovery of deuterium (^2H). Urey was born and educated in rural Indiana. After earning a BS in zoology from the University of Montana in 1917, Urey changed career directions. He earned his PhD in chemistry at Berkeley with G. N. Lewis and subsequently worked with Niels Bohr in Copenhagen. During World War II, Urey was the director of war research for the Atom Bomb Project at Columbia University. In later years, his research

> focused on the evolution of life. In 1953, he and his graduate student, Stanley Miller, showed that organic compounds, including amino acids, could be formed by passing an electric discharge through a mixture of compounds thought to be present in the atmosphere of primitive Earth.

Because the normal boiling point of D_2O is 101.4°C (compared to 100.0°C for H_2O), evaporation or fractional distillation can be used to increase the concentration of deuterium in a sample of water by the selective removal of the more volatile H_2O. Thus bodies of water that have no outlet, such as the Great Salt Lake and the Dead Sea, which maintain their level solely by evaporation, have significantly higher concentrations of deuterated water than does lake or seawater with at least one outlet. A more efficient way to obtain water highly enriched in deuterium is by prolonged electrolysis of an aqueous solution. Because a deuteron (D^+) has twice the mass of a proton (H^+), it diffuses more slowly toward the electrode surface. Consequently, the gas evolved at the cathode is enriched in H, the species that diffuses more rapidly, favoring the formation of H_2 over D_2 or HD. Meanwhile, the solution becomes enriched in deuterium. Deuterium-rich water is called heavy water because the density of D_2O (1.1044 g/cm^3 at 25°C) is greater than that of H_2O (0.99978 g/cm^3). Heavy water was an important constituent of early nuclear reactors.

Because deuterons diffuse so much more slowly, D_2O will not support life and is actually toxic if administered to mammals in large amounts. The rate-limiting step in many important reactions catalyzed by enzymes involves proton transfer. The transfer of D^+ is so slow compared with that of H^+ because bonds to D break more slowly than those to H, so the delicate balance of reactions in the cell is disrupted. Nonetheless, deuterium and tritium are important research tools for biochemists. By incorporating these isotopes into specific positions in selected molecules, where they act as labels, or tracers, biochemists can follow the path of a molecule through an organism or a cell. Tracers can also be used to provide information about the mechanism of enzymatic reactions.

Bonding in Hydrogen and Hydrogen-Containing Compounds

The 1s^1 electron configuration of hydrogen indicates a single valence electron. Because the 1s orbital has a maximum capacity of two electrons, hydrogen can form compounds with other elements in three ways (Figure 18.3.1):

1. **Losing its electron to form a proton (H^+) with an empty 1s orbital.** The proton is a Lewis acid that can accept a pair of electrons from another atom to form an electron-pair bond. In the acid–base reactions, the proton always binds to a lone pair of electrons on an atom in another molecule to form a polar covalent bond. If the lone pair of electrons belongs to an oxygen atom of a water molecule, the result is the hydronium ion (H_3O^+).
2. **Accepting an electron to form a hydride ion ($H^−$), which has a filled 1s^2 orbital.** Hydrogen reacts with relatively electropositive metals, such as the alkali metals (group 1) and alkaline earth metals (group 2), to form ionic hydrides, which contain metal cations and $H^−$ ions.
3. **Sharing its electron with an electron on another atom to form an electron-pair bond.** With a half-filled 1s^1 orbital, the hydrogen atom can interact with singly occupied orbitals on other atoms to form either a covalent or a polar covalent electron-pair bond, depending on the electronegativity of the other atom.

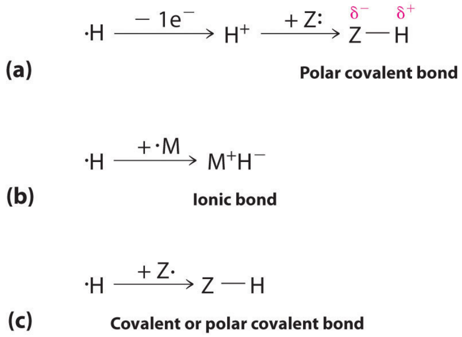

Figure 18.3.1: Three Types of Bonding in Compounds of Hydrogen. Because of its 1s^1 electron configuration and the fact that the 1s orbital can accommodate no more than two electrons, hydrogen can (a) bond to other elements by losing an electron to form a proton, which can accept a pair of electrons from a more electronegative atom to form a polar covalent bond; (b) gain an electron from an electropositive metal to form a hydride ion, resulting in an ionic hydride; or (c) share its half-filled 1s orbital with a half-filled orbital on another atom to form a covalent or a polar covalent electron-pair bond.

Hydrogen can also act as a bridge between two atoms. One familiar example is the **hydrogen bond**, an electrostatic interaction between a hydrogen bonded to an electronegative atom and an atom that has one or more lone pairs of electrons (Figure 18.3.2). An example of this kind of interaction is the hydrogen bonding network found in water (Figure 18.3.2). Hydrogen can also form a

three-center bond (or electron-deficient bond), in which a hydride bridges two electropositive atoms. Compounds that contain hydrogen bonded to boron and similar elements often have this type of bonding. The B–H–B units found in boron hydrides cannot be described in terms of localized electron-pair bonds.

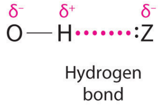

Figure 18.3.2: The Hydrogen Bond. The covalent bond between hydrogen and a very electronegative element, such as nitrogen, oxygen, or fluorine, is highly polar. The resulting partial positive charge on H allows it to interact with a lone pair of electrons on another atom to form a hydrogen bond, which is typically a linear arrangement of the three atoms, with the hydrogen atom placed asymmetrically between the two heavier atoms.

Because the H atom in the middle of such a unit can accommodate a maximum of only two electrons in its 1s orbital, the B–H–B unit can be described as containing a hydride that interacts simultaneously with empty sp^3 orbitals on two boron atoms (Figure 18.3.3). In these bonds, only two bonding electrons are used to hold three atoms together, making them electron-deficient bonds. You encountered a similar phenomenon in the discussion of π bonding in ozone and the nitrite ion. Recall that in both these cases, we used the presence of two electrons in a π molecular orbital extending over three atoms to explain the fact that the two O–O bond distances in ozone and the two N–O bond distances in nitrite are the same, which otherwise can be explained only by the use of resonance structures.

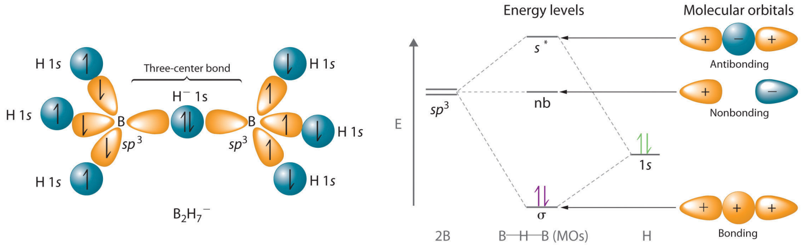

Figure 18.3.3: A Three-Center Bond Uses Two Electrons to Link Three Atoms. In the B–H–B unit shown, a hydride, with a filled 1s orbital, interacts simultaneously with empty sp^3 hybrids on the boron atoms of two BH_3 units to give three molecular orbitals. The two bonding electrons occupy the lowest-energy (σ) bonding orbital, thereby holding all three atoms together.

> *Hydrogen can lose its electron to form H^+, accept an electron to form H^-, share its electron, hydrogen bond, or form a three-center bond.*

Synthesis, Reactions, and Compounds of Hydrogen

The first known preparation of elemental hydrogen was in 1671, when Robert Boyle dissolved iron in dilute acid and obtained a colorless, odorless, gaseous product. Hydrogen was finally identified as an element in 1766, when Henry Cavendish showed that water was the sole product of the reaction of the gas with oxygen. The explosive properties of mixtures of hydrogen with air were not discovered until early in the 18th century; they partially caused the spectacular explosion of the hydrogen-filled dirigible Hindenburg in 1937 (Figure 18.3.4). Due to its extremely low molecular mass, hydrogen gas is difficult to condense to a liquid (boiling point = 20.3 K), and solid hydrogen has one of the lowest melting points known (13.8 K).

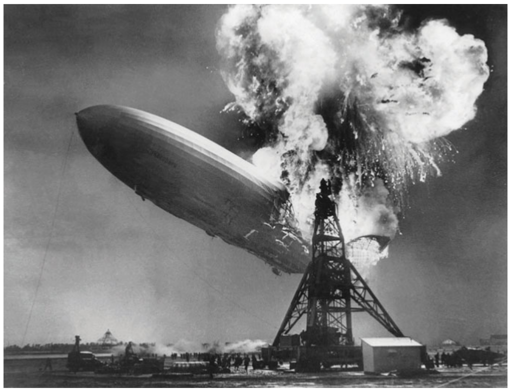

Figure 18.3.4: The Explosive Properties of Hydrogen. When mixed with air and ignited by a spark, hydrogen gas can explode. The photograph shows the German dirigible Hindenburg on fire at Lakehurst, New Jersey, in 1937, after its hydrogen compartment was accidentally ignited as a consequence of an electrical discharge that caused the dirigible's flammable skin to catch fire.

The most common way to produce small amounts of highly pure hydrogen gas in the laboratory was discovered by Boyle: reacting an active metal (M), such as iron, magnesium, or zinc, with dilute acid:

$$M_{(s)} + 2H^+_{(aq)} \rightarrow H_{2(g)} + M^{2+}_{(aq)} \tag{18.3.1}$$

Hydrogen gas can also be generated by reacting metals such as aluminum or zinc with a strong base:

$$\mathrm{Al(s) + OH^-(aq) + 3H_2O(l) \rightarrow \frac{3}{2}H_2(g) + [Al(OH)_4]^-(aq)} \tag{18.3.2}$$

Solid commercial drain cleaners such as Drano use this reaction to generate gas bubbles that help break up clogs in a drainpipe. Hydrogen gas is also produced by reacting ionic hydrides with water. Because ionic hydrides are expensive, however, this reaction is generally used for only specialized purposes, such as producing HD gas by reacting a hydride with D_2O:

$$MH_{(s)} + D_2O(l) \rightarrow HD_{(g)} + M^+(aq) + OD^-_{(aq)} \tag{18.3.3}$$

On an industrial scale, H_2 is produced from methane by means of catalytic steam reforming, a method used to convert hydrocarbons to a mixture of CO and H_2 known as synthesis gas, or syngas. The process is carried out at elevated temperatures (800°C) in the presence of a nickel catalyst:

$$\mathrm{CH_4(g) + H_2O(g) \xrightarrow{Ni} CO(g) + 3H_2(g)} \tag{18.3.4}$$

Most of the elements in the periodic table form binary compounds with hydrogen, which are collectively referred to as hydrides. Binary hydrides in turn can be classified in one of three ways, each with its own characteristic properties. Covalent hydrides contain hydrogen bonded to another atom via a covalent bond or a polar covalent bond. Covalent hydrides are usually molecular substances that are relatively volatile and have low melting points. Ionic hydrides contain the hydride ion as the anion with cations derived from electropositive metals. Like most ionic compounds, they are typically nonvolatile solids that contain three-dimensional lattices of cations and anions. Unlike most ionic compounds, however, they often decompose to H_2(g) and the parent metal after heating. Metallic hydrides are formed by hydrogen and less electropositive metals such as the transition metals. The properties of metallic hydrides are usually similar to those of the parent metal. Consequently, metallic hydrides are best viewed as metals that contain many hydrogen atoms present as interstitial impurities.

> *Covalent hydrides are relatively volatile and have low melting points; ionic hydrides are generally nonvolatile solids in a lattice framework.*

Summary and Key Takeaway

Hydrogen can lose an electron to form a proton, gain an electron to form a hydride ion, or form a covalent bond or polar covalent electron-pair bond. The three isotopes of hydrogen—protium (^{1}H or H), deuterium (^{2}H or D), and tritium (^{3}H or T)—have different physical properties. Deuterium and tritium can be used as tracers, substances that enable biochemists to follow the path of a molecule through an organism or a cell. Hydrogen can form compounds that contain a proton (H^+), a hydride ion (H^-), an electron-pair bond to H, a hydrogen bond, or a three-center bond (or electron-deficient bond), in which two electrons are shared between three atoms. Hydrogen gas can be generated by reacting an active metal with dilute acid, reacting Al or Zn with a strong base, or industrially by catalytic steam reforming, which produces synthesis gas, or syngas.

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18.4: Group 2A Elements

Learning Objectives

- To describe how to isolate the alkaline earth metals.
- To be familiar with the reactions, compounds, and complexes of the alkaline earth metals.

Like the alkali metals, the alkaline earth metals are so reactive that they are never found in elemental form in nature. Because they form +2 ions that have very negative reduction potentials, large amounts of energy are needed to isolate them from their ores. Four of the six group 2 elements—magnesium (Mg), calcium (Ca), strontium (Sr), and barium (Ba)—were first isolated in the early 19th century by Sir Humphry Davy, using a technique similar to the one he used to obtain the first alkali metals. In contrast to the alkali metals, however, compounds of the alkaline earth metals had been recognized as unique for many centuries. In fact, the name alkali comes from the Arabic al-qili, meaning “ashes,” which were known to neutralize acids. Medieval alchemists found that a portion of the ashes would melt on heating, and these substances were later identified as the carbonates of sodium and potassium (M_2CO_3). The ashes that did not melt (but did dissolve in acid), originally called alkaline earths, were subsequently identified as the alkaline earth oxides (MO). In 1808, Davy was able to obtain pure samples of Mg, Ca, Sr, and Ba by electrolysis of their chlorides or oxides.

Beryllium (Be), the lightest alkaline earth metal, was first obtained in 1828 by Friedrich Wöhler in Germany and simultaneously by Antoine Bussy in France. The method used by both men was reduction of the chloride by the potent “new” reductant, potassium:

$$\mathrm{BeCl_2(s) + 2K(s) \xrightarrow{\Delta} Be(s) + 2KCl(s)} \tag{18.4.1}$$

Radium was discovered in 1898 by Pierre and Marie Curie, who processed tons of residue from uranium mines to obtain about 120 mg of almost pure $RaCl_2$. Marie Curie was awarded the Nobel Prize in Chemistry in 1911 for its discovery. Because of its low abundance and high radioactivity however, radium has few uses.

Preparation of the Alkaline Earth Metals

The alkaline earth metals are produced for industrial use by electrolytic reduction of their molten chlorides, as indicated in this equation for calcium:

$$CaCl_{2\,(l)} \rightarrow Ca_{(l)} + Cl_{2\,(g)} \tag{18.4.2}$$

The group 2 metal chlorides are obtained from a variety of sources. For example, $BeCl_2$ is produced by reacting HCl with beryllia (BeO), which is obtained from the semiprecious stone beryl $[Be_3Al_2(SiO_3)_6]$.

A crystal of beryl. Beryl is a gemstone and an important source of beryllium.

Chemical reductants can also be used to obtain the group 2 elements. For example, magnesium is produced on a large scale by heating a form of limestone called dolomite ($CaCO_3 \cdot MgCO_3$) with an inexpensive iron/silicon alloy at 1150°C. Initially CO_2 is released, leaving behind a mixture of CaO and MgO; Mg^{2+} is then reduced:

$$2CaO \cdot MgO_{(s)} + Fe/Si_{(s)} \rightarrow 2Mg(l) + Ca_2SiO_{4\,(s)} + Fe(s) \tag{18.4.3}$$

An early source of magnesium was an ore called magnesite ($MgCO_3$) from the district of northern Greece called Magnesia. Strontium was obtained from strontianite ($SrCO_3$) found in a lead mine in the town of Strontian in Scotland. The alkaline earth metals are somewhat easier to isolate from their ores, as compared to the alkali metals, because their carbonate and some sulfate and hydroxide salts are insoluble.

A crystal of strontianite. Both strontianite, one of the most important strontium ores, and strontium are named after the town of Strontian, Scotland, the location of one of the first mines for strontium ores.

General Properties of the Alkaline Earth Metals

Several important properties of the alkaline earth metals are summarized in Table 18.4.1. Although many of these properties are similar to those of the alkali metals (Table 18.4.1), certain key differences are attributable to the differences in the valence electron configurations of the two groups (ns^2 for the alkaline earth metals versus ns^1 for the alkali metals).

Table 18.4.1: Selected Properties of the Group 2 Elements

	Beryllium	**Magnesium**	**Calcium**	**Strontium**	**Barium**	**Radium**
atomic symbol	Be	Mg	Ca	Sr	Ba	Ra
atomic number	4	12	20	38	56	88
atomic mass	9.01	24.31	40.08	87.62	137.33	226
valence electron configuration	$2s^2$	$3s^2$	$4s^2$	$5s^2$	$6s^2$	$7s^2$
melting point/boiling point (°C)	1287/2471	650/1090	842/1484	777/1382	727/1897	700/—
density (g/cm^3) at 25°C	1.85	1.74	1.54	2.64	3.62	~5
atomic radius (pm)	112	145	194	219	253	—
first ionization energy (kJ/mol)	900	738	590	549	503	—
most common oxidation state	+2	+2	+2	+2	+2	+2
ionic radius (pm)*	45	72	100	118	135	—
electron affinity (kJ/mol)	≥ 0	≥ 0	−2	−5	−14	—
electronegativity	1.6	1.3	1.0	1.0	0.9	0.9
standard electrode potential (E°, V)	−1.85	−2.37	−2.87	−2.90	−2.91	−2.8
product of reaction with O_2	BeO	MgO	CaO	SrO	BaO_2	—
type of oxide	amphoteric	weakly basic	basic	basic	basic	—

*The values cited are for six-coordinate ions except for Be^{2+}, for which the value for the four-coordinate ion is given.

	Beryllium	**Magnesium**	**Calcium**	**Strontium**	**Barium**	**Radium**
product of reaction with N_2	none	Mg_3N_2	Ca_3N_2	Sr_3N_2	Ba_3N_2	—
product of reaction with X_2	BeX_2	MgX_2	CaX_2	SrX_2	BaX_2	—
product of reaction with H_2	none	MgH_2	CaH_2	SrH_2	BaH_2	—

*The values cited are for six-coordinate ions except for Be^{2+}, for which the value for the four-coordinate ion is given.

As with the alkali metals, the atomic and ionic radii of the alkaline earth metals increase smoothly from Be to Ba, and the ionization energies decrease. As we would expect, the first ionization energy of an alkaline earth metal, with an ns^2 valence electron configuration, is always significantly greater than that of the alkali metal immediately preceding it. The group 2 elements do exhibit some anomalies, however. For example, the density of Ca is less than that of Be and Mg, the two lightest members of the group, and Mg has the lowest melting and boiling points. In contrast to the alkali metals, the heaviest alkaline earth metal (Ba) is the strongest reductant, and the lightest (Be) is the weakest. The standard electrode potentials of Ca and Sr are not very different from that of Ba, indicating that the opposing trends in ionization energies and hydration energies are of roughly equal importance.

One major difference between the group 1 and group 2 elements is their electron affinities. With their half-filled ns orbitals, the alkali metals have a significant affinity for an additional electron. In contrast, the alkaline earth metals generally have little or no tendency to accept an additional electron because their ns valence orbitals are already full; an added electron would have to occupy one of the vacant np orbitals, which are much higher in energy.

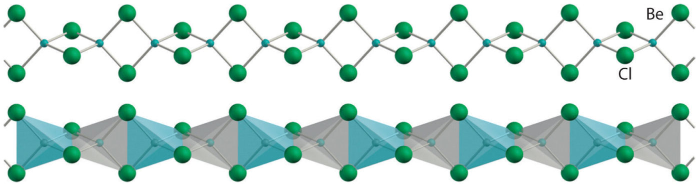
Reactions and Compounds of the Alkaline Earth Metals

With their low first and second ionization energies, the group 2 elements almost exclusively form ionic compounds that contain M^{2+} ions. As expected, however, the lightest element (Be), with its higher ionization energy and small size, forms compounds that are largely covalent. Some compounds of Mg^{2+} also have significant covalent character. Hence organometallic compounds like those discussed for Li in group 1 are also important for Be and Mg in group 2.

> *The group 2 elements almost exclusively form ionic compounds containing M^{2+} ions.*

All alkaline earth metals react vigorously with the halogens (group 17) to form the corresponding halides (MX_2). Except for the beryllium halides, these compounds are all primarily ionic in nature, containing the M^{2+} cation and two X^- anions. The beryllium halides, with properties more typical of covalent compounds, have a polymeric halide-bridged structure in the solid state, as shown for $BeCl_2$. These compounds are volatile, producing vapors that contain the linear X–Be–X molecules predicted by the valence-shell electron-pair repulsion (VSEPR) model. As expected for compounds with only four valence electrons around the central atom, the beryllium halides are potent Lewis acids. They react readily with Lewis bases, such as ethers, to form tetrahedral adducts in which the central beryllium is surrounded by an octet of electrons:

$$BeCl_{2(s)} + 2(CH_3CH_2)_2O_{(l)} \rightarrow BeCl_2[O(CH_2CH_3)_2]_{2(soln)} \tag{18.4.4}$$



Solid beryllium chloride ($BeCl_2$). The solid has a polymeric, halide-bridged structure.

> *Because of their higher ionization energy and small size, both Be and Mg form organometallic compounds.*

The reactions of the alkaline earth metals with oxygen are less complex than those of the alkali metals. All group 2 elements except barium react directly with oxygen to form the simple oxide MO. Barium forms barium peroxide (BaO_2) because the larger O_2^{2-} ion is better able to separate the large Ba^{2+} ions in the crystal lattice. In practice, only BeO is prepared by direct reaction with oxygen, and this reaction requires finely divided Be and high temperatures because Be is relatively inert. The other alkaline earth oxides are usually prepared by the thermal decomposition of carbonate salts:

$$\mathrm{MCO_3(s) \xrightarrow{\Delta} MO(s) + CO_2(g)} \tag{18.4.5}$$

The reactions of the alkaline earth metals with the heavier chalcogens (Y) are similar to those of the alkali metals. When the reactants are present in a 1:1 ratio, the binary chalcogenides (MY) are formed; at lower M:Y ratios, salts containing polychalcogenide ions (Y_n^{2-}) are formed.

In the reverse of Equation 18.4.5, the oxides of Ca, Sr, and Ba react with CO_2 to regenerate the carbonate. Except for BeO, which has significant covalent character and is therefore amphoteric, all the alkaline earth oxides are basic. Thus they react with water to form the hydroxides—$M(OH)_2$:

$$MO_{(s)} + H_2O_{(l)} \rightarrow M^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{18.4.6}$$

and they dissolve in aqueous acid. Hydroxides of the lighter alkaline earth metals are insoluble in water, but their solubility increases as the atomic number of the metal increases. Because BeO and MgO are much more inert than the other group 2 oxides, they are used as refractory materials in applications involving high temperatures and mechanical stress. For example, MgO (melting point = 2825°C) is used to coat the heating elements in electric ranges.

The carbonates of the alkaline earth metals also react with aqueous acid to give CO_2 and H_2O:

$$MCO_{3(s)} + 2H^+_{(aq)} \rightarrow M^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)} \tag{18.4.7}$$

The reaction in Equation 18.4.7is the basis of antacids that contain MCO_3, which is used to neutralize excess stomach acid.

The trend in the reactivities of the alkaline earth metals with nitrogen is the opposite of that observed for the alkali metals. Only the lightest element (Be) does not react readily with N_2 to form the nitride (M_3N_2), although finely divided Be will react at high temperatures. The higher lattice energy due to the highly charged M^{2+} and N^{3-} ions is apparently sufficient to overcome the chemical inertness of the N_2 molecule, with its N≡N bond. Similarly, all the alkaline earth metals react with the heavier group 15 elements to form binary compounds such as phosphides and arsenides with the general formula M_3Z_2.

> *Higher lattice energies cause the alkaline earth metals to be more reactive than the alkali metals toward group 15 elements.*

When heated, all alkaline earth metals, except for beryllium, react directly with carbon to form ionic carbides with the general formula MC_2. The most important alkaline earth carbide is calcium carbide (CaC_2), which reacts readily with water to produce acetylene. For many years, this reaction was the primary source of acetylene for welding and lamps on miners' helmets. In contrast, beryllium reacts with elemental carbon to form Be_2C, which formally contains the C^{4-} ion (although the compound is covalent). Consistent with this formulation, reaction of Be_2C with water or aqueous acid produces methane:

$$Be_2C_{(s)} + 4H_2O_{(l)} \rightarrow 2Be(OH)_{2(s)} + CH_{4(g)} \tag{18.4.8}$$

Beryllium does not react with hydrogen except at high temperatures (1500°C), although BeH_2 can be prepared at lower temperatures by an indirect route. All the heavier alkaline earth metals (Mg through Ba) react directly with hydrogen to produce the binary hydrides (MH_2). The hydrides of the heavier alkaline earth metals are ionic, but both BeH_2 and MgH_2 have polymeric structures that reflect significant covalent character. All alkaline earth hydrides are good reducing agents that react rapidly with water or aqueous acid to produce hydrogen gas:

$$CaH_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + 2H_{2(g)} \tag{18.4.9}$$

Like the alkali metals, the heavier alkaline earth metals are sufficiently electropositive to dissolve in liquid ammonia. In this case, however, two solvated electrons are formed per metal atom, and no equilibriums involving metal dimers or metal anions are known. Also, like the alkali metals, the alkaline earth metals form a wide variety of simple ionic salts with oxoanions, such as carbonate, sulfate, and nitrate. The nitrate salts tend to be soluble, but the carbonates and sulfates of the heavier alkaline earth metals are quite insoluble because of the higher lattice energy due to the doubly charged cation and anion. The solubility of the carbonates and the sulfates decreases rapidly down the group because hydration energies decrease with increasing cation size.

> *The solubility of alkaline earth carbonate and sulfates decrease down the group because the hydration energies decrease.*

Complexes of the Alkaline Earth Metals

Because of their higher positive charge (+2) and smaller ionic radii, the alkaline earth metals have a much greater tendency to form complexes with Lewis bases than do the alkali metals. This tendency is most important for the lightest cation (Be^{2+}) and decreases rapidly with the increasing radius of the metal ion.

> *The alkaline earth metals have a substantially greater tendency to form complexes with Lewis bases than do the alkali metals.*

The chemistry of Be^{2+} is dominated by its behavior as a Lewis acid, forming complexes with Lewis bases that produce an octet of electrons around beryllium. For example, Be^{2+} salts dissolve in water to form acidic solutions that contain the tetrahedral $[Be(H_2O)_4]^{2+}$ ion. Because of its high charge-to-radius ratio, the Be^{2+} ion polarizes coordinated water molecules, thereby increasing their acidity:

$$[Be(H_2O)_4]^{2+}_{(aq)} \rightarrow [Be(H_2O)_3(OH)]^{+}_{(aq)} + H^{+}_{(aq)} \tag{18.4.10}$$

Similarly, in the presence of a strong base, beryllium and its salts form the tetrahedral hydroxo complex: $[Be(OH)_4]^{2-}$. Hence beryllium oxide is amphoteric. Beryllium also forms a very stable tetrahedral fluoride complex: $[BeF_4]^{2-}$. Recall that beryllium halides behave like Lewis acids by forming adducts with Lewis bases (Equation 18.4.4).

The heavier alkaline earth metals also form complexes, but usually with a coordination number of 6 or higher. Complex formation is most important for the smaller cations (Mg^{2+} and Ca^{2+}). Thus aqueous solutions of Mg^{2+} contain the octahedral $[Mg(H_2O)_6]^{2+}$ ion. Like the alkali metals, the alkaline earth metals form complexes with neutral cyclic ligands like the crown ethers and cryptands discussed in Section 21.3.

Organometallic Compounds Containing Group 2 Elements

Like the alkali metals, the lightest alkaline earth metals (Be and Mg) form the most covalent-like bonds with carbon, and they form the most stable organometallic compounds. Organometallic compounds of magnesium with the formula RMgX, where R is an alkyl or aryl group and X is a halogen, are universally called Grignard reagents, after Victor Grignard (1871–1935), the French chemist who discovered them. Grignard reagents can be used to synthesize various organic compounds, such as alcohols, aldehydes, ketones, carboxylic acids, esters, thiols, and amines.

Uses of the Alkaline Earth Metals

Elemental magnesium is the only alkaline earth metal that is produced on a large scale (about 5 × 10^5 tn per year). Its low density (1.74 g/cm^3 compared with 7.87 g/cm^3 for iron and 2.70 g/cm^3 for aluminum) makes it an important component of the lightweight metal alloys used in aircraft frames and aircraft and automobile engine parts (Figure 18.4.1). Most commercial aluminum actually contains about 5% magnesium to improve its corrosion resistance and mechanical properties. Elemental magnesium also serves as an inexpensive and powerful reductant for the production of a number of metals, including titanium, zirconium, uranium, and even beryllium, as shown in the following equation:

$$TiCl_{4\ (l)} + 2Mg(s) \rightarrow Ti_{(s)} + 2MgCl_{2\ (s)} \tag{18.4.11}$$

The only other alkaline earth that is widely used as the metal is beryllium, which is extremely toxic. Ingestion of beryllium or exposure to beryllium-containing dust causes a syndrome called berylliosis, characterized by severe inflammation of the respiratory tract or other tissues. A small percentage of beryllium dramatically increases the strength of copper or nickel alloys, which are used in nonmagnetic, nonsparking tools (such as wrenches and screwdrivers), camera springs, and electrical contacts. The low atomic number of beryllium gives it a very low tendency to absorb x-rays and makes it uniquely suited for applications involving radioactivity. Both elemental Be and BeO, which is a high-temperature ceramic, are used in nuclear reactors, and the windows on all x-ray tubes and sources are made of beryllium foil.

Figure 18.4.1: Magnesium Alloys Are Lightweight and Corrosion Resistant. Because magnesium is about five times lighter than steel and 50% lighter than aluminum, it was long considered the “material of the future,” as shown in this 1950 concept Buick LeSabre sports car made almost entirely of magnesium and aluminum alloys. Modern aluminum alloys usually contain about 5% magnesium to improve their corrosion resistance and mechanical properties.

Millions of tons of calcium compounds are used every year. As discussed in earlier chapters, $CaCl_2$ is used as “road salt” to lower the freezing point of water on roads in cold temperatures. In addition, $CaCO_3$ is a major component of cement and an ingredient in many commercial antacids. “Quicklime” (CaO), produced by heating $CaCO_3$ (Equation 18.4.5), is used in the steel industry to remove oxide impurities, make many kinds of glass, and neutralize acidic soil. Other applications of group 2 compounds described in earlier chapters include the medical use of $BaSO_4$ in “barium milkshakes” for identifying digestive problems by x-rays and the use of various alkaline earth compounds to produce the brilliant colors seen in fireworks.

✓ Example 18.4.1

For each application, choose the most appropriate substance based on the properties and reactivities of the alkaline earth metals and their compounds. Explain your choice in each case. Use any tables you need in making your decision, such as K_{sp} values (Table 17.1), lattice energies (Table 8.1), and band-gap energies.

a. To neutralize excess stomach acid that causes indigestion, would you use $BeCO_3$, $CaCO_3$, or $BaCO_3$?
b. To remove CO_2 from the atmosphere in a space capsule, would you use MgO, CaO, or BaO?
c. As a component of the alloy in an automotive spark plug electrode, would you use Be, Ca, or Ba?

Given: application and selected alkaline earth metals

Asked for: most appropriate substance for each application

Strategy:

Based on the discussion in this section and any relevant information elsewhere in this book, determine which substance is most appropriate for the indicated use.

Solution

a. All the alkaline earth carbonates will neutralize an acidic solution by Equation 18.4.7. Because beryllium and its salts are toxic, however, $BeCO_3$ cannot be used as an antacid. Of the remaining choices, $CaCO_3$ is somewhat more soluble than $BaCO_3$ (according to the K_{sp} values in Table 17.1), suggesting that it will act more rapidly. Moreover, the formula mass of $CaCO_3$ is 100.1 amu, whereas that of $BaCO_3$ is almost twice as large. Therefore, neutralizing a given amount of acid would require twice the mass of $BaCO_3$ compared with $CaCO_3$. Furthermore, reaction of $BaCO_3$ with acid produces a solution containing Ba^{2+} ions, which are toxic. (Ba^{2+} is a stimulant that can cause ventricular fibrillation of the heart.) Finally, $CaCO_3$ is produced on a vast scale, so $CaCO_3$ is likely to be significantly less expensive than any barium compound. Consequently, $CaCO_3$ is the best choice for an antacid.
b. This application involves reacting CO_2 with an alkaline earth oxide to form the carbonate, which is the reverse of the thermal decomposition reaction in which MCO_3 decomposes to CO_2 and the metal oxide MO (Equation 18.4.5). Owing to their higher lattice energies, the smallest alkaline earth metals should form the most stable oxides. Hence their carbonates should decompose at the lowest temperatures, as is observed ($BeCO_3$ decomposes at 100°C; $BaCO_3$ at 1360°C). If the carbonate with the smallest alkaline earth metal decomposes most readily, we would expect the reverse reaction (formation of a carbonate) to occur most readily with the largest metal cation (Ba^{2+}). Hence BaO is the best choice.

c. The alloy in a spark plug electrode must release electrons and promote their flow across the gap between the electrodes at high temperatures. Of the three metals listed, Ba has the lowest ionization energy and thus releases electrons most readily. Heating a barium-containing alloy to high temperatures will cause some ionization to occur, providing the initial step in forming a spark.

? Exercise 18.4.1

Which of the indicated alkaline earth metals or their compounds is most appropriate for each application?

a. drying agent for removing water from the atmosphere—$CaCl_2$, $MgSO_4$, or BaF_2
b. removal of scale deposits (largely $CaCO_3$) in water pipes—HCl(aq) or $H_2SO_4(aq)$
c. removal of traces of N_2 from purified argon gas—Be, Ca, or Ba

Answer

a. $MgSO_4$
b. HCl
c. Ba

✓ Example 18.4.2

Predict the products of each reaction and then balance each chemical equation.

a. CaO(s) + HCl(g) →
b. MgO(s) + excess $OH^-(aq)$ →
c. $\mathrm{CaH_2(s) + TiO_2(s)} \overset{\Delta}{\longrightarrow}$

Given: reactants

Asked for: products and balanced chemical equation

Strategy:

Follow the procedure given in Example 3 to predict the products of each reaction and then balance each chemical equation.

Solution

a. **A** Gaseous HCl is an acid, and CaO is a basic oxide that contains the O^{2-} ion. This is therefore an acid–base reaction that produces $CaCl_2$ and H_2O.

B The balanced chemical equation is

$$CaO_{(s)} + 2HCl_{(g)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)} \tag{18.4.12}$$

b. **A** Magnesium oxide is a basic oxide, so it can either react with water to give a basic solution or dissolve in an acidic solution. Hydroxide ion is also a base. Because we have two bases but no acid, an acid–base reaction is impossible. A redox reaction is not likely because MgO is neither a good oxidant nor a good reductant.

B We conclude that no reaction occurs.

c. **A** Because CaH_2 contains the hydride ion (H^-), it is a good reductant. It is also a strong base because H^- ions can react with H^+ ions to form H_2. Titanium oxide (TiO_2) is a metal oxide that contains the metal in its highest oxidation state (+4 for a group 4 metal); it can act as an oxidant by accepting electrons. We therefore predict that a redox reaction will occur, in which H^- is oxidized and Ti^{4+} is reduced. The most probable reduction product is metallic titanium, but what is the oxidation product? Oxygen must appear in the products, and both CaO and H_2O are stable compounds. The +1 oxidation state of hydrogen in H_2O is a sign that an oxidation has occurred ($2H^- \rightarrow 2H^+ + 4e^-$).

B The balanced chemical equation is

$$\mathrm{CaH_2(s) + TiO_2(s) \overset{\Delta}{\longrightarrow} Ti(s) + CaO(s) + H_2O(l)}$$

We could also write the products as Ti(s) + $Ca(OH)_2(s)$.

? Exercise 18.4.2

Predict the products of each reaction and then balance each chemical equation.

a. $BeCl_2(s) + Mg(s) \xrightarrow{\Delta}$
b. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow$
c. $BeO(s) + OH^-(aq) + H_2O(l) \rightarrow$

Answer

a. $BeCl_2(s) + Mg(s) \xrightarrow{\Delta} Be(s) + MgCl_2(s)$
b. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$
c. $BeO(s) + 2OH^-(aq) + H_2O(l) \rightarrow [Be(OH)_4]^{2-}(aq)$

Summary

Group 2 elements almost exclusively form ionic compounds containing the M^{2+} ion, they are more reactive toward group 15 elements, and they have a greater tendency to form complexes with Lewis bases than do the alkali metals. Pure samples of most of the alkaline earth metals can be obtained by electrolysis of the chlorides or oxides. Beryllium was first obtained by the reduction of its chloride; radium chloride, which is radioactive, was obtained through a series of reactions and separations. In contrast to the alkali metals, the alkaline earth metals generally have little or no affinity for an added electron. All alkaline earth metals react with the halogens to produce the corresponding halides, with oxygen to form the oxide (except for barium, which forms the peroxide), and with the heavier chalcogens to form chalcogenides or polychalcogenide ions. All oxides except BeO react with CO_2 to form carbonates, which in turn react with acid to produce CO_2 and H_2O. Except for Be, all the alkaline earth metals react with N_2 to form nitrides, and all react with carbon and hydrogen to form carbides and hydrides. Alkaline earth metals dissolve in liquid ammonia to give solutions that contain two solvated electrons per metal atom. The alkaline earth metals have a greater tendency than the alkali metals to form complexes with crown ethers, cryptands, and other Lewis bases. The most important alkaline earth organometallic compounds are Grignard reagents (RMgX), which are used to synthesize organic compounds.

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18.5: Group 3A Elements

Learning Objectives

- To understand the trends in properties and the reactivity of the group 13 elements.

Group 13 is the first group to span the dividing line between metals and nonmetals, so its chemistry is more diverse than that of groups 1 and 2, which include only metallic elements. Except for the lightest element (boron), the group 13 elements are all relatively electropositive; that is, they tend to lose electrons in chemical reactions rather than gain them. Although group 13 includes aluminum, the most abundant metal on Earth, none of these elements was known until the early 19th century because they are never found in nature in their free state. Elemental boron and aluminum, which were first prepared by reducing B_2O_3 and $AlCl_3$, respectively, with potassium, could not be prepared until potassium had been isolated and shown to be a potent reductant. Indium (In) and thallium (Tl) were discovered in the 1860s by using spectroscopic techniques, long before methods were available for isolating them. Indium, named for its indigo (deep blue-violet) emission line, was first observed in the spectrum of zinc ores, while thallium (from the Greek thallos, meaning "a young, green shoot of a plant") was named for its brilliant green emission line. Gallium (Ga; Mendeleev's eka-aluminum) was discovered in 1875 by the French chemist Paul Émile Lecoq de Boisbaudran during a systematic search for Mendeleev's "missing" element in group 13.

> *Group 13 elements are never found in nature in their free state.*

Preparation and General Properties of the Group 13 Elements

As reductants, the group 13 elements are less powerful than the alkali metals and alkaline earth metals. Nevertheless, their compounds with oxygen are thermodynamically stable, and large amounts of energy are needed to isolate even the two most accessible elements—boron and aluminum—from their oxide ores.

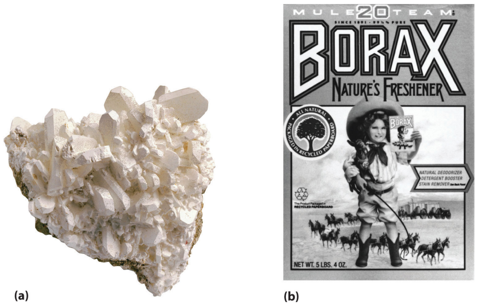


Figure 18.5.1: Borax Deposits. *(a) Concentrated deposits of crystalline borax [$Na_2B_4O_5(OH)_4{\cdot}8H_2O$] are found in ancient lake beds, such as the Mojave Desert and Death Valley in the western United States. (b) Borax is used in various cleaning products, including 20 Mule Team Borax, a laundry detergent named for the teams of 20 mules that hauled wagons full of borax from desert deposits to railroad terminals in the 1880s.*

Although boron is relatively rare (it is about 10,000 times less abundant than aluminum), concentrated deposits of borax [$Na_2B_4O_5(OH)_4{\cdot}8H_2O$] are found in ancient lake beds (Figure 18.5.1) and were used in ancient times for making glass and glazing pottery. Boron is produced on a large scale by reacting borax with acid to produce boric acid [$B(OH)_3$], which is then dehydrated to the oxide (B_2O_3). Reduction of the oxide with magnesium or sodium gives amorphous boron that is only about 95% pure:

$$\mathrm{Na_2B_4O_5(OH)_4\cdot 8H_2O(s) \xrightarrow{acid} B(OH)_3(s) \xrightarrow{\Delta} B_2O_3(s)} \tag{18.5.1}$$

$$\mathrm{B_2O_3(s) + 3Mg(s) \xrightarrow{\Delta} 2B(s) + 3MgO(s)} \tag{18.5.2}$$

Pure, crystalline boron, however, is extremely difficult to obtain because of its high melting point (2300°C) and the highly corrosive nature of liquid boron. It is usually prepared by reducing pure BCl_3 with hydrogen gas at high temperatures or by the thermal decomposition of boron hydrides such as diborane (B_2H_6):

$$\mathrm{BCl_3(g) + \frac{3}{2}H_2(g) \rightarrow B(s) + 3HCl(g)} \tag{18.5.3}$$

$$B_2H_{6(g)} \rightarrow 2B_{(s)} + 3H_{2(g)} \tag{18.5.4}$$

The reaction shown in Equation 18.5.3 is used to prepare boron fibers, which are stiff and light. Hence they are used as structural reinforcing materials in objects as diverse as the US space shuttle and the frames of lightweight bicycles that are used in races such as the Tour de France. Boron is also an important component of many ceramics and heat-resistant borosilicate glasses, such as Pyrex, which is used for ovenware and laboratory glassware.

In contrast to boron, deposits of aluminum ores such as bauxite, a hydrated form of Al_2O_3, are abundant. With an electrical conductivity about twice that of copper on a weight for weight basis, aluminum is used in more than 90% of the overhead electric power lines in the United States. However, because aluminum–oxygen compounds are stable, obtaining aluminum metal from bauxite is an expensive process. Aluminum is extracted from oxide ores by treatment with a strong base, which produces the soluble hydroxide complex $[Al(OH)_4]^-$. Neutralization of the resulting solution with gaseous CO_2 results in the precipitation of $Al(OH)_3$:

$$2[Al(OH)_4]^-_{(aq)} + CO_{2(g)} \rightarrow 2Al(OH)_{3(s)} + CO^{2-}_{3(aq)} + H_2O_{(l)} \tag{18.5.5}$$

Thermal dehydration of $Al(OH)_3$ produces Al_2O_3, and metallic aluminum is obtained by the electrolytic reduction of Al_2O_3 using the **Hall–Heroult process**. Of the group 13 elements, only aluminum is used on a large scale: for example, each Boeing 777 airplane is about 50% aluminum by mass.

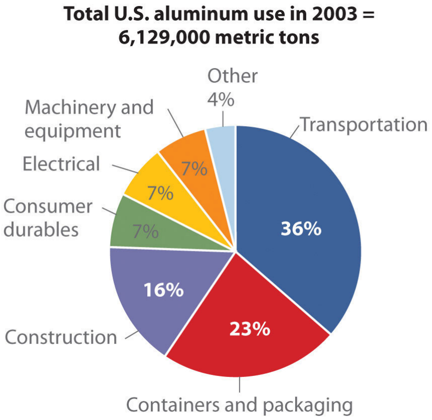


Figure 18.5.2: Source: Thomas D. Kelly and Grecia R. Matos, “Historical Statistics for Mineral and Material Commodities in the United States,” US Geological Survey Data Series 140, 2010, accessed July 20, 2011, pubs.usgs.gov/ds/2005/140/.

The other members of group 13 are rather rare: gallium is approximately 5000 times less abundant than aluminum, and indium and thallium are even scarcer. Consequently, these metals are usually obtained as by-products in the processing of other metals. The extremely low melting point of gallium (29.6°C), however, makes it easy to separate from aluminum. Due to its low melting point and high boiling point, gallium is used as a liquid in thermometers that have a temperature range of almost 2200°C. Indium and thallium, the heavier group 13 elements, are found as trace impurities in sulfide ores of zinc and lead. Indium is used as a crushable seal for high-vacuum cryogenic devices, and its alloys are used as low-melting solders in electronic circuit boards. Thallium, on the other hand, is so toxic that the metal and its compounds have few uses. Both indium and thallium oxides are released in flue dust when sulfide ores are converted to metal oxides and SO_2. Until relatively recently, these and other toxic elements were allowed to disperse in the air, creating large “dead zones” downwind of a smelter. The flue dusts are now trapped and serve as a relatively rich source of elements such as In and Tl (as well as Ge, Cd, Te, and As).

Table 18.5.1 summarizes some important properties of the group 13 elements. Notice the large differences between boron and aluminum in size, ionization energy, electronegativity, and standard reduction potential, which is consistent with the observation that boron behaves chemically like a nonmetal and aluminum like a metal. All group 13 elements have ns^2np^1 valence electron configurations, and all tend to lose their three valence electrons to form compounds in the +3 oxidation state. The heavier elements in the group can also form compounds in the +1 oxidation state formed by the formal loss of the single np valence electron. Because the group 13 elements generally contain only six valence electrons in their neutral compounds, these compounds are all moderately strong Lewis acids.

Table 18.5.1: Selected Properties of the Group 13 Elements

Property	Boron	Aluminum*	Gallium	Indium	Thallium

Property	Boron	Aluminum*	Gallium	Indium	Thallium
atomic symbol	B	Al	Ga	In	Tl
atomic number	5	13	31	49	81
atomic mass (amu)	10.81	26.98	69.72	114.82	204.38
valence electron configuration[†]	$2s^22p^1$	$3s^23p^1$	$4s^24p^1$	$5s^25p^1$	$6s^26p^1$
melting point/boiling point (°C)	2075/4000	660/2519	29.7/2204	156.6/2072	304/1473
density (g/cm^3) at 25°C	2.34	2.70	5.91	7.31	11.8
atomic radius (pm)	87	118	136	156	156
first ionization energy (kJ/mol)	801	578	579	558	589
most common oxidation state	+3	+3	+3	+3	+1
ionic radius (pm)[‡]	−25	54	62	80	162
electron affinity (kJ/mol)	−27	−42	−40	−39	−37
electronegativity	2.0	1.6	1.8	1.8	1.8
standard reduction potential (E°, V)	−0.87	−1.66	−0.55	−0.34	+0.741 of $M^{3+}(aq)$
product of reaction with O_2	B_2O_3	Al_2O_3	Ga_2O_3	In_2O_3	Tl_2O
type of oxide	acidic	amphoteric	amphoteric	amphoteric	basic
product of reaction with N_2	BN	AlN	GaN	InN	none
product of reaction with X_2[§]	BX_3	Al_2X_6	Ga_2X_6	In_2X_6	TlX

*This is the name used in the United States; the rest of the world inserts an extra i and calls it aluminium.

[†] The configuration shown does not include filled d and f subshells.

[‡] The values cited are for six-coordinate ions in the most common oxidation state, except for Al^{3+}, for which the value for the four-coordinate ion is given. The B^{3+} ion is not a known species; the radius cited is an estimated four-coordinate value.

[§] X is Cl, Br, or I. Reaction with F_2 gives the trifluorides (MF_3) for all group 13 elements.

> *Neutral compounds of the group 13 elements are electron deficient, so they are generally moderately strong Lewis acids.*

In contrast to groups 1 and 2, the group 13 elements show no consistent trends in ionization energies, electron affinities, and reduction potentials, whereas electronegativities actually increase from aluminum to thallium. Some of these anomalies, especially for the series Ga, In, Tl, can be explained by the increase in the effective nuclear charge (Z_{eff}) that results from poor shielding of the nuclear charge by the filled $(n − 1)d^{10}$ and $(n − 2)f^{14}$ subshells. Consequently, although the actual nuclear charge increases by

32 as we go from indium to thallium, screening by the filled 5d and 4f subshells is so poor that Z_{eff} increases significantly from indium to thallium. Thus the first ionization energy of thallium is actually greater than that of indium.

> *Anomalies in periodic trends among Ga, In, and Tl can be explained by the increase in the effective nuclear charge due to poor shielding.*

Reactions and Compounds of Boron

Elemental boron is a semimetal that is remarkably unreactive; in contrast, the other group 13 elements all exhibit metallic properties and reactivity. We therefore consider the reactions and compounds of boron separately from those of other elements in the group. All group 13 elements have fewer valence electrons than valence orbitals, which generally results in delocalized, metallic bonding. With its high ionization energy, low electron affinity, low electronegativity, and small size, however, boron does not form a metallic lattice with delocalized valence electrons. Instead, boron forms unique and intricate structures that contain multicenter bonds, in which a pair of electrons holds together three or more atoms.

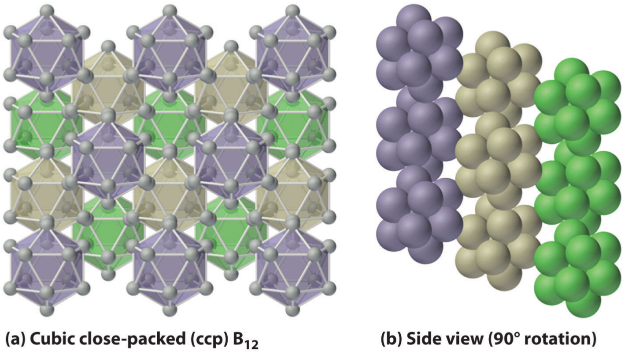


Figure 18.5.3: Solid Boron Contains B_{12} Icosahedra. Unlike metallic solids, elemental boron consists of a regular array of B_{12} icosahedra rather than individual boron atoms. Note that each boron atom in the B_{12} icosahedron is connected to five other boron atoms within the B_{12} unit. (a) The allotrope of boron with the simplest structure is α-rhombohedral boron, which consists of B_{12} octahedra in an almost cubic close-packed lattice. (b) A side view of the structure shows that icosahedra do not pack as efficiently as spheres, making the density of solid boron less than expected.

> *Elemental boron forms multicenter bonds, whereas the other group 13 elements exhibit metallic bonding.*

The basic building block of elemental boron is not the individual boron atom, as would be the case in a metal, but rather the B_{12} icosahedron. Because these icosahedra do not pack together very well, the structure of solid boron contains voids, resulting in its low density (Figure 18.5.3). Elemental boron can be induced to react with many nonmetallic elements to give binary compounds that have a variety of applications. For example, plates of boron carbide (B_4C) can stop a 30-caliber, armor-piercing bullet, yet they weigh 10%–30% less than conventional armor. Other important compounds of boron with nonmetals include boron nitride (BN), which is produced by heating boron with excess nitrogen (Equation 18.5.6); boron oxide (B_2O_3), which is formed when boron is heated with excess oxygen (Equation 18.5.7); and the boron trihalides (BX_3), which are formed by heating boron with excess halogen (Equation 18.5.8).

$$2B(s) + N_2(g) \xrightarrow{\Delta} 2BN(s) \tag{18.5.6}$$

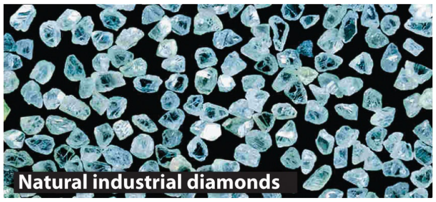
$$4B(s) + 3O_2(g) \xrightarrow{\Delta} 2B_2O_3(s) \tag{18.5.7}$$

$$2B(s) + 3X_2(g) \xrightarrow{\Delta} 2BX_3(g) \tag{18.5.8}$$

As is typical of elements lying near the dividing line between metals and nonmetals, many compounds of boron are amphoteric, dissolving in either acid or base.

Boron nitride is similar in many ways to elemental carbon. With eight electrons, the B–N unit is isoelectronic with the C–C unit, and B and N have the same average size and electronegativity as C. The most stable form of BN is similar to graphite, containing six-membered B_3N_3 rings arranged in layers. At high temperature and pressure, hexagonal BN converts to a cubic structure similar to diamond, which is one of the hardest substances known. Boron oxide (B_2O_3) contains layers of trigonal planar BO_3 groups (analogous to BX_3) in which the oxygen atoms bridge two boron atoms. It dissolves many metal and nonmetal oxides, including

SiO_2, to give a wide range of commercially important borosilicate glasses. A small amount of CoO gives the deep blue color characteristic of “cobalt blue” glass.



At high temperatures, boron also reacts with virtually all metals to give metal borides that contain regular three-dimensional networks, or clusters, of boron atoms. The structures of two metal borides—ScB_{12} and CaB_6—are shown in Figure 18.5.4. Because metal-rich borides such as ZrB_2 and TiB_2 are hard and corrosion resistant even at high temperatures, they are used in applications such as turbine blades and rocket nozzles.

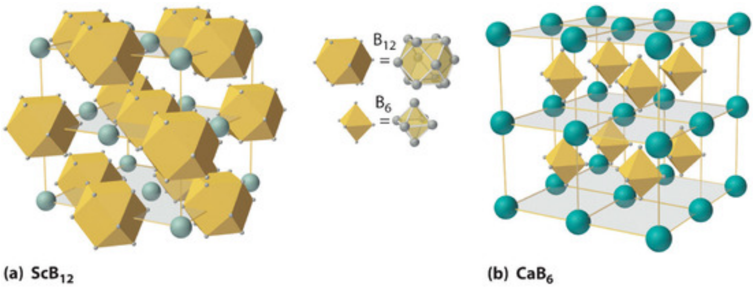


Figure 18.5.4: The Structures of $ScB_{12}$and CaB_6, Two Boron-Rich Metal Borides. *(a) The structure of ScB_{12} consists of B_{12} clusters and Sc atoms arranged in a faced-centered cubic lattice similar to that of NaCl, with B_{12}units occupying the anion positions and scandium atoms the cation positions. The B12 units here are not icosahedra but cubooctahedra, with alternating square and triangular faces. (b) The structure of CaB_6 consists of octahedral B_6 clusters and calcium atoms arranged in a body-centered cubic lattice similar to that of CsCl, with B_6 units occupying the anion positions and calcium atoms the cation positions.*

Boron hydrides were not discovered until the early 20th century, when the German chemist Alfred Stock undertook a systematic investigation of the binary compounds of boron and hydrogen, although binary hydrides of carbon, nitrogen, oxygen, and fluorine have been known since the 18th century. Between 1912 and 1936, Stock oversaw the preparation of a series of boron–hydrogen compounds with unprecedented structures that could not be explained with simple bonding theories. All these compounds contain multicenter bonds. The simplest example is diborane (B_2H_6), which contains two bridging hydrogen atoms (part (a) in Figure 18.5.5. An extraordinary variety of polyhedral boron–hydrogen clusters is now known; one example is the $B_{12}H_{12}{}^{2-}$ ion, which has a polyhedral structure similar to the icosahedral B_{12} unit of elemental boron, with a single hydrogen atom bonded to each boron atom.

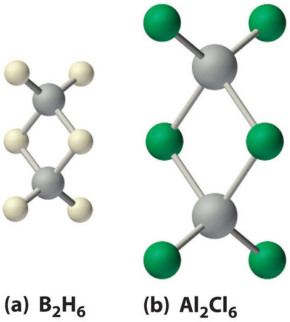
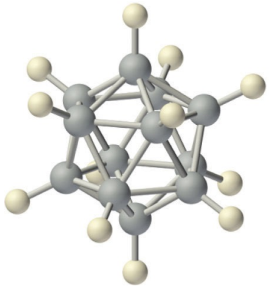
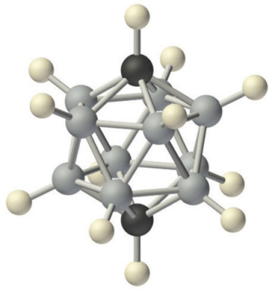


Figure 18.5.5: The Structures of Diborane (B_2H_6) and Aluminum Chloride (Al_2Cl_6). (a) The hydrogen-bridged dimer B_2H_6 contains two three-center, two-electron bonds as described for the $B_2H_7{}^-$ ion in Figure 21.5. (b) In contrast, the bonding in the halogen-bridged dimer Al_2Cl_6 can be described in terms of electron-pair bonds, in which a chlorine atom bonded to one aluminum atom acts as a Lewis base by donating a lone pair of electrons to another aluminum atom, which acts as a Lewis acid.

A related class of polyhedral clusters, the carboranes, contain both CH and BH units; an example is shown here. Replacing the hydrogen atoms bonded to carbon with organic groups produces substances with novel properties, some of which are currently being investigated for their use as liquid crystals and in cancer chemotherapy.



$B_{12}H_{12}^{2-}$



$B_{10}C_2H_{12}$

The enthalpy of combustion of diborane (B_2H_6) is −2165 kJ/mol, one of the highest values known:

$$B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(s)} + 3H_2O(l) \qquad \Delta H_{comb} = -2165\ kJ/mol \tag{18.5.9}$$

Consequently, the US military explored using boron hydrides as rocket fuels in the 1950s and 1960s. This effort was eventually abandoned because boron hydrides are unstable, costly, and toxic, and, most important, B_2O_3 proved to be highly abrasive to rocket nozzles. Reactions carried out during this investigation, however, showed that boron hydrides exhibit unusual reactivity.

Because boron and hydrogen have almost identical electronegativities, the reactions of boron hydrides are dictated by minor differences in the distribution of electron density in a given compound. In general, two distinct types of reaction are observed: electron-rich species such as the BH_4^- ion are reductants, whereas electron-deficient species such as B_2H_6 act as oxidants.

✓ Example 18.5.1

For each reaction, explain why the given products form.

a. $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(l)$
b. $BCl_3(l) + 3H_2O(l) \rightarrow B(OH)_3(aq) + 3HCl(aq)$
c. $2BI_3(s) + 3H_2(g) \xrightarrow{\Delta} \frac{1}{6}B_{12}(s) + 6HI(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution

a. Molecular oxygen is an oxidant. If the other reactant is a potential reductant, we expect that a redox reaction will occur. Although B_2H_6 contains boron in its highest oxidation state (+3), it also contains hydrogen in the −1 oxidation state (the hydride ion). Because hydride is a strong reductant, a redox reaction will probably occur. We expect that H^- will be oxidized to H^+ and O_2 will be reduced to O^{2-}, but what are the actual products? A reasonable guess is B_2O_3 and H_2O, both stable compounds.
b. Neither BCl_3 nor water is a powerful oxidant or reductant, so a redox reaction is unlikely; a hydrolysis reaction is more probable. Nonmetal halides are acidic and react with water to form a solution of the hydrohalic acid and a nonmetal oxide or hydroxide. In this case, the most probable boron-containing product is boric acid [$B(OH)_3$].
c. We normally expect a boron trihalide to behave like a Lewis acid. In this case, however, the other reactant is elemental hydrogen, which usually acts as a reductant. The iodine atoms in BI_3 are in the lowest accessible oxidation state (−1), and boron is in the +3 oxidation state. Consequently, we can write a redox reaction in which hydrogen is oxidized and boron is reduced. Because compounds of boron in lower oxidation states are rare, we expect that boron will be reduced to elemental boron. The other product of the reaction must therefore be HI.

Exercise 18.5.1

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $B_2H_6(g) + H_2O(l) \xrightarrow{\Delta}$
b. $BBr_3(l) + O_2(g) \rightarrow$
c. $B_2O_3(s) + Ca(s) \xrightarrow{\Delta}$

Answer

a. $B_2H_6(g) + H_2O(l) \xrightarrow{\Delta} 2B(OH)_3(s) + 6H_2(g)$
b. $BBr_3(l) + O_2(g) \rightarrow$ no reaction
c. $6B_2O_3(s) + 18Ca(s) \xrightarrow{\Delta} B_{12}(s) + 18CaO(s)$

Reactions and Compounds of the Heavier Group 13 Elements

All four of the heavier group 13 elements (Al, Ga, In, and Tl) react readily with the halogens to form compounds with a 1:3 stoichiometry:

$$2M_{(s)} + 3X_{2(s,l,g)} \rightarrow 2MX_{3(s)} \text{ or } M_2X_6 \tag{18.5.10}$$

The reaction of Tl with iodine is an exception: although the product has the stoichiometry TlI_3, it is not thallium(III) iodide, but rather a thallium(I) compound, the Tl^+ salt of the triiodide ion (I_3^-). This compound forms because iodine is not a powerful enough oxidant to oxidize thallium to the +3 oxidation state.

Of the halides, only the fluorides exhibit behavior typical of an ionic compound: they have high melting points (>950°C) and low solubility in nonpolar solvents. In contrast, the trichorides, tribromides, and triiodides of aluminum, gallium, and indium, as well as $TlCl_3$ and $TlBr_3$, are more covalent in character and form halogen-bridged dimers (part (b) in Figure 18.5.4). Although the structure of these dimers is similar to that of diborane (B_2H_6), the bonding can be described in terms of electron-pair bonds rather than the delocalized electron-deficient bonding found in diborane. Bridging halides are poor electron-pair donors, so the group 13 trihalides are potent Lewis acids that react readily with Lewis bases, such as amines, to form a Lewis acid–base adduct:

$$Al_2Cl_{6(soln)} + 2(CH_3)_3N_{(soln)} \rightarrow 2(CH_3)_3N : AlCl_{3(soln)} \tag{18.5.11}$$

In water, the halides of the group 13 metals hydrolyze to produce the metal hydroxide (\[M(OH)_3\)):

$$MX_{3(s)} + 3H_2O_{(l)} \rightarrow M(OH)_{3(s)} + 3HX_{(aq)} \tag{18.5.12}$$

In a related reaction, $Al_2(SO_4)_3$ is used to clarify drinking water by the precipitation of hydrated $Al(OH)_3$, which traps particulates. The halides of the heavier metals (In and Tl) are less reactive with water because of their lower charge-to-radius ratio. Instead of forming hydroxides, they dissolve to form the hydrated metal complex ions: $[M(H_2O)_6]^{3+}$.

> *Of the group 13 halides, only the fluorides behave as typical ionic compounds.*

Like boron (Equation 18.5.7), all the heavier group 13 elements react with excess oxygen at elevated temperatures to give the trivalent oxide (M_2O_3), although Tl_2O_3 is unstable:

$$4M(s) + 3O_2(g) \xrightarrow{\Delta} 2M_2O_3(s) \tag{18.5.13}$$

Aluminum oxide (Al_2O_3), also known as alumina, is a hard, high-melting-point, chemically inert insulator used as a ceramic and as an abrasive in sandpaper and toothpaste. Replacing a small number of Al^{3+} ions in crystalline alumina with Cr^{3+} ions forms the gemstone ruby, whereas replacing Al^{3+} with a mixture of Fe^{2+}, Fe^{3+}, and Ti^{4+} produces blue sapphires. The gallium oxide compound $MgGa_2O_4$ gives the brilliant green light familiar to anyone who has ever operated a xerographic copy machine. All the oxides dissolve in dilute acid, but Al_2O_3 and Ga_2O_3 are amphoteric, which is consistent with their location along the diagonal line of the periodic table, also dissolving in concentrated aqueous base to form solutions that contain $M(OH)_4^-$ ions.

> *Group 13 trihalides are potent Lewis acids that react with Lewis bases to form a Lewis acid–base adduct.*

Aluminum, gallium, and indium also react with the other group 16 elements (chalcogens) to form chalcogenides with the stoichiometry M_2Y_3. However, because Tl(III) is too strong an oxidant to form a stable compound with electron-rich anions such as S^{2-}, Se^{2-}, and Te^{2-}, thallium forms only the thallium(I) chalcogenides with the stoichiometry Tl_2Y. Only aluminum, like boron, reacts directly with N_2 (at very high temperatures) to give AlN, which is used in transistors and microwave devices as a nontoxic heat sink because of its thermal stability; GaN and InN can be prepared using other methods. All the metals, again except Tl, also react with the heavier group 15 elements (pnicogens) to form the so-called III–V compounds, such as GaAs. These are semiconductors, whose electronic properties, such as their band gaps, differ from those that can be achieved using either pure or doped group 14 elements. For example, nitrogen- and phosphorus-doped gallium arsenide ($GaAs_{1-x-y}P_xN_y$) is used in the displays of calculators and digital watches.

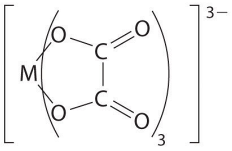
> *All group 13 oxides dissolve in dilute acid, but Al_2O_3 and Ga_2O_3 are amphoteric.*

Unlike boron, the heavier group 13 elements do not react directly with hydrogen. Only the aluminum and gallium hydrides are known, but they must be prepared indirectly; AlH_3 is an insoluble, polymeric solid that is rapidly decomposed by water, whereas GaH_3 is unstable at room temperature.

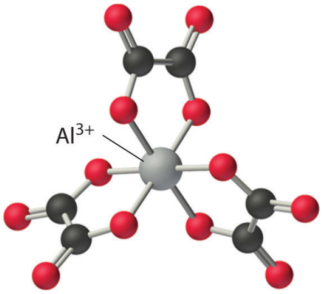
Complexes of Group 13 Elements

Boron has a relatively limited tendency to form complexes, but aluminum, gallium, indium, and, to some extent, thallium form many complexes. Some of the simplest are the hydrated metal ions [$M(H_2O)_6{}^{3+}$], which are relatively strong Brønsted–Lowry acids that can lose a proton to form the $M(H_2O)_5(OH)^{2+}$ ion:

$$[M(H_2O)_6]^{3+}_{(aq)} \rightarrow M(H_2O)_5(OH)^{2+}_{(aq)} + H^+_{(aq)} \tag{18.5.14}$$



Oxalate ion



Al^{3+}–oxalate complex

Group 13 metal ions also form stable complexes with species that contain two or more negatively charged groups, such as the oxalate ion. The stability of such complexes increases as the number of coordinating groups provided by the ligand increases.

✓ Example 18.5.2

For each reaction, explain why the given products form.

a. $2Al(s) + Fe_2O_3(s) \xrightarrow{\Delta} 2Fe(l) + Al_2O_3(s)$

b. $2Ga(s) + 6H_2O(l) + 2OH^-(aq) \xrightarrow{\Delta} 3H_2(g) + 2Ga(OH)_4^-(aq)$

c. $In_2Cl_6(s) \xrightarrow{H_2O(l)} 2In^{3+}(aq) + 6Cl^-(aq)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution

a. Aluminum is an active metal and a powerful reductant, and Fe_2O_3 contains Fe(III), a potential oxidant. Hence a redox reaction is probable, producing metallic Fe and Al_2O_3. Because Al is a main group element that lies above Fe, which is a transition element, it should be a more active metal than Fe. Thus the reaction should proceed to the right. In fact, this is the thermite reaction, which is so vigorous that it produces molten Fe and can be used for welding.
b. Gallium lies immediately below aluminum in the periodic table and is amphoteric, so it will dissolve in either acid or base to produce hydrogen gas. Because gallium is similar to aluminum in many of its properties, we predict that gallium will dissolve in the strong base.
c. The metallic character of the group 13 elements increases with increasing atomic number. Indium trichloride should therefore behave like a typical metal halide, dissolving in water to form the hydrated cation.

? Exercise 18.5.2

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $LiH(s) + Al_2Cl_6(soln) \rightarrow$
b. $Al_2O_3(s) + OH^-(aq) \rightarrow$
c. $Al(s) + N_2(g) \xrightarrow{\Delta}$
d. $Ga_2Cl_6(soln) + Cl^-(soln) \rightarrow$

Answer

a. $8LiH(s) + Al_2Cl_6(soln) \rightarrow 2LiAlH_4(soln) + 6LiCl(s)$
b. $Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4{}^-(aq)$
c. $2Al(s) + N_2(g) \xrightarrow{\Delta} 2AlN(s)$
d. $Ga_2Cl_6(soln) + 2Cl^-(soln) \rightarrow 2GaCl_4{}^-(soln)$

Summary

Compounds of the group 13 elements with oxygen are thermodynamically stable. Many of the anomalous properties of the group 13 elements can be explained by the increase in Z_{eff} moving down the group. Isolation of the group 13 elements requires a large amount of energy because compounds of the group 13 elements with oxygen are thermodynamically stable. Boron behaves chemically like a nonmetal, whereas its heavier congeners exhibit metallic behavior. Many of the inconsistencies observed in the properties of the group 13 elements can be explained by the increase in Z_{eff} that arises from poor shielding of the nuclear charge by the filled $(n - 1)d^{10}$ and $(n - 2)f^{14}$ subshells. Instead of forming a metallic lattice with delocalized valence electrons, boron forms unique aggregates that contain multicenter bonds, including metal borides, in which boron is bonded to other boron atoms to form three-dimensional networks or clusters with regular geometric structures. All neutral compounds of the group 13 elements are electron deficient and behave like Lewis acids. The trivalent halides of the heavier elements form halogen-bridged dimers that contain electron-pair bonds, rather than the delocalized electron-deficient bonds characteristic of diborane. Their oxides dissolve in dilute acid, although the oxides of aluminum and gallium are amphoteric. None of the group 13 elements reacts directly with hydrogen, and the stability of the hydrides prepared by other routes decreases as we go down the group. In contrast to boron, the heavier group 13 elements form a large number of complexes in the +3 oxidation state.

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18.6: Group 4A Elements

Learning Objectives

- To understand the trends in properties and reactivity of the group 14 elements.

The elements of group 14 show a greater range of chemical behavior than any other family in the periodic table. Three of the five elements—carbon, tin, and lead—have been known since ancient times. For example, some of the oldest known writings are Egyptian hieroglyphics written on papyrus with ink made from lampblack, a finely divided carbon soot produced by the incomplete combustion of hydrocarbons (Figure 18.6.1). Activated carbon is an even more finely divided form of carbon that is produced from the thermal decomposition of organic materials, such as sawdust. Because it adsorbs many organic and sulfur-containing compounds, activated carbon is used to decolorize foods, such as sugar, and to purify gases and wastewater.

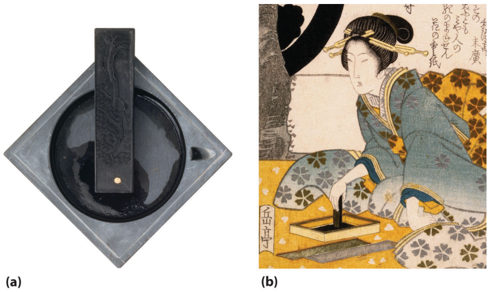


Figure 18.6.1: Very Small Particles of Noncrystalline Carbon Are Used to Make Black Ink. *(a) Since ancient times, ink sticks have been the major source of black ink in Asia. Plant oils or resinous woods such as pine are burned, and the resulting soot (lampblack) is collected, mixed with binders such as animal glues and minerals, compressed into a solid stick, and allowed to dry. Liquid ink is made by rubbing the ink stick against the surface of a special stone ink dish with small amounts of water. (b) A 19th-century Japanese painting illustrates how ink is made from an ink stick.*

Tin and lead oxides and sulfides are easily reduced to the metal by heating with charcoal, a discovery that must have occurred by accident when prehistoric humans used rocks containing their ores for a cooking fire. However, because tin and copper ores are often found together in nature, their alloy—bronze—was probably discovered before either element, a discovery that led to the Bronze Age. The heaviest element in group 14, lead, is such a soft and malleable metal that the ancient Romans used thin lead foils as writing tablets, as well as lead cookware and lead pipes for plumbing. (Recall that the atomic symbols for tin and lead come from their Latin names: Sn for stannum and Pb for plumbum.)

Although the first glasses were prepared from silica (silicon oxide, SiO_2) around 1500 BC, elemental silicon was not prepared until 1824 because of its high affinity for oxygen. Jöns Jakob Berzelius was finally able to obtain amorphous silicon by reducing Na_2SiF_6 with molten potassium. The crystalline element, which has a shiny blue-gray luster, was not isolated until 30 yr later. The last member of the group 14 elements to be discovered was germanium, which was found in 1886 in a newly discovered silver-colored ore by the German chemist Clemens Winkler, who named the element in honor of his native country.

Preparation and General Properties of the Group 14 Elements

The natural abundance of the group 14 elements varies tremendously. Elemental carbon, for example, ranks only 17th on the list of constituents of Earth’s crust. Pure graphite is obtained by reacting coke, an amorphous form of carbon used as a reductant in the production of steel, with silica to give silicon carbide (SiC). This is then thermally decomposed at very high temperatures (2700°C) to give graphite:

$$\mathrm{SiO_2(s) + 3C(s) \xrightarrow{\Delta} SiC(s) + 2CO(g)} \tag{18.6.1}$$

$$\mathrm{SiC(s) \xrightarrow{\Delta} Si(s) + C(graphite)} \tag{18.6.2}$$

One allotrope of carbon, diamond, is metastable under normal conditions, with a $\Delta G°_f$ of 2.9 kJ/mol versus graphite. At pressures greater than 50,000 atm, however, the diamond structure is favored and is the most stable form of carbon. Because the structure of diamond is more compact than that of graphite, its density is significantly higher (3.51 g/cm^3 versus 2.2 g/cm^3). Because of its high thermal conductivity, diamond powder is used to transfer heat in electronic devices.

The most common sources of diamonds on Earth are ancient volcanic pipes that contain a rock called kimberlite, a lava that solidified rapidly from deep inside the Earth. Most kimberlite formations, however, are much newer than the diamonds they contain. In fact, the relative amounts of different carbon isotopes in diamond show that diamond is a chemical and geological "fossil" older than our solar system, which means that diamonds on Earth predate the existence of our sun. Thus diamonds were most likely created deep inside Earth from primordial grains of graphite present when Earth was formed (part (a) in Figure $18.6.2$). Gem-quality diamonds can now be produced synthetically and have chemical, optical, and physical characteristics identical to those of the highest-grade natural diamonds.

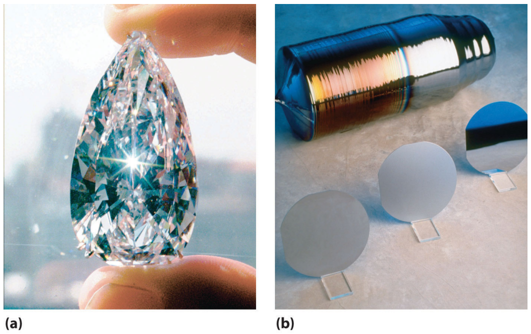


Figure 18.6.2: Crystalline Samples of Carbon and Silicon, the Lightest Group 14 Elements. (a) The 78.86-carat Ahmadabad diamond, a historic Indian gem purchased in Gujarat in the 17th century by the French explorer Jean-Baptiste Tavernier and sold in 1995 for $4.3 million, is a rare example of a large single crystal of diamond, the less-stable allotrope of carbon. (b) Large single crystals of highly purified silicon are the basis of the modern electronics industry. They are sliced into very thin wafers that are highly polished and then cut into smaller pieces for use as chips.

Although oxygen is the most abundant element on Earth, the next most abundant is silicon, the next member of group 14. Pure silicon is obtained by reacting impure silicon with Cl_2 to give $SiCl_4$, followed by the fractional distillation of the impure $SiCl_4$ and reduction with H_2:

$$\mathrm{SiCl_4(l) + 2H_2(g) \xrightarrow{\Delta} Si(s) + 4HCl(g)} \tag{18.6.3}$$

Several million tons of silicon are annually produced with this method. Amorphous silicon containing residual amounts of hydrogen is used in photovoltaic devices that convert light to electricity, and silicon-based solar cells are used to power pocket calculators, boats, and highway signs, where access to electricity by conventional methods is difficult or expensive. Ultrapure silicon and germanium form the basis of the modern electronics industry (part (b) in Figure $18.6.2$).

In contrast to silicon, the concentrations of germanium and tin in Earth's crust are only 1–2 ppm. The concentration of lead, which is the end product of the nuclear decay of many radionuclides, is 13 ppm, making lead by far the most abundant of the heavy group 14 elements. No concentrated ores of germanium are known; like indium, germanium is generally recovered from flue dusts obtained by processing the ores of metals such as zinc. Because germanium is essentially transparent to infrared radiation, it is used in optical devices.

Tin and lead are soft metals that are too weak for structural applications, but because tin is flexible, corrosion resistant, and nontoxic, it is used as a coating in food packaging. A "tin can," for example, is actually a steel can whose interior is coated with a thin layer (1–2 µm) of metallic tin. Tin is also used in superconducting magnets and low-melting-point alloys such as solder and pewter. Pure lead is obtained by heating galena (PbS) in air and reducing the oxide (PbO) to the metal with carbon, followed by electrolytic deposition to increase the purity:

$$\mathrm{PbS(s) + \frac{3}{2}O_2(g) \xrightarrow{\Delta} PbO(s) + SO_2(g)} \tag{18.6.4}$$

$$\mathrm{PbO(s) + C(s) \xrightarrow{\Delta} Pb(l) + CO(g)} \tag{18.6.5}$$

or

$$\mathrm{PbO(s) + CO(g) \xrightarrow{\Delta} Pb(l) + CO_2(g)} \tag{18.6.6}$$

By far the single largest use of lead is in lead storage batteries. The group 14 elements all have ns^2np^2 valence electron configurations. All form compounds in which they formally lose either the two np and the two ns valence electrons or just the two np valence electrons, giving a +4 or +2 oxidation state, respectively. Because covalent bonds decrease in strength with increasing atomic size and the ionization energies for the heavier elements of the group are higher than expected due to a higher Z_{eff}, the relative stability of the +2 oxidation state increases smoothly from carbon to lead.

> *The relative stability of the +2 oxidation state increases, and the tendency to form catenated compounds decreases, from carbon to lead in group 14.*

Recall that many carbon compounds contain multiple bonds formed by π overlap of singly occupied 2p orbitals on adjacent atoms. Compounds of silicon, germanium, tin, and lead with the same stoichiometry as those of carbon, however, tend to have different structures and properties. For example, CO_2 is a gas that contains discrete O=C=O molecules, whereas the most common form of SiO_2 is the high-melting solid known as quartz, the major component of sand. Instead of discrete SiO_2 molecules, quartz contains a three-dimensional network of silicon atoms that is similar to the structure of diamond but with an oxygen atom inserted between each pair of silicon atoms. Thus each silicon atom is linked to four other silicon atoms by bridging oxygen atoms.

The tendency to catenate—to form chains of like atoms—decreases rapidly as we go down group 14 because bond energies for both the E–E and E–H bonds decrease with increasing atomic number (where E is any group 14 element). Consequently, inserting a CH_2 group into a linear hydrocarbon such as n-hexane is exergonic ($\Delta G° = -45$ kJ/mol), whereas inserting an SiH_2 group into the silicon analogue of n-hexane (Si_6H_{14}) actually costs energy ($\Delta G° \approx +25$ kJ/mol). As a result of this trend, the thermal stability of catenated compounds decreases rapidly from carbon to lead.

In Table 18.6.1 "Selected Properties of the Group 14 Elements" we see, once again, that there is a large difference between the lightest element (C) and the others in size, ionization energy, and electronegativity. As in group 13, the second and third elements (Si and Ge) are similar, and there is a reversal in the trends for some properties, such as ionization energy, between the fourth and fifth elements (Sn and Pb). As for group 13, these effects can be explained by the presence of filled (n − 1)d and (n − 2)f subshells, whose electrons are relatively poor at screening the outermost electrons from the higher nuclear charge.

Table 18.6.1: Selected Properties of the Group 14 Elements

Property	Carbon	Silicon	Germanium	Tin	Lead
atomic symbol	C	Si	Ge	Sn	Pb
atomic number	6	14	32	50	82
atomic mass (amu)	12.01	28.09	72.64	118.71	207.2
valence electron configuration*	$2s^22p^2$	$3s^23p^2$	$4s^24p^2$	$5s^25p^2$	$6s^26p^2$
melting point/boiling point (°C)	4489 (at 10.3 MPa)/3825	1414/3265	939/2833	232/2602	327/1749
density (g/cm^3) at 25°C	2.2 (graphite), 3.51 (diamond)	2.33	5.32	7.27(white)	11.30
atomic radius (pm)	77 (diamond)	111	125	145	154
first ionization energy (kJ/mol)	1087	787	762	709	716
most common oxidation state	+4	+4	+4	+4	+4
ionic radius (pm)†	≈29	≈40	53	69	77.5

*The configuration shown does not include filled d and f subshells.

†The values cited are for six-coordinate +4 ions in the most common oxidation state, except for C^{4+} and Si^{4+}, for which values for the four-coordinate ion are estimated.

‡X is Cl, Br, or I. Reaction with F_2 gives the tetrafluorides (EF_4) for all group 14 elements, where E represents any group 14 element.

Property	Carbon	Silicon	Germanium	Tin	Lead
electron affinity (kJ/mol)	−122	−134	−119	−107	−35
electronegativity	2.6	1.9	2.0	2.0	1.8
standard reduction potential (E°, V) (for EO_2 → E in acidic solution)	0.21	−0.86	−0.18	−0.12	0.79
product of reaction with O_2	CO_2, CO	SiO_2	GeO_2	SnO_2	PbO
type of oxide	acidic (CO_2)	acidic neutral (CO)	amphoteric	amphoteric	amphoteric
product of reaction with N_2	none	Si_3N_4	none	Sn_3N_4	none
product of reaction with X_2‡	CX_4	SiX_4	GeX_4	SnX_4	PbX_2
product of reaction with H_2	CH_4	none	none	none	none

*The configuration shown does not include filled d and f subshells.

†The values cited are for six-coordinate +4 ions in the most common oxidation state, except for C^{4+} and Si^{4+}, for which values for the four-coordinate ion are estimated.

‡X is Cl, Br, or I. Reaction with F_2 gives the tetrafluorides (EF_4) for all group 14 elements, where E represents any group 14 element.

> The group 14 elements follow the same pattern as the group 13 elements in their periodic properties.

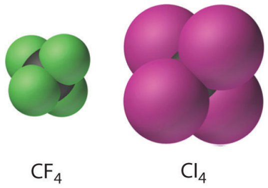
Reactions and Compounds of Carbon

Carbon is the building block of all organic compounds, including biomolecules, fuels, pharmaceuticals, and plastics, whereas inorganic compounds of carbon include metal carbonates, which are found in substances as diverse as fertilizers and antacid tablets, halides, oxides, carbides, and carboranes. Like boron in group 13, the chemistry of carbon differs sufficiently from that of its heavier congeners to merit a separate discussion.

The structures of the allotropes of carbon—diamond, graphite, fullerenes, and nanotubes—are distinct, but they all contain simple electron-pair bonds (Figure 7.18). Although it was originally believed that fullerenes were a new form of carbon that could be prepared only in the laboratory, fullerenes have been found in certain types of meteorites. Another possible allotrope of carbon has also been detected in impact fragments of a carbon-rich meteorite; it appears to consist of long chains of carbon atoms linked by alternating single and triple bonds, $(–C≡C–C≡C–)_n$. Carbon nanotubes ("buckytubes") are being studied as potential building blocks for ultramicroscale detectors and molecular computers and as tethers for space stations. They are currently used in electronic devices, such as the electrically conducting tips of miniature electron guns for flat-panel displays in portable computers.

Although all the carbon tetrahalides (CX_4) are known, they are generally not obtained by the direct reaction of carbon with the elemental halogens (X_2) but by indirect methods such as the following reaction, where X is Cl or Br:

$$CH_{4(g)} + 4X_{2(g)} \rightarrow CX_{4(l,s)} + 4HX_{(g)} \tag{18.6.7}$$



The carbon tetrahalides all have the tetrahedral geometry predicted by the valence-shell electron-pair repulsion (VSEPR) model, as shown for CCl_4 and CI_4. Their stability decreases rapidly as the halogen increases in size because of poor orbital overlap and increased crowding. Because the C–F bond is about 25% stronger than a C–H bond, fluorocarbons are thermally and chemically more stable than the corresponding hydrocarbons, while having a similar hydrophobic character. A polymer of tetrafluoroethylene ($F_2C{=}CF_2$), analogous to polyethylene, is the nonstick Teflon lining found on many cooking pans, and similar compounds are used to make fabrics stain resistant (such as Scotch-Gard) or waterproof but breathable (such as Gore-Tex).

> *The stability of the carbon tetrahalides decreases with increasing size of the halogen due to increasingly poor orbital overlap and crowding.*

Carbon reacts with oxygen to form either CO or CO_2, depending on the stoichiometry. Carbon monoxide is a colorless, odorless, and poisonous gas that reacts with the iron in hemoglobin to form an Fe–CO unit, which prevents hemoglobin from binding, transporting, and releasing oxygen in the blood (see Figure 23.26). In the laboratory, carbon monoxide can be prepared on a small scale by dehydrating formic acid with concentrated sulfuric acid:

$$\mathrm{HCO_2H(l)} \xrightarrow{\mathrm{H_2SO_4(l)}} \mathrm{CO(g)} + \mathrm{H_3O^+(aq)} + \mathrm{HSO_4^-} \tag{18.6.8}$$

Carbon monoxide also reacts with the halogens to form the oxohalides (COX_2). Probably the best known of these is phosgene ($Cl_2C{=}O$), which is highly poisonous and was used as a chemical weapon during World War I:

$$\mathrm{CO(g)} + \mathrm{Cl_2(g)} \xrightarrow{\Delta} \mathrm{Cl_2C{=}O(g)} \tag{18.6.9}$$

Despite its toxicity, phosgene is an important industrial chemical that is prepared on a large scale, primarily in the manufacture of polyurethanes.

Carbon dioxide can be prepared on a small scale by reacting almost any metal carbonate or bicarbonate salt with a strong acid. As is typical of a nonmetal oxide, CO_2 reacts with water to form acidic solutions containing carbonic acid (H_2CO_3). In contrast to its reactions with oxygen, reacting carbon with sulfur at high temperatures produces only carbon disulfide (CS_2):

$$\mathrm{C(s)} + 2\mathrm{S(g)} \xrightarrow{\Delta} \mathrm{CS_2(g)} \tag{18.6.10}$$

The selenium analog CSe_2 is also known. Both have the linear structure predicted by the VSEPR model, and both are vile smelling (and in the case of CSe_2, highly toxic), volatile liquids. The sulfur and selenium analogues of carbon monoxide, CS and CSe, are unstable because the C≡Y bonds (Y is S or Se) are much weaker than the C≡O bond due to poorer π orbital overlap.

> *π bonds between carbon and the heavier chalcogenides are weak due to poor orbital overlap.*

Binary compounds of carbon with less electronegative elements are called carbides. The chemical and physical properties of carbides depend strongly on the identity of the second element, resulting in three general classes: ionic carbides, interstitial carbides, and covalent carbides. The reaction of carbon at high temperatures with electropositive metals such as those of groups 1 and 2 and aluminum produces ionic carbides, which contain discrete metal cations and carbon anions. The identity of the anions depends on the size of the second element. For example, smaller elements such as beryllium and aluminum give methides such as Be_2C and Al_4C_3, which formally contain the C^{4-} ion derived from methane (CH_4) by losing all four H atoms as protons. In contrast, larger metals such as sodium and calcium give carbides with stoichiometries of Na_2C_2 and CaC_2. Because these carbides contain the C^{4-} ion, which is derived from acetylene (HC≡CH) by losing both H atoms as protons, they are more properly called acetylides. Reacting ionic carbides with dilute aqueous acid results in protonation of the anions to give the parent hydrocarbons: CH_4 or C_2H_2. For many years, miners’ lamps used the reaction of calcium carbide with water to produce a steady supply of acetylene, which was ignited to provide a portable lantern.

19th-century miner's lamp. The lamp uses burning acetylene, produced by the slow reaction of calcium carbide with water, to provide light.

The reaction of carbon with most transition metals at high temperatures produces interstitial carbides. Due to the less electropositive nature of the transition metals, these carbides contain covalent metal–carbon interactions, which result in different properties: most interstitial carbides are good conductors of electricity, have high melting points, and are among the hardest substances known. Interstitial carbides exhibit a variety of nominal compositions, and they are often nonstoichiometric compounds whose carbon content can vary over a wide range. Among the most important are tungsten carbide (WC), which is used industrially in high-speed cutting tools, and cementite (Fe_3C), which is a major component of steel.

Elements with an electronegativity similar to that of carbon form covalent carbides, such as silicon carbide (SiC; Equation ???) and boron carbide (B_4C). These substances are extremely hard, have high melting points, and are chemically inert. For example, silicon carbide is highly resistant to chemical attack at temperatures as high as 1600°C. Because it also maintains its strength at high temperatures, silicon carbide is used in heating elements for electric furnaces and in variable-temperature resistors.

> *Carbides formed from group 1 and 2 elements are ionic. Transition metals form interstitial carbides with covalent metal–carbon interactions, and covalent carbides are chemically inert.*

✓ Example 18.6.1

For each reaction, explain why the given product forms.

a. $CO(g) + Cl_2(g) \rightarrow Cl_2C{=}O(g)$
b. $CO(g) + BF_3(g) \rightarrow F_3B{:}C{\equiv}O(g)$
c. $Sr(s) + 2C(s) \xrightarrow{\Delta} SrC_2(s)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. Because the carbon in CO is in an intermediate oxidation state (+2), CO can be either a reductant or an oxidant; it is also a Lewis base. The other reactant (Cl_2) is an oxidant, so we expect a redox reaction to occur in which the carbon of CO is further oxidized. Because Cl_2 is a two-electron oxidant and the carbon atom of CO can be oxidized by two electrons to the +4 oxidation state, the product is phosgene ($Cl_2C{=}O$).
b. Unlike Cl_2, BF_3 is not a good oxidant, even though it contains boron in its highest oxidation state (+3). Nor can BF_3 behave like a reductant. Like any other species with only six valence electrons, however, it is certainly a Lewis acid. Hence an acid–base reaction is the most likely alternative, especially because we know that CO can use the lone pair of electrons on carbon to act as a Lewis base. The most probable reaction is therefore the formation of a Lewis acid–base adduct.

c. Typically, both reactants behave like reductants. Unless one of them can also behave like an oxidant, no reaction will occur. We know that Sr is an active metal because it lies far to the left in the periodic table and that it is more electropositive than carbon. Carbon is a nonmetal with a significantly higher electronegativity; it is therefore more likely to accept electrons in a redox reaction. We conclude, therefore, that Sr will be oxidized, and C will be reduced. Carbon forms ionic carbides with active metals, so the reaction will produce a species formally containing either C^{4-} or C_2^{2-}. Those that contain C^{4-} usually involve small, highly charged metal ions, so Sr^{2+} will produce the acetylide (SrC_2) instead.

? Exercise 18.6.1

Predict the products of the reactions and write a balanced chemical equation for each reaction.

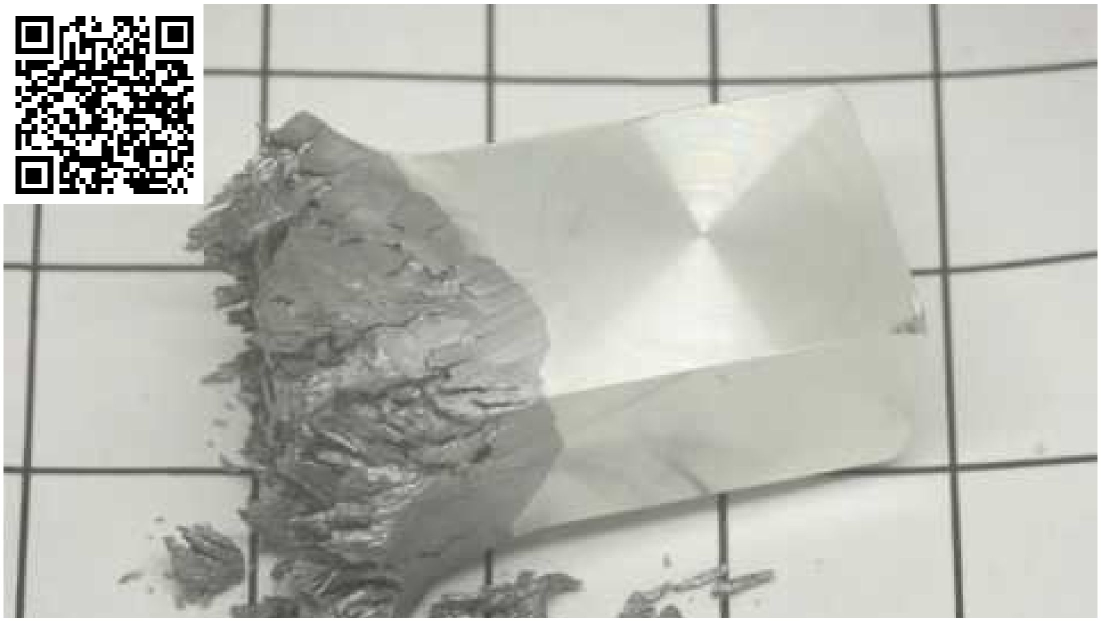
a. $C(s) + \text{excess } O_2(g) \xrightarrow{\Delta}$
b. $C(s) + H_2O(l) \rightarrow$
c. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow$

Answer

a. $C(s) + \text{excess } O_2(g) \xrightarrow{\Delta} CO_2(g)$
b. $C(s) + H_2O(l) \rightarrow$ no reaction
c. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow CO_2(g) + NaHSO_4(aq) + H_2O(l)$

Reactions and Compounds of the Heavier Group 14 Elements

Although silicon, germanium, tin, and lead in their +4 oxidation states often form binary compounds with the same stoichiometry as carbon, the structures and properties of these compounds are usually significantly different from those of the carbon analogues. Silicon and germanium are both semiconductors with structures analogous to diamond. Tin has two common allotropes: white (β) tin has a metallic lattice and metallic properties, whereas gray (α) tin has a diamond-like structure and is a semiconductor. The metallic β form is stable above 13.2°C, and the nonmetallic α form is stable below 13.2°C. Lead is the only group 14 element that is metallic in both structure and properties under all conditions.



***Video 18.6.1**: Time lapse tin pest reaction.*

Based on its position in the periodic table, we expect silicon to be amphoteric. In fact, it dissolves in strong aqueous base to produce hydrogen gas and solutions of silicates, but the only aqueous acid that it reacts with is hydrofluoric acid, presumably due to the formation of the stable SiF_6^{2-} ion. Germanium is more metallic in its behavior than silicon. For example, it dissolves in hot oxidizing acids, such as HNO_3 and H_2SO_4, but in the absence of an oxidant, it does not dissolve in aqueous base. Although tin has an even more metallic character than germanium, lead is the only element in the group that behaves purely as a metal. Acids do not readily attack it because the solid acquires a thin protective outer layer of a Pb^{2+} salt, such as $PbSO_4$.

All group 14 dichlorides are known, and their stability increases dramatically as the atomic number of the central atom increases. Thus CCl_2 is dichlorocarbene, a highly reactive, short-lived intermediate that can be made in solution but cannot be isolated in pure form using standard techniques; $SiCl_2$ can be isolated at very low temperatures, but it decomposes rapidly above −150°C, and $GeCl_2$ is relatively stable at temperatures below 20°C. In contrast, $SnCl_2$ is a polymeric solid that is indefinitely stable at room temperature, whereas $PbCl_2$ is an insoluble crystalline solid with a structure similar to that of $SnCl_2$.

> *The stability of the group 14 dichlorides increases dramatically from carbon to lead.*

Although the first four elements of group 14 form tetrahalides (MX_4) with all the halogens, only fluorine is able to oxidize lead to the +4 oxidation state, giving PbF_4. The tetrahalides of silicon and germanium react rapidly with water to give amphoteric oxides (where M is Si or Ge):

$$MX_{4(s,l)} + 2H_2O_{(l)} \rightarrow MO_{2(s)} + 4HX_{(aq)} \tag{18.6.11}$$

In contrast, the tetrahalides of tin and lead react with water to give hydrated metal ions. Because of the stability of its +2 oxidation state, lead reacts with oxygen or sulfur to form PbO or PbS, respectively, whereas heating the other group 14 elements with excess O_2 or S_8 gives the corresponding dioxides or disulfides, respectively. The dioxides of the group 14 elements become increasingly basic as we go down the group.

> *The dioxides of the group 14 elements become increasingly basic down the group.*

Because the Si–O bond is even stronger than the C–O bond (~452 kJ/mol versus ~358 kJ/mol), silicon has a strong affinity for oxygen. The relative strengths of the C–O and Si–O bonds contradict the generalization that bond strengths decrease as the bonded atoms become larger. This is because we have thus far assumed that a formal single bond between two atoms can always be described in terms of a single pair of shared electrons. In the case of Si–O bonds, however, the presence of relatively low-energy, empty d orbitals on Si and nonbonding electron pairs in the p or sp^n hybrid orbitals of O results in a partial π bond (Figure 18.6.3). Due to its partial π double bond character, the Si–O bond is significantly stronger and shorter than would otherwise be expected. A similar interaction with oxygen is also an important feature of the chemistry of the elements that follow silicon in the third period (P, S, and Cl). Because the Si–O bond is unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.

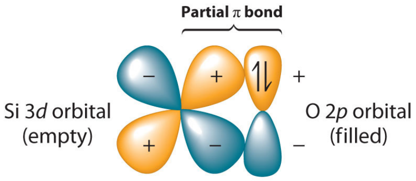
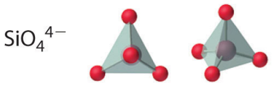


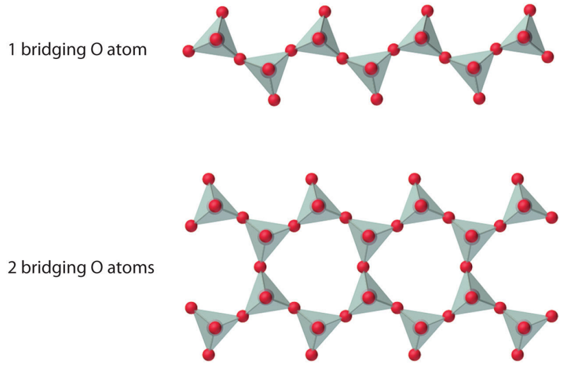
Figure 18.6.3: π Bonding between Silicon and Oxygen. Silicon has relatively low-energy, empty 3d orbitals that can interact with filled 2p hybrid orbitals on oxygen. This interaction results in a partial π bond in which both electrons are supplied by oxygen, giving the Si–O bond partial double bond character and making it significantly stronger (and shorter) than expected for a single bond.

> *Because silicon–oxygen bonds are unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.*

Compounds with anions that contain only silicon and oxygen are called silicates, whose basic building block is the SiO_4^{4-} unit:



The number of oxygen atoms shared between silicon atoms and the way in which the units are linked vary considerably in different silicates. Converting one of the oxygen atoms from terminal to bridging generates chains of silicates, while converting two oxygen atoms from terminal to bridging generates double chains. In contrast, converting three or four oxygens to bridging generates a variety of complex layered and three-dimensional structures, respectively.



In a large and important class of materials called aluminosilicates, some of the Si atoms are replaced by Al atoms to give aluminosilicates such as zeolites, whose three-dimensional framework structures have large cavities connected by smaller tunnels (Figure 18.6.4). Because the cations in zeolites are readily exchanged, zeolites are used in laundry detergents as water-softening agents: the more loosely bound Na^+ ions inside the zeolite cavities are displaced by the more highly charged Mg^{2+} and Ca^{2+} ions present in hard water, which bind more tightly. Zeolites are also used as catalysts and for water purification.

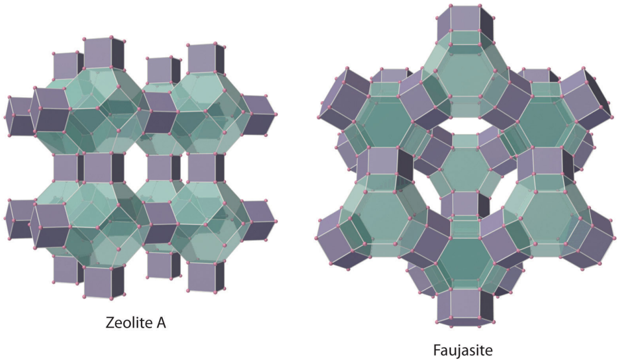


Figure 18.6.4: Zeolites Are Aluminosilicates with Large Cavities Connected by Channels. The cavities normally contain hydrated cations that are loosely bound to the oxygen atoms of the negatively charged framework by electrostatic interactions. The sizes and arrangements of the channels and cavities differ in different types of zeolites. For example, in zeolite A the aluminosilicate cages are arranged in a cubic fashion, and the channels connecting the cavities intersect at right angles. In contrast, the cavities in faujasite are much larger, and the channels intersect at 120° angles. In these idealized models, the oxygen atoms that connect each pair of silicon atoms have been omitted.

Silicon and germanium react with nitrogen at high temperature to form nitrides (M_3N_4):

$$3Si_{(l)}+2N_{2(g)}\rightarrow Si_3N_{4(s)} \tag{18.6.12}$$

Silicon nitride has properties that make it suitable for high-temperature engineering applications: it is strong, very hard, and chemically inert, and it retains these properties to temperatures of about 1000°C.

Because of the diagonal relationship between boron and silicon, metal silicides and metal borides exhibit many similarities. Although metal silicides have structures that are as complex as those of the metal borides and carbides, few silicides are structurally similar to the corresponding borides due to the significantly larger size of Si (atomic radius 111 pm versus 87 pm for B). Silicides of active metals, such as Mg_2Si, are ionic compounds that contain the $Si^{4−}$ ion. They react with aqueous acid to form silicon hydrides such as SiH_4:

$$Mg_2Si_{(s)}+4H^+_{(aq)}\rightarrow 2Mg^{2+}_{(aq)}+SiH_{4(g)} \tag{18.6.13}$$

Unlike carbon, catenated silicon hydrides become thermodynamically less stable as the chain lengthens. Thus straight-chain and branched silanes (analogous to alkanes) are known up to only n = 10; the germanium analogues (germanes) are known up to n = 9. In contrast, the only known hydride of tin is SnH_4, and it slowly decomposes to elemental Sn and H_2 at room temperature. The simplest lead hydride (PbH_4) is so unstable that chemists are not even certain it exists. Because E=E and E≡E bonds become weaker with increasing atomic number (where E is any group 14 element), simple silicon, germanium, and tin analogues of alkenes, alkynes, and aromatic hydrocarbons are either unstable (Si=Si and Ge=Ge) or unknown. Silicon-based life-forms are therefore likely to be found only in science fiction.

> *The stability of group 14 hydrides decreases down the group, and E=E and E≡E bonds become weaker.*

The only important organic derivatives of lead are compounds such as tetraethyllead [$(CH_3CH_2)_4Pb$]. Because the Pb–C bond is weak, these compounds decompose at relatively low temperatures to produce alkyl radicals (R·), which can be used to control the rate of combustion reactions. For 60 yr, hundreds of thousands of tons of lead were burned annually in automobile engines, producing a mist of lead oxide particles along the highways that constituted a potentially serious public health problem. (Example 6 in Section 22.3 examines this problem.) The use of catalytic converters reduced the amount of carbon monoxide, nitrogen oxides, and hydrocarbons released into the atmosphere through automobile exhausts, but it did nothing to decrease lead emissions. Because lead poisons catalytic converters, however, its use as a gasoline additive has been banned in most of the world.

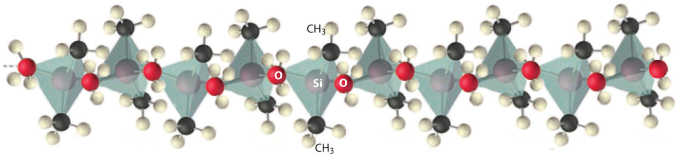


Figure 18.6.5 Silicones Are Polymers with Long Chains of Alternating Silicon and Oxygen Atoms. The structure of a linear silicone polymer is similar to that of quartz, but two of the oxygen atoms attached to each silicon atom are replaced by the carbon atoms of organic groups, such as the methyl groups ($–CH_3$) shown here. The terminal silicon atoms are bonded to three methyl groups. Silicones can be oily, waxy, flexible, or elastic, depending on the chain length, the extent of cross-linking between the chains, and the type of organic group.

Compounds that contain Si–C and Si–O bonds are stable and important. High-molecular-mass polymers called silicones contain an $(Si–O–)_n$ backbone with organic groups attached to Si (Figure 18.6.5). The properties of silicones are determined by the chain length, the type of organic group, and the extent of cross-linking between the chains. Without cross-linking, silicones are waxes or oils, but cross-linking can produce flexible materials used in sealants, gaskets, car polishes, lubricants, and even elastic materials, such as the plastic substance known as Silly Putty.

A child playing with Silly Putty, a silicone polymer with unusual mechanical properties. Gentle pressure causes Silly Putty to flow or stretch, but it cannot be flattened when hit with a hammer. This is called a "Non-Newtonian Fluid"

✓ Example 18.6.2

For each reaction, explain why the given products form.

a. $Pb(s) + Cl_2(g) \rightarrow PbCl_2(s)$
b. $Mg_2Si(s) + 4H_2O(l) \rightarrow SiH_4(g) + 2Mg(OH)_2(s)$
c. $GeO_2(s) + 4OH^-(aq) \rightarrow GeO_4^{4-}(aq) + 2H_2O(l)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. Lead is a metal, and chlorine is a nonmetal that is a strong oxidant. Thus we can expect a redox reaction to occur in which the metal acts as a reductant. Although lead can form compounds in the +2 and +4 oxidation states, Pb^{4+} is a potent oxidant (the inert-pair effect). Because lead prefers the +2 oxidation state and chlorine is a weaker oxidant than fluorine, we expect $PbCl_2$ to be the product.
b. This is the reaction of water with a metal silicide, which formally contains the Si^{4-} ion. Water can act as either an acid or a base. Because the other compound is a base, we expect an acid–base reaction to occur in which water acts as an acid. Because Mg_2Si contains Si in its lowest possible oxidation state, however, an oxidation–reduction reaction is also a possibility. But water is a relatively weak oxidant, so an acid–base reaction is more likely. The acid (H_2O) transfers a proton to the base (Si^{4-}), which can accept four protons to form SiH_4. Proton transfer from water produces the OH^{-} ion, which will combine with Mg^{2+} to give magnesium hydroxide.
c. We expect germanium dioxide (GeO_2) to be amphoteric because of the position of germanium in the periodic table. It should dissolve in strong aqueous base to give an anionic species analogous to silicate.

? Exercise 18.6.2

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $PbO_2(s) \xrightarrow{\Delta}$
b. $GeCl_4(s) + H_2O(l) \rightarrow$
c. $Sn(s) + HCl(aq) \rightarrow$

Answer

a. $PbO_2(s) \xrightarrow{\Delta} PbO(s) + \frac{1}{2}O_2(g)$
b. $GeCl_4(s) + 2H_2O(l) \rightarrow GeO_2(s) + 4HCl(aq)$
c. $Sn(s) + 2HCl(aq) \rightarrow Sn^{2+}(aq) + H_2(g) + 2Cl^{-}(aq)$

Summary

The group 14 elements show the greatest diversity in chemical behavior of any group; covalent bond strengths decease with increasing atomic size, and ionization energies are greater than expected, increasing from C to Pb. The group 14 elements show the greatest range of chemical behavior of any group in the periodic table. Because the covalent bond strength decreases with increasing atomic size and greater-than-expected ionization energies due to an increase in Z_{eff}, the stability of the +2 oxidation state increases from carbon to lead. The tendency to form multiple bonds and to catenate decreases as the atomic number increases. The stability of the carbon tetrahalides decreases as the halogen increases in size because of poor orbital overlap and steric crowding. Carbon forms three kinds of carbides with less electronegative elements: ionic carbides, which contain metal cations and C^{4-} (methide) or $C_2{}^{2-}$ (acetylide) anions; interstitial carbides, which are characterized by covalent metal–carbon interactions and are among the hardest substances known; and covalent carbides, which have three-dimensional covalent network structures that make them extremely hard, high melting, and chemically inert. Consistent with periodic trends, metallic behavior increases down the group. Silicon has a tremendous affinity for oxygen because of partial Si–O π bonding. Dioxides of the group 14 elements become increasingly basic down the group and their metallic character increases. Silicates contain anions that consist of only silicon and oxygen. Aluminosilicates are formed by replacing some of the Si atoms in silicates by Al atoms; aluminosilicates with three-dimensional framework structures are called zeolites. Nitrides formed by reacting silicon or germanium with nitrogen are strong, hard, and chemically inert. The hydrides become thermodynamically less stable down the group. Moreover, as atomic size increases, multiple bonds between or to the group 14 elements become weaker. Silicones, which contain an Si–O backbone and Si–C bonds, are high-molecular-mass polymers whose properties depend on their compositions.

Contributors and Attributions

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    - Anonymous

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18.7: The Group 5A Elements

Learning Objectives

- To understand the trends in properties and reactivity of the group 15 elements: the pnicogens.

Like the group 14 elements, the lightest member of group 15, nitrogen, is found in nature as the free element, and the heaviest elements have been known for centuries because they are easily isolated from their ores. Antimony (Sb) was probably the first of the pnicogens to be obtained in elemental form and recognized as an element. Its atomic symbol comes from its Roman name: stibium. It is found in stibnite (Sb_2S_3), a black mineral that has been used as a cosmetic (an early form of mascara) since biblical times, and it is easily reduced to the metal in a charcoal fire (Figure 18.7.1). The Egyptians used antimony to coat copper objects as early as the third millennium BC, and antimony is still used in alloys to improve the tonal quality of bells.

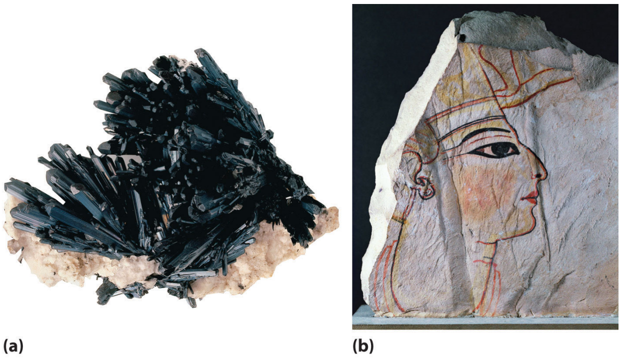


Figure 18.7.1: The Ancient Egyptians Used Finely Ground Antimony Sulfide for Eye Makeup. (a) Crystals of the soft black mineral stibnite (Sb_2S_3) on a white mineral matrix. (b) A fragment of an Egyptian painting on limestone from the 16th–13th centuries BC shows the use of ground stibnite ("kohl") as black eye shadow. Small vases of ground stibnite have been found among the funeral goods buried with Egyptian pharaohs.

In the form of its yellow sulfide ore, orpiment (As_2S_3), arsenic (As) has been known to physicians and professional assassins since ancient Greece, although elemental arsenic was not isolated until centuries later. The history of bismuth (Bi), in contrast, is more difficult to follow because early alchemists often confused it with other metals, such as lead, tin, antimony, and even silver (due to its slightly pinkish-white luster). Its name comes from the old German wismut, meaning "white metal." Bismuth was finally isolated in the 15th century, and it was used to make movable type for printing shortly after the invention of the Gutenberg printing process in 1440. Bismuth is used in printing because it is one of the few substances known whose solid state is less dense than the liquid. Consequently, its alloys expand as they cool, filling a mold completely and producing crisp, clear letters for typesetting.

Phosphorus was discovered in 1669 by the German alchemist Hennig Brandt, who was looking for the "philosophers' stone," a mythical substance capable of converting base metals to silver or gold. Believing that human urine was the source of the key ingredient, Brandt obtained several dozen buckets of urine, which he allowed to putrefy. The urine was distilled to dryness at high temperature and then condensed; the last fumes were collected under water, giving a waxy white solid that had unusual properties. For example, it glowed in the dark and burst into flames when removed from the water. (Unfortunately for Brandt, however, it did not turn lead into gold.) The element was given its current name (from the Greek phos, meaning "light," and phoros, meaning "bringing") in the 17th century. For more than a century, the only way to obtain phosphorus was the distillation of urine, but in 1769 it was discovered that phosphorus could be obtained more easily from bones. During the 19th century, the demand for phosphorus for matches was so great that battlefields and paupers' graveyards were systematically scavenged for bones. Early matches were pieces of wood coated with elemental phosphorus that were stored in an evacuated glass tube and ignited when the tube was broken (which could cause unfortunate accidents if the matches were kept in a pocket!).

Unfortunately, elemental phosphorus is volatile and highly toxic. It is absorbed by the teeth and destroys bone in the jaw, leading to a painful and fatal condition called "phossy jaw," which for many years was accepted as an occupational hazard of working in the match industry.

Although nitrogen is the most abundant element in the atmosphere, it was the last of the pnicogens to be obtained in pure form. In 1772, Daniel Rutherford, working with Joseph Black (who discovered CO_2), noticed that a gas remained when CO_2 was removed from a combustion reaction. Antoine Lavoisier called the gas azote, meaning "no life," because it did not support life. When it was discovered that the same element was also present in nitric acid and nitrate salts such as KNO_3 (nitre), it was named nitrogen. About 90% of the nitrogen produced today is used to provide an inert atmosphere for processes or reactions that are oxygen sensitive, such as the production of steel, petroleum refining, and the packaging of foods and pharmaceuticals.

Preparation and General Properties of the Group 15 Elements

Because the atmosphere contains several trillion tons of elemental nitrogen with a purity of about 80%, it is a huge source of nitrogen gas. Distillation of liquefied air yields nitrogen gas that is more than 99.99% pure, but small amounts of very pure nitrogen gas can be obtained from the thermal decomposition of sodium azide:

$$2NaN_3(s) \xrightarrow{\Delta} 2Na(l) + 3N_2(g) \tag{18.7.1}$$

In contrast, Earth's crust is relatively poor in nitrogen. The only important nitrogen ores are large deposits of KNO_3 and $NaNO_3$ in the deserts of Chile and Russia, which were apparently formed when ancient alkaline lakes evaporated. Consequently, virtually all nitrogen compounds produced on an industrial scale use atmospheric nitrogen as the starting material. Phosphorus, which constitutes only about 0.1% of Earth's crust, is much more abundant in ores than nitrogen. Like aluminum and silicon, phosphorus is always found in combination with oxygen, and large inputs of energy are required to isolate it.

The other three pnicogens are much less abundant: arsenic is found in Earth's crust at a concentration of about 2 ppm, antimony is an order of magnitude less abundant, and bismuth is almost as rare as gold. All three elements have a high affinity for the chalcogens and are usually found as the sulfide ores (M_2S_3), often in combination with sulfides of other heavy elements, such as copper, silver, and lead. Hence a major source of antimony and bismuth is flue dust obtained by smelting the sulfide ores of the more abundant metals.

In group 15, as elsewhere in the p block, we see large differences between the lightest element (N) and its congeners in size, ionization energy, electron affinity, and electronegativity (Table 18.7.1). The chemical behavior of the elements can be summarized rather simply: nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. With their ns^2np^3 valence electron configurations, all form compounds by losing either the three np valence electrons to form the +3 oxidation state or the three np and the two ns valence electrons to give the +5 oxidation state, whose stability decreases smoothly from phosphorus to bismuth. In addition, the relatively large magnitude of the electron affinity of the lighter pnicogens enables them to form compounds in the −3 oxidation state (such as NH_3 and PH_3), in which three electrons are formally added to the neutral atom to give a filled np subshell. Nitrogen has the unusual ability to form compounds in nine different oxidation states, including −3, +3, and +5. Because neutral covalent compounds of the trivalent pnicogens contain a lone pair of electrons on the central atom, they tend to behave as Lewis bases.

Table 18.7.1: Selected Properties of the Group 15 Elements

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
atomic symbol	N	P	As	Sb	Bi
atomic number	7	15	33	51	83
atomic mass (amu)	14.01	30.97	74.92	121.76	209.98
valence electron configuration*	$2s^22p^3$	$3s^23p^3$	$4s^24p^3$	$5s^25p^3$	$6s^26p^3$
melting point/boiling point (°C)	−210/−196	44.15/281^c	817 (at 3.70 MPa)/603 (sublimes)†	631/1587	271/1564
density (g/cm^3) at 25°C	1.15 (g/L)	1.82†	5.75‡	6.68	9.79

*The configuration shown does not include filled d and f subshells. †For white phosphorus. ‡For gray arsenic. §The values cited are for six-coordinate ions in the indicated oxidation states. The N^{5+}, P^{5+}, and As^{5+} ions are not known species. $^{\|}$The chemical form of the elements in these oxidation states varies considerably. For N, the reaction is $NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$; for P and As, it is $H_3EO_4 + 2H^+ + 2e^- \rightarrow H_3EO_3 + H_2O$; and for Sb it is $Sb_2O_5 + 4e^- + 10H^+ \rightarrow 2Sb^{3+} + 5H_2O$.

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
atomic radius (pm)	56	98	114	133	143
first ionization energy (kJ/mol)	1402	1012	945	831	703
common oxidation state(s)	−3 to +5	+5, +3, −3	+5, +3	+5, +3	+3
ionic radius (pm)[§]	146 (−3), 16 (+3)	212 (−3), 44 (+3)	58 (+3)	76 (+3), 60 (+5)	103 (+3)
electron affinity (kJ/mol)	0	−72	−78	−101	−91
electronegativity	3.0	2.2	2.2	2.1	1.9
standard reduction potential (E°, V) ($E^V \rightarrow E^{III}$ in acidic solution)[‖]	+0.93	−0.28	+0.56	+0.65	—
product of reaction with O_2	NO_2, NO	P_4O_6, P_4O_{10}	As_4O_6	Sb_2O_5	Bi_2O_3
type of oxide	acidic (NO_2), neutral (NO, N_2O)	acidic	acidic	amphoteric	basic
product of reaction with N_2	—	none	none	none	none
product of reaction with X_2	none	PX_3, PX_5	AsF_5, AsX_3	SbF_5, $SbCl_5$, $SbBr_3$, SbI_3	BiF_5, BiX_3
product of reaction with H_2	none	none	none	none	none

[*] The configuration shown does not include filled d and f subshells. [†] For white phosphorus. [‡] For gray arsenic. [§] The values cited are for six-coordinate ions in the indicated oxidation states. The N^{5+}, P^{5+}, and As^{5+} ions are not known species. [‖] The chemical form of the elements in these oxidation states varies considerably. For N, the reaction is $NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$; for P and As, it is $H_3EO_4 + 2H^+ + 2e^- \rightarrow H_3EO_3 + H_2O$; and for Sb it is $Sb_2O_5 + 4e^- + 10H^+ \rightarrow 2Sb^{3+} + 5H_2O$.

> *In group 15, the stability of the +5 oxidation state decreases from P to Bi.*

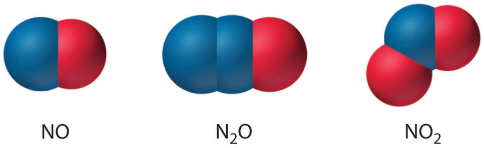
> *Because neutral covalent compounds of the trivalent group 15 elements have a lone pair of electrons on the central atom, they tend to be Lewis bases.*

Reactions and Compounds of Nitrogen

Like carbon, nitrogen has four valence orbitals (one 2s and three 2p), so it can participate in at most four electron-pair bonds by using sp^3 hybrid orbitals. Unlike carbon, however, nitrogen does not form long chains because of repulsive interactions between lone pairs of electrons on adjacent atoms. These interactions become important at the shorter internuclear distances encountered with the smaller, second-period elements of groups 15, 16, and 17. Stable compounds with N–N bonds are limited to chains of no more than three N atoms, such as the azide ion (N_3^-).

Nitrogen is the only pnicogen that normally forms multiple bonds with itself and other second-period elements, using π overlap of adjacent np orbitals. Thus the stable form of elemental nitrogen is N_2, whose N≡N bond is so strong ($D_{N\equiv N}$ = 942 kJ/mol) compared with the N–N and N=N bonds ($D_{N–N}$ = 167 kJ/mol; $D_{N=N}$ = 418 kJ/mol) that all compounds containing N–N and N=N bonds are thermodynamically unstable with respect to the formation of N_2. In fact, the formation of the N≡N bond is so thermodynamically favored that virtually all compounds containing N–N bonds are potentially explosive.

Again in contrast to carbon, nitrogen undergoes only two important chemical reactions at room temperature: it reacts with metallic lithium to form lithium nitride, and it is reduced to ammonia by certain microorganisms. At higher temperatures, however, N_2 reacts with more electropositive elements, such as those in group 13, to give binary nitrides, which range from covalent to ionic in character. Like the corresponding compounds of carbon, binary compounds of nitrogen with oxygen, hydrogen, or other nonmetals are usually covalent molecular substances.



Few binary molecular compounds of nitrogen are formed by direct reaction of the elements. At elevated temperatures, N_2 reacts with H_2 to form ammonia, with O_2 to form a mixture of NO and NO_2, and with carbon to form cyanogen (N≡C–C≡N); elemental nitrogen does not react with the halogens or the other chalcogens. Nonetheless, all the binary nitrogen halides (NX_3) are known. Except for NF_3, all are toxic, thermodynamically unstable, and potentially explosive, and all are prepared by reacting the halogen with NH_3 rather than N_2. Both nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are thermodynamically unstable, with positive free energies of formation. Unlike NO, NO_2 reacts readily with excess water, forming a 1:1 mixture of nitrous acid (HNO_2) and nitric acid (HNO_3):

$$2\,NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq) \tag{18.7.2}$$

Nitrogen also forms N_2O (dinitrogen monoxide, or nitrous oxide), a linear molecule that is isoelectronic with CO_2 and can be represented as $^{-}N{=}N^{+}{=}O$. Like the other two oxides of nitrogen, nitrous oxide is thermodynamically unstable. The structures of the three common oxides of nitrogen are as follows:

> *Few binary molecular compounds of nitrogen are formed by the direct reaction of the elements.*

At elevated temperatures, nitrogen reacts with highly electropositive metals to form ionic nitrides, such as Li_3N and Ca_3N_2. These compounds consist of ionic lattices formed by M^{n+} and N^{3-} ions. Just as boron forms interstitial borides and carbon forms interstitial carbides, with less electropositive metals nitrogen forms a range of interstitial nitrides, in which nitrogen occupies holes in a close-packed metallic structure. Like the interstitial carbides and borides, these substances are typically very hard, high-melting materials that have metallic luster and conductivity.

Nitrogen also reacts with semimetals at very high temperatures to produce covalent nitrides, such as Si_3N_4 and BN, which are solids with extended covalent network structures similar to those of graphite or diamond. Consequently, they are usually high melting and chemically inert materials.

Ammonia (NH_3) is one of the few thermodynamically stable binary compounds of nitrogen with a nonmetal. It is not flammable in air, but it burns in an O_2 atmosphere:

$$4\,NH_3(g) + 3\,O_2(g) \rightarrow 2\,N_2(g) + 6\,H_2O(g) \tag{18.7.3}$$

About 10% of the ammonia produced annually is used to make fibers and plastics that contain amide bonds, such as nylons and polyurethanes, while 5% is used in explosives, such as ammonium nitrate, TNT (trinitrotoluene), and nitroglycerine. Large amounts of anhydrous liquid ammonia are used as fertilizer.

Nitrogen forms two other important binary compounds with hydrogen. Hydrazoic acid (HN_3), also called hydrogen azide, is a colorless, highly toxic, and explosive substance. Hydrazine (N_2H_4) is also potentially explosive; it is used as a rocket propellant and to inhibit corrosion in boilers.

> *B, C, and N all react with transition metals to form interstitial compounds that are hard, high-melting materials.*

✓ Example 18.7.1

For each reaction, explain why the given products form when the reactants are heated.

a. $Sr(s) + N_2O(g) \xrightarrow{\Delta} SrO(s) + N_2(g)$
b. $NH_4NO_2(s) \xrightarrow{\Delta} N_2(g) + 2H_2O(g)$
c. $Pb(NO_3)_2(s) \xrightarrow{\Delta} PbO_2(s) + 2NO_2(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. As an alkali metal, strontium is a strong reductant. If the other reactant can act as an oxidant, then a redox reaction will occur. Nitrous oxide contains nitrogen in a low oxidation state (+1), so we would not normally consider it an oxidant. Nitrous oxide is, however, thermodynamically unstable ($\Delta H°_f > 0$ and $\Delta G°_f > 0$), and it can be reduced to N_2, which is a stable species. Consequently, we predict that a redox reaction will occur.
b. When a substance is heated, a decomposition reaction probably will occur, which often involves the release of stable gases. In this case, ammonium nitrite contains nitrogen in two different oxidation states (−3 and +3), so an internal redox reaction is a possibility. Due to its thermodynamic stability, N_2 is the probable nitrogen-containing product, whereas we predict that H and O will combine to form H_2O.
c. Again, this is probably a thermal decomposition reaction. If one element is in an usually high oxidation state and another in a low oxidation state, a redox reaction will probably occur. Lead nitrate contains the Pb^{2+} cation and the nitrate anion, which contains nitrogen in its highest possible oxidation state (+5). Hence nitrogen can be reduced, and we know that lead can be oxidized to the +4 oxidation state. Consequently, it is likely that lead(II) nitrate will decompose to lead(IV) oxide and nitrogen dioxide when heated. Even though PbO_2 is a powerful oxidant, the release of a gas such as NO_2 can often drive an otherwise unfavorable reaction to completion (Le Chatelier's principle). Note, however, that PbO_2 will probably decompose to PbO at high temperatures.

? Exercise 23.3.1

Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $NO(g) + H_2O(l) \xrightarrow{\Delta}$
b. $NH_4NO_3(s) \xrightarrow{\Delta}$
c. $Sr(s) + N_2(g) \rightarrow$

Answer

a. $NO(g) + H_2O(l) \xrightarrow{\Delta}$ no reaction
b. $NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(g)$
c. $3Sr(s) + N_2(g) \rightarrow Sr_3N_2(s)$

Reactions and Compounds of the Heavier Pnicogens

Like the heavier elements of group 14, the heavier pnicogens form catenated compounds that contain only single bonds, whose stability decreases rapidly as we go down the group. For example, phosphorus exists as multiple allotropes, the most common of which is white phosphorus, which consists of P_4 tetrahedra and behaves like a typical nonmetal. As is typical of a molecular solid, white phosphorus is volatile, has a low melting point (44.1°C), and is soluble in nonpolar solvents. It is highly strained, with bond angles of only 60°, which partially explains why it is so reactive and so easily converted to more stable allotropes. Heating white phosphorus for several days converts it to red phosphorus, a polymer that is air stable, virtually insoluble, denser than white phosphorus, and higher melting, properties that make it much safer to handle. A third allotrope of phosphorus, black phosphorus, is prepared by heating the other allotropes under high pressure; it is even less reactive, denser, and higher melting than red phosphorus. As expected from their structures, white phosphorus is an electrical insulator, and red and black phosphorus are semiconductors. The three heaviest pnicogens—arsenic, antimony, and bismuth—all have a metallic luster, but they are brittle (not ductile) and relatively poor electrical conductors.

> *As in group 14, the heavier group 15 elements form catenated compounds that contain only single bonds, whose stability decreases as we go down the group.*

The reactivity of the heavier pnicogens decreases as we go down the column. Phosphorus is by far the most reactive of the pnicogens, forming binary compounds with every element in the periodic table except antimony, bismuth, and the noble gases. Phosphorus reacts rapidly with O_2, whereas arsenic burns in pure O_2 if ignited, and antimony and bismuth react with O_2 only when heated. None of the pnicogens reacts with nonoxidizing acids such as aqueous HCl, but all dissolve in oxidizing acids such as HNO_3. Only bismuth behaves like a metal, dissolving in HNO_3 to give the hydrated Bi^{3+} cation.

> *The reactivity of the heavier group 15 elements decreases as we go down the column.*

The heavier pnicogens can use energetically accessible 3d, 4d, or 5d orbitals to form dsp^3 or d^2sp^3 hybrid orbitals for bonding. Consequently, these elements often have coordination numbers of 5 or higher. Phosphorus and arsenic form halides (e.g., $AsCl_5$) that are generally covalent molecular species and behave like typical nonmetal halides, reacting with water to form the corresponding oxoacids (in this case, H_3AsO_4). All the pentahalides are potent Lewis acids that can expand their coordination to accommodate the lone pair of a Lewis base:

$$\mathrm{AsF_5(soln) + F^-(soln) \rightarrow AsF_6^-(soln)} \tag{18.7.4}$$

In contrast, bismuth halides have extended lattice structures and dissolve in water to produce hydrated ions, consistent with the stronger metallic character of bismuth.

Except for BiF_3, which is essentially an ionic compound, the trihalides are volatile covalent molecules with a lone pair of electrons on the central atom. Like the pentahalides, the trihalides react rapidly with water. In the cases of phosphorus and arsenic, the products are the corresponding acids, H_3PO_3 and H_3AsO_3, where E is P or As:

$$\mathrm{EX_3(l) + 3\,H_2O(l) \rightarrow H_3EO_3(aq) + 3\,HX(aq)} \tag{18.7.5}$$

Phosphorus halides are also used to produce insecticides, flame retardants, and plasticizers.

> *Phosphorus has the greatest ability to form π bonds with elements such as O, N, and C.*

With energetically accessible d orbitals, phosphorus and, to a lesser extent, arsenic are able to form π bonds with second-period atoms such as N and O. This effect is even more important for phosphorus than for silicon, resulting in very strong P–O bonds and even stronger P=O bonds. The first four elements in group 15 also react with oxygen to produce the corresponding oxide in the +3 oxidation state. Of these oxides, P_4O_6 and As_4O_6 have cage structures formed by inserting an oxygen atom into each edge of the P_4 or As_4 tetrahedron (part (a) in Figure 18.7.2), and they behave like typical nonmetal oxides. For example, P_4O_6 reacts with water to form phosphorous acid (H_3PO_3). Consistent with its position between the nonmetal and metallic oxides, Sb_4O_6 is amphoteric, dissolving in either acid or base. In contrast, Bi_2O_3 behaves like a basic metallic oxide, dissolving in acid to give solutions that contain the hydrated Bi^{3+} ion. The two least metallic elements of the heavier pnicogens, phosphorus and arsenic, form very stable oxides with the formula E_4O_{10} in the +5 oxidation state (part (b) in Figure 18.7.2 In contrast, Bi_2O_5 is so unstable that there is no absolute proof it exists.

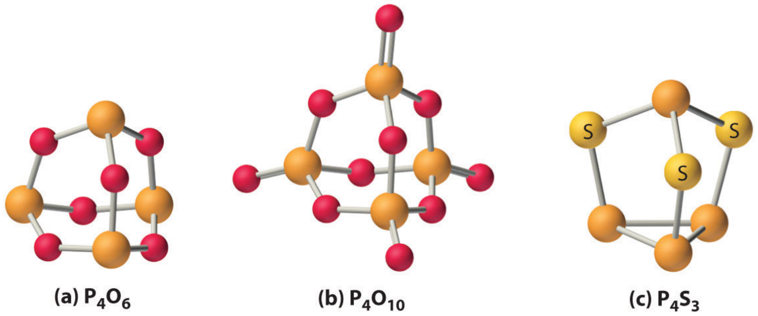


Figure 18.7.2: The Structures of Some Cage Compounds of Phosphorus. (a, b) The structures of P_4O_6 and P_4O_{10} are both derived from the structure of white phosphorus (P_4) by inserting an oxygen atom into each of the six edges of the P_4 tetrahedron; P_4O_{10} contains an additional terminal oxygen atom bonded to each phosphorus atom. (c) The structure of P_4S_3 is also derived from the structure of P_4 by inserting three sulfur atoms into three adjacent edges of the tetrahedron.

The heavier pnicogens form sulfides that range from molecular species with three-dimensional cage structures, such as P_4S_3 (part (c) in Figure 18.7.2), to layered or ribbon structures, such as Sb_2S_3 and Bi_2S_3, which are semiconductors. Reacting the heavier pnicogens with metals produces substances whose properties vary with the metal content. Metal-rich phosphides (such as M_4P) are hard, high-melting, electrically conductive solids with a metallic luster, whereas phosphorus-rich phosphides (such as MP_{15}) are lower melting and less thermally stable because they contain catenated P_n units. Many organic or organometallic compounds of the heavier pnicogens containing one to five alkyl or aryl groups are also known. Because of the decreasing strength of the pnicogen–carbon bond, their thermal stability decreases from phosphorus to bismuth.

> *The thermal stability of organic or organometallic compounds of group 15 decreases down the group due to the decreasing strength of the pnicogen–carbon bond.*

✓ Example 18.7.2

For each reaction, explain why the given products form.

a. $\mathrm{Bi(s)} + \frac{3}{2}\mathrm{Br(l)} \rightarrow \mathrm{BiBr_3(s)}$
b. $2(CH_3)_3As(l) + O_2(g) \rightarrow 2(CH_3)_3As{=}O(s)$
c. $PBr_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HBr(aq)$
d. $As(s) + Ga(s) \xrightarrow{\Delta} GaAs(s)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution

a. Bromine is an oxidant, and bismuth is a metal that can be oxidized. Hence a redox reaction is likely to occur. To identify the product, recall that bismuth can form compounds in either the +3 or +5 oxidation state. The heaviest pnicogen, bismuth is rather difficult to oxidize to the +5 oxidation state because of the inert-pair effect. Hence the product will probably be bismuth(III) bromide.
b. Trimethylarsine, with a lone pair of electrons on the arsenic atom, can act as either a Lewis base or a reductant. If arsenic is oxidized by two electrons, then oxygen must be reduced, most probably by two electrons to the −2 oxidation state. Because As(V) forms strong bonds to oxygen due to π bonding, the expected product is $(CH_3)_3As{=}O$.
c. Phosphorus tribromide is a typical nonmetal halide. We expect it to react with water to produce an oxoacid of P(III) and the corresponding hydrohalic acid.Because of the strength of the P=O bond, phosphorous acid (H_3PO_3) is actually $HP(O)(OH)_2$, which contains a P=O bond and a P–H bond.
d. Gallium is a metal with a strong tendency to act as a reductant and form compounds in the +3 oxidation state. In contrast, arsenic is a semimetal. It can act as a reductant to form compounds in the +3 or +5 oxidation state, or it can act as an oxidant, accepting electrons to form compounds in the −3 oxidation state. If a reaction occurs, then a binary compound will

probably form with a 1:1 ratio of the elements. GaAs is an example of a III-V compound, many of which are used in the electronics industry.

? Exercise 18.7.2

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $PCl_5(s) + H_2O(l) \rightarrow$
b. $Bi_2O_5(s) \xrightarrow{\Delta}$
c. $Ca_3P_2(s) + H^+(aq) \rightarrow$
d. $NaNH_2(s) + PH_3(soln) \rightarrow$

Answer

a. $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$
b. $Bi_2O_5(s) \xrightarrow{\Delta} Bi_2O_3(s) + O_2(g)$
c. $Ca_3P_2(s) + 6H^+(aq) \rightarrow 2PH_3(g) + 3Ca^{2+}(aq)$
d. $NaNH_2(s) + PH_3(soln) \rightarrow NaPH_2(s) + NH_3(soln)$

Summary

The reactivity of the heavier group 15 elements decreases down the group, as does the stability of their catenated compounds. In group 15, nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. Nitrogen forms compounds in nine different oxidation states. The stability of the +5 oxidation state decreases from phosphorus to bismuth because of the inert-pair effect. Due to their higher electronegativity, the lighter pnicogens form compounds in the −3 oxidation state. Because of the presence of a lone pair of electrons on the pnicogen, neutral covalent compounds of the trivalent pnicogens are Lewis bases. Nitrogen does not form stable catenated compounds because of repulsions between lone pairs of electrons on adjacent atoms, but it does form multiple bonds with other second-period atoms. Nitrogen reacts with electropositive elements to produce solids that range from covalent to ionic in character. Reaction with electropositive metals produces ionic nitrides, reaction with less electropositive metals produces interstitial nitrides, and reaction with semimetals produces covalent nitrides. The reactivity of the pnicogens decreases with increasing atomic number. Compounds of the heavier pnicogens often have coordination numbers of 5 or higher and use dsp^3 or d^2sp^3 hybrid orbitals for bonding. Because phosphorus and arsenic have energetically accessible d orbitals, these elements form π bonds with second-period atoms such as O and N. Phosphorus reacts with metals to produce phosphides. Metal-rich phosphides are hard, high-melting, electrically conductive solids with metallic luster, whereas phosphorus-rich phosphides, which contain catenated phosphorus units, are lower melting and less thermally stable.

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18.8: The Chemistry of Nitrogen

Like the group 14 elements, the lightest member of group 15, nitrogen, is found in nature as the free element, and the heaviest elements have been known for centuries because they are easily isolated from their ores. Although nitrogen is the most abundant element in the atmosphere, it was the last of the pnicogens (Group 15 elements) to be obtained in pure form. In 1772, Daniel Rutherford, working with Joseph Black (who discovered CO_2), noticed that a gas remained when CO_2 was removed from a combustion reaction. Antoine Lavoisier called the gas azote, meaning “no life,” because it did not support life. When it was discovered that the same element was also present in nitric acid and nitrate salts such as KNO_3 (nitre), it was named nitrogen. About 90% of the nitrogen produced today is used to provide an inert atmosphere for processes or reactions that are oxygen sensitive, such as the production of steel, petroleum refining, and the packaging of foods and pharmaceuticals.

Preparation and General Properties of Nitrogen

Because the atmosphere contains several trillion tons of elemental nitrogen with a purity of about 80%, it is a huge source of nitrogen gas. Distillation of liquefied air yields nitrogen gas that is more than 99.99% pure, but small amounts of very pure nitrogen gas can be obtained from the thermal decomposition of sodium azide:

$$2\,\mathrm{NaN_3(s)} \xrightarrow{\Delta} 2\,\mathrm{Na(l)} + 3\,\mathrm{N_2(g)} \tag{18.8.1}$$

In contrast, Earth’s crust is relatively poor in nitrogen. The only important nitrogen ores are large deposits of KNO_3 and $NaNO_3$ in the deserts of Chile and Russia, which were apparently formed when ancient alkaline lakes evaporated. Consequently, virtually all nitrogen compounds produced on an industrial scale use atmospheric nitrogen as the starting material. Phosphorus, which constitutes only about 0.1% of Earth’s crust, is much more abundant in ores than nitrogen. Like aluminum and silicon, phosphorus is always found in combination with oxygen, and large inputs of energy are required to isolate it.

Reactions and Compounds of Nitrogen

Like carbon, nitrogen has four valence orbitals (one 2s and three 2p), so it can participate in at most four electron-pair bonds by using sp^3 hybrid orbitals. Unlike carbon, however, nitrogen does not form long chains because of repulsive interactions between lone pairs of electrons on adjacent atoms. These interactions become important at the shorter internuclear distances encountered with the smaller, second-period elements of groups 15, 16, and 17. Stable compounds with N–N bonds are limited to chains of no more than three N atoms, such as the azide ion (N_3^-).

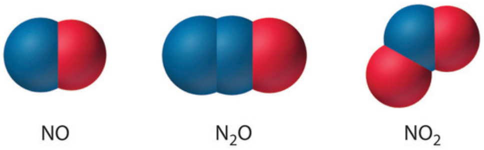
Nitrogen is the only pnicogen that normally forms multiple bonds with itself and other second-period elements, using π overlap of adjacent np orbitals. Thus the stable form of elemental nitrogen is N_2, whose N≡N bond is so strong ($D_{N\equiv N}$ = 942 kJ/mol) compared with the N–N and N=N bonds ($D_{N–N}$ = 167 kJ/mol; $D_{N=N}$ = 418 kJ/mol) that all compounds containing N–N and N=N bonds are thermodynamically unstable with respect to the formation of N_2. In fact, the formation of the N≡N bond is so thermodynamically favored that virtually all compounds containing N–N bonds are potentially explosive.

Again in contrast to carbon, nitrogen undergoes only two important chemical reactions at room temperature: it reacts with metallic lithium to form lithium nitride, and it is reduced to ammonia by certain microorganisms. At higher temperatures, however, N_2 reacts with more electropositive elements, such as those in group 13, to give binary nitrides, which range from covalent to ionic in character. Like the corresponding compounds of carbon, binary compounds of nitrogen with oxygen, hydrogen, or other nonmetals are usually covalent molecular substances.

Few binary molecular compounds of nitrogen are formed by direct reaction of the elements. At elevated temperatures, N_2 reacts with H_2 to form ammonia, with O_2 to form a mixture of NO and NO_2, and with carbon to form cyanogen (N≡C–C≡N); elemental nitrogen does not react with the halogens or the other chalcogens. Nonetheless, all the binary nitrogen halides (NX_3) are known. Except for NF_3, all are toxic, thermodynamically unstable, and potentially explosive, and all are prepared by reacting the halogen with NH_3 rather than N_2. Both nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are thermodynamically unstable, with positive free energies of formation. Unlike NO, NO_2 reacts readily with excess water, forming a 1:1 mixture of nitrous acid (HNO_2) and nitric acid (HNO_3):

$$2\,\mathrm{NO_2(g)} + \mathrm{H_2O(l)} \longrightarrow \mathrm{HNO_2(aq)} + \mathrm{HNO_3(aq)} \tag{18.8.2}$$

Nitrogen also forms N_2O (dinitrogen monoxide, or nitrous oxide), a linear molecule that is isoelectronic with CO_2 and can be represented as $^-N=N^+=O$. Like the other two oxides of nitrogen, nitrous oxide is thermodynamically unstable. The structures of the three common oxides of nitrogen are as follows:



> *Few binary molecular compounds of nitrogen are formed by the direct reaction of the elements.*

At elevated temperatures, nitrogen reacts with highly electropositive metals to form ionic nitrides, such as $\mathrm{Li_3N}$ and $\mathrm{Ca_3N_2}$. These compounds consist of ionic lattices formed by $\mathrm{M^{n^+}}$ and $\mathrm{N^{3-}}$ ions. Just as boron forms interstitial borides and carbon forms interstitial carbides, with less electropositive metals nitrogen forms a range of interstitial nitrides, in which nitrogen occupies holes in a close-packed metallic structure. Like the interstitial carbides and borides, these substances are typically very hard, high-melting materials that have metallic luster and conductivity.

Nitrogen also reacts with semimetals at very high temperatures to produce covalent nitrides, such as $\mathrm{Si_3N_4}$ and BN, which are solids with extended covalent network structures similar to those of graphite or diamond. Consequently, they are usually high melting and chemically inert materials.

Ammonia (NH_3) is one of the few thermodynamically stable binary compounds of nitrogen with a nonmetal. It is not flammable in air, but it burns in an $\mathrm{O_2}$ atmosphere:

$$4\,\mathrm{NH_3(g)} + 3\,\mathrm{O_2(g)} \longrightarrow 2\,\mathrm{N_2(g)} + 6\,\mathrm{H_2O(g)} \tag{18.8.3}$$

About 10% of the ammonia produced annually is used to make fibers and plastics that contain amide bonds, such as nylons and polyurethanes, while 5% is used in explosives, such as ammonium nitrate, TNT (trinitrotoluene), and nitroglycerine. Large amounts of anhydrous liquid ammonia are used as fertilizer.

Nitrogen forms two other important binary compounds with hydrogen. Hydrazoic acid ($\mathrm{HN_3}$), also called hydrogen azide, is a colorless, highly toxic, and explosive substance. Hydrazine ($\mathrm{N_2H_4}$) is also potentially explosive; it is used as a rocket propellant and to inhibit corrosion in boilers.

> *B, C, and N all react with transition metals to form interstitial compounds that are hard, high-melting materials.*

✓ Example 18.8.1

For each reaction, explain why the given products form when the reactants are heated.

a. $\mathrm{Sr(s)} + \mathrm{N_2O(g)} \xrightarrow{\Delta} \mathrm{SrO(s)} + \mathrm{N_2(g)}$
b. $\mathrm{NH_4NO_2(s)} \xrightarrow{\Delta} \mathrm{N_2(g)} + 2\,\mathrm{H_2O(g)}$
c. $\mathrm{Pb(NO_3)_2(s)} \xrightarrow{\Delta} \mathrm{PbO_2(s)} + 2\,\mathrm{NO_2(g)}$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. As an alkali metal, strontium is a strong reductant. If the other reactant can act as an oxidant, then a redox reaction will occur. Nitrous oxide contains nitrogen in a low oxidation state (+1), so we would not normally consider it an oxidant. Nitrous oxide is, however, thermodynamically unstable ($\Delta H°_f > 0$ and $\Delta G°_f > 0$), and it can be reduced to N_2, which is a stable species. Consequently, we predict that a redox reaction will occur.

b. When a substance is heated, a decomposition reaction probably will occur, which often involves the release of stable gases. In this case, ammonium nitrite contains nitrogen in two different oxidation states (−3 and +3), so an internal redox reaction is a possibility. Due to its thermodynamic stability, N_2 is the probable nitrogen-containing product, whereas we predict that H and O will combine to form H_2O.

c. Again, this is probably a thermal decomposition reaction. If one element is in an usually high oxidation state and another in a low oxidation state, a redox reaction will probably occur. Lead nitrate contains the Pb^{2+} cation and the nitrate anion, which contains nitrogen in its highest possible oxidation state (+5). Hence nitrogen can be reduced, and we know that lead can be oxidized to the +4 oxidation state. Consequently, it is likely that lead(II) nitrate will decompose to lead(IV) oxide and nitrogen dioxide when heated. Even though PbO_2 is a powerful oxidant, the release of a gas such as NO_2 can often drive an otherwise unfavorable reaction to completion (Le Chatelier's principle). Note, however, that PbO_2 will probably decompose to PbO at high temperatures.

? Exercise 18.8.1

Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $\mathrm{NO(g) + H_2O(l) \xrightarrow{\Delta}}$

b. $\mathrm{NH_4NO_3(s) \xrightarrow{\Delta}}$

c. $\mathrm{Sr(s) + N_2(g) \longrightarrow}$

Answer

a. $\mathrm{NO(g) + H_2O(l) \xrightarrow{\Delta} no reaction}$

b. $\mathrm{NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2\,H_2O(g)}$

c. $\mathrm{3\,Sr(s) + N_2(g) \longrightarrow Sr_3N_2(s)}$

Summary

Nitrogen behaves chemically like nonmetals, Nitrogen forms compounds in nine different oxidation states. Nitrogen does not form stable catenated compounds because of repulsions between lone pairs of electrons on adjacent atoms, but it does form multiple bonds with other second-period atoms. Nitrogen reacts with electropositive elements to produce solids that range from covalent to ionic in character. Reaction with electropositive metals produces ionic nitrides, reaction with less electropositive metals produces interstitial nitrides, and reaction with semimetals produces covalent nitrides.

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18.9: The Chemistry of Phosphorus

Learning Objectives

- Compare properties of Group 15 elements.
- Explain the major application of phosphate.
- Describe the equilibria of the ionization of phosphoric acid.

Phosphorus (P) is an essential part of life as we know it. Without the phosphates in biological molecules such as ATP, ADP and DNA, we would not be alive. Phosphorus compounds can also be found in the minerals in our bones and teeth. It is a necessary part of our diet. In fact, we consume it in nearly all of the foods we eat. Phosphorus is quite reactive. This quality of the element makes it an ideal ingredient for matches because it is so flammable. Phosphorus is a vital element for plants and that is why we put phosphates in our fertilizer to help them maximize their growth.

Introduction

Phosphorus plays a big role in our existence but it can also be dangerous. When fertilizers containing phosphorus enter the water, it produces rapid algae growth. This can lead to eutrophication of lakes and rivers; i.e., the ecosystem has an increase of chemical nutrients and this can led to negative environmental effects. With all the excess phosphorus, plants grow rapidly then die, causing a lack of oxygen in the water and an overall reduction of water quality. It is thus necessary to remove excess phosphorus from our wastewater. The process of removing the phosphorus is done chemically by reacting the phosphorus with compounds such as ferric chloride, ferric sulfate, and aluminum sulfate or aluminum chlorohydrate. Phosphorus, when combined with aluminum or iron, becomes an insoluble salt. The solubility equilibrium constants of $FePO_4$ and $AlPO_4$ are 1.3x10^{-22} and 5.8x10^{-19}, respectively. With solubilitys this low, the resulting precipitates can then be filtered out.

Figure 1. Phosphates can lead to excessive algae growth, which can be undesirable

Another example of the dangers of phosphorus is in the production of matches. The flammable nature and cheap manufacturing of white phosphorus made it possible to easily make matches around the turn of the 20th century. However, white phosphorus is highly toxic. Many workers in match factories developed brain damage and a disease called "phosphorus necrosis of the jaw" from exposure to toxic phosphorus vapors. Excess phosphorus accumulation caused their bone tissue to die and rot away. For this reason, we now use red phosphorus or phosphorus sesquisulfide in "safety" matches.

Discovery of Phosphorus

Named from the Greek word phosphoros ("bringer of light"), elemental phosphorus is not found in its elemental form because this form is quite reactive. Because of this factor it took a long period of time for it to be "discovered". The first recorded isolation of phosphorus was by alchemist Hennig Brand in 1669, involving about 60 pails of urine. After letting a large amount of urine putrefy for a long time, Brand distilled the liquid to a paste, heated the paste, discarded the salt formed, and put the remaining substance under cold water to form solid white phosphorus. Brand's process was not very efficient; the salt he discarded actually contained most of the phosphorus. Nevertheless, he obtained some pure, elemental phosphorus for his efforts. Others of the time improved the efficiency of the process by adding sand, but still continued to discard the salt. Later, phosphorus was manufactured from bone ash. Currently, the process for manufacturing phosphorus does not involve large amounts of putrefied urine or bone ash. Instead, manufacturers use calcium phosphate and coke (Emsley).

Allotropes of Phosphorus

Phosphorus is a nonmetal, solid at room temperature, and a poor conductor of heat and electricity. Phosphorus occurs in at least 10 allotropic forms, the most common (and reactive) of which is so-called white (or yellow) phosphorus, which looks like a waxy solid or plastic. It is very reactive and will spontaneously inflame in air, so it is stored under water. The other common form of phosphorus is red phosphorus, which is much less reactive and is one of the components on the striking surface of a match book. Red phosphorus can be converted to white phosphorus by careful heating.

White phosphorus consists of P_4 molecules, whereas the crystal structure of red phosphorus has a complicated network of bonding. White phosphorus has to be stored in water to prevent natural combustion, but red phosphorus is stable in air.

Figure 2: The four common allotropes of phosphorus. from Wikipedia.

When burned, red phosphorus also forms the same oxides as those obtained in the burning of white phosphosrus, P_4O_6 when air supply is limited, and P_4O_{10} when sufficient air is present.

Diphosphorus (P_2)

Diphosphorus (P_2) is the gaseous form of phosphorus that is thermodynamically stable above 1200 °C and until 2000 °C. It can be generated by heating white phosphorus (see below) to 1100 K and is very reactive with a bond-dissociation energy (117 kcal/mol or 490 kJ/mol) half that of dinitrogen (N_2).

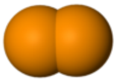

Figure 2: Diphosphorus molecule. (CC-SA-BY 3.0; Wikipedia)

White Phosphorus (P_4)

White phosphorus (P_4) has a tetrahedral structure. It is soft and waxy, but insoluble in water. Its glow occurs as a result of its vapors slowly being oxidized by the air. It is so thermodynamically unstable that it combusts in air. It was once used in fireworks and the U.S. military still uses it in incendiary bombs.

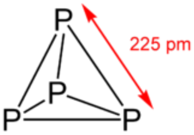

Figure 3: Structure of white phosphorus. (CC-SA-BY 3.0; Wikipedia)

This Youtube video link shows various experiments with white phosphorus, which help show the physical and chemical properties of it. It also shows white phosphorus combusting with air.

Red Phosphorus and Violet Phosphorus (Polymeric)

Red Phosphorus has more atoms linked together in a network than white phosphorus does, which makes it much more stable. It is not quite as flammable, but given enough energy it still reacts with air. For this reason, we now use red phosphorus in matches.

Figure 4: red phosphorus is in safety matches. (CC-SA-BY 3.0; Wikipedia)

Violet phosphorus is obtained from heating and crystallizing red phosphorus in a certain way. The phosphorus forms pentagonal "tubes".

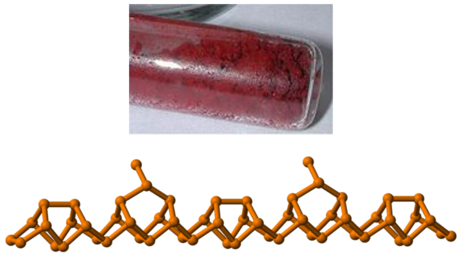

Figure 5. Structure of Violet Phosphorus. (CC-SA-BY 3.0; Wikipedia)

Black Phosphorus (Polymeric)

Black phosphorus is the most stable form; the atoms are linked together in puckered sheets, like graphite. Because of these structural similarities black phosphorus is also flaky like graphite and possesses other similar properties.

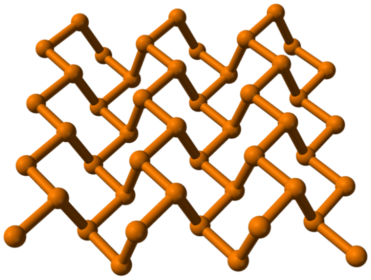

Figure 6. Ball-and-stick model of a sheet of phosphorus atoms in black phosphorus. (CC-SA-BY 3.0; Wikipedia)

Isotopes of Phosphorus

There are many isotopes of phosphorus, only one of which is stable (^{31}P). The rest of the isotopes are radioactive with generally very short half-lives, which vary from a few nanoseconds to a few seconds. Two of the radioactive phosphorus isotopes have longer half-lives: ^{32}P has a half-life of 14 days and ^{33}P has a half-life of 25 days. These half-lives are long enough to be useful for analysis, and for this reason the isotopes can be used to mark DNA.

^{32}P played an important role in the 1952 Hershey-Chase Experiment. In this experiment, Alfred Hershey and Martha Chase used radioactive isotopes of phosphorus and sulfur to determine that DNA was genetic material and not proteins. Sulfur can be found in proteins but not DNA, and phosphorus can be found in DNA but not proteins. This made phosphorus and sulfur effective markers of DNA and protein, respectively. The experiment was set up as follows: Hershey and Chase grew one sample of a virus in the presence of radioactive ^{35}S and another sample of a virus in the presence of ^{32}P. Then, they allowed both samples to infect bacteria. They blended the ^{35}S and the ^{32}P samples separately and centrifuged the two samples. Centrifuging separated the genetic material from the non-genetic material. The genetic material penetrated the solid that contained the bacterial cells at the bottom of the tube while the non-genetic material remained in the liquid. By analyzing their radioactive markers, Hershey and Chase found that the ^{32}P remained with the bacteria, and the ^{35}S remained in the supernatant liquid. These results were confirmed by further tests involving the radioactive phosphorus..

Phosphorus and Life

We get most elements from nature in the form of minerals. In nature, phosphorus exists in the form of phosphates. Rocks containing phosphate are fluoroapatite ($3\,Ca_3(PO_4)_2 \cdot CaF_2$), chloroapaptite, ($3\,Ca_3(PO_4)_2 \cdot CaCl_2$), and hydroxyapatite ($3\,Ca_3(PO_4)_2 \cdot Ca(OH)_2$). These minerals are very similar to the bones and teeth. The arrangements of atoms and ions of bones and teeth are similar to those of the phosphate-containing rocks. In fact, when the OH^- ions of the teeth are replaced by F^-, the teeth resist decay. This discovery led to a series of social and economical issues.

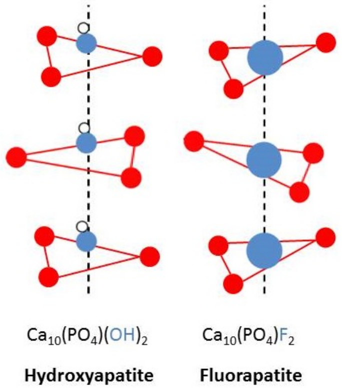

Figure 6: (left) Fluoride ions (F^-) replace hydroxyl groups (OH^-) in hydroxyapatite to form fluorapatite in the tooth enamel. (right) A portion of the apatite crystal lattice is depicted showing the replacement of hydroxide by fluoride (big blue circles). (Public Domain; Delmar Larsen).

Nitrogen, phosphorus and potassium are key ingredients for plants, and their contents are key in all forms of fertilizers. From an industrial and economical viewpoint, phosphorus-containing compounds are important commodities. Thus, the chemistry of phosphorus has academic, commercial and industrial interests.

Chemistry of Phosphorus

As a member of the Nitrogen Family, Group 15 on the Periodic Table, phosphorus has 5 valence shell electrons available for bonding. Its valence shell configuration is 3s^{2}3p^3. Phosphorus forms mostly covalent bonds. Any phosphorus rock can be used for the production of elemental phosphorus. Crushed phosphate rocks and sand (SiO_2) react at 1700 K to give phosphorus oxide, P_4O_{10}:

$$2\,Ca_3(PO_4)_2 + 6\,SiO_2 \rightarrow P_4O_{10} + 6\,CaSiO_3 \tag{18.9.1}$$

P_4O_{10} can be reduced by carbon:

$$P_4O_{10} + 10\,C \rightarrow P_4 + 10\,CO. \tag{18.9.2}$$

Waxy solids of white phosphorus are molecular crystals consisting of P_4 molecules. They have an interesting property in that they undergo spontaneous combustion in air:

$$P_4 + 5\,O_2 \rightarrow P_4O_{10} \tag{18.9.3}$$

The structure of P_4 can be understood by thinking of the electronic configuration ($s^2\,p^3$) of P in bond formation. Sharing three electrons with other P atoms gives rise to the 6 $P-P$ bonds, leaving a lone pair occupying the 4th position in a distorted tetrahedron.

When burned with insufficient oxygen, P_4O_6 is formed:

$$P_4 + 3\,O_2 \rightarrow P_4O_6 \tag{18.9.4}$$

Into each of the $P-P$ bonds, an O atom is inserted.

Burning phosphorus with excess oxygen results in the formation of P_4O_{10}. An additional O atom is attached to the P directly:

$$P_4 + 5\,O_2 \rightarrow P_4O_{10} \tag{18.9.5}$$

Thus, the oxides P_4O_6 and P_4O_{10} share interesting features. Oxides of phosphorus, P_4O_{10}, dissolve in water to give phosphoric acid,

$$P_4O_{10} + 6\,H_2O \rightarrow 4\,H_3PO_4 \tag{18.9.6}$$

Phosphoric acid is a polyprotic acid, and it ionizes in three stages:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \tag{18.9.7}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \tag{18.9.8}$$

$$\mathrm{HPO_4^{2-}} \rightarrow \mathrm{H^+} + \mathrm{PO_4^{3-}} \tag{18.9.9}$$

Phosphoric Acid

Phosphoric acid is a polyprotic acid, which makes it an ideal buffer. It gets harder and harder to separate the hydrogen from the phosphate, making the pK$_a$ values increase in basicity: 2.12, 7.21, and 12.67. The conjugate bases $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} can be mixed to form buffer solutions.

Table 1: Ionization constants for the successive deprotonation of phosphoric acid states

Reaction	Dissociation Constant
$H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO^{4-}$	$K_{a1}=7.5\text{x}10^{-3}$
$H_2PO_4^- + H_2O \rightarrow H_3O^+ + HPO_4^{2-}$	$K_{a2}=6.2\text{x}10^{-8}$
$H_2PO_4^- + H_2O \rightarrow H_3O^+ + PO_4^{3-}$	$K_{a3}=2.14\text{x}10^{-13}$
Overall: $H_3PO_4 + 3H_2O \rightarrow 3H_3O^+ + PO_4^{3-}$	

Past and Present Uses of Phosphorus

Commercially, phosphorus compounds are used in the manufacture of phosphoric acid (H_3PO_4) (found in soft drinks and used in fertilizer compounding). Other compounds find applications in fireworks and, of course, phosphorescent compounds which glow in the dark. Phosphorus compounds are currently used in foods, toothpaste, baking soda, matches, pesticides, nerve gases, and fertilizers. Phosphoric acid is not only used in buffer solutions; it is also a key ingredient of Coca Cola and other sodas! Phosphorus compounds were once used in detergents as a water softener until they raised concerns about pollution and eutrophication. Pure phosphorus was once prescribed as a medicine and an aphrodisiac until doctors realized it was poisonous (Emsley).

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Questions

1. About 85% of the total industrial output of phosphoric acid is used
   a. in the detergent industry
   b. to produce buffer solutions
   c. in the paint industry
   d. to produce superphosphate fertilizers
   e. in the manufacture of plastics
2. What is the product when phosphorus pentoxide $\mathrm{P_4O_{10}}$ reacts with water? Give the formula of the product.
3. What is the phosphorus-containing product when $\mathrm{PCl_3}$ reacts with water? Give the formula.

Solutions

1. *Answer...* d

   The middle number, (for example, 6-5-8) specifies the percentage of phosphorus compound in a fertilizer. Phosphorus is an important element for plant life.

2. *Answer* $\mathrm{H_3PO_4}$

$$\mathrm{P_4O_{10}} + 6\,\mathrm{H_2O} \rightarrow 4\,\mathrm{H_3PO_4}$$

3. *Answer* $\mathrm{H_3PO_3}$

$$\mathrm{PCl_3} + 3\,\mathrm{H_2O} \rightarrow \mathrm{H_3PO_3} + 3\,\mathrm{HCl}$$

   This is a weaker acid than $\mathrm{H_3PO_4}$.

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18.10: The Group 6A Elements

Learning Objectives

- To understand the trends in properties and reactivity of the group 16 elements: the chalcogens.

The chalcogens are the first group in the p block to have no stable metallic elements. All isotopes of polonium (Po), the only metal in group 16, are radioactive, and only one element in the group, tellurium (Te), can even be described as a semimetal. As in groups 14 and 15, the lightest element of group 16, oxygen, is found in nature as the free element.

Of the group 16 elements, only sulfur was known in ancient times; the others were not discovered until the late 18th and 19th centuries. Sulfur is frequently found as yellow crystalline deposits of essentially pure S_8 in areas of intense volcanic activity or around hot springs. As early as the 15th century BC, sulfur was used as a fumigant in Homeric Greece because, when burned, it produces SO_2 fumes that are toxic to most organisms, including vermin hiding in the walls and under the floors of houses. Hence references to sulfur are common in ancient literature, frequently in the context of religious purification. In fact, the association of sulfur with the divine was so pervasive that the prefixes thio- (meaning “sulfur”) and theo- (meaning “god”) have the same root in ancient Greek. Though used primarily in the production of sulfuric acid, sulfur is also used to manufacture gunpowder and as a cross-linking agent for rubber, which enables rubber to hold its shape but retain its flexibility.

> *Group 16 is the first group in the p block with no stable metallic elements.*

Oxygen was not discovered until 1771, when the Swedish pharmacist Carl Wilhelm Scheele found that heating compounds such as KNO_3, Ag_2CO_3, and HgO produced a colorless, odorless gas that supported combustion better than air. The results were not published immediately, however, so Scheele’s work remained unknown until 1777. Unfortunately, this was nearly two years after a paper by the English chemist Joseph Priestley had been published, describing the isolation of the same gas by using a magnifying glass to focus the sun’s rays on a sample of HgO. Oxygen is used primarily in the steel industry during the conversion of crude iron to steel using the Bessemer process. Another important industrial use of oxygen is in the production of TiO_2, which is commonly used as a white pigment in paints, paper, and plastics.

Figure 18.10.1: A crystalline sulfur deposit. This sulfur deposit is located around a volcanic vent in Kilauea Crater, Hawaii.

Tellurium was discovered accidentally in 1782 by the Austrian chemist Franz Joseph Müller von Reichenstein, the chief surveyor of mines in Transylvania who was also responsible for the analysis of ore samples. The silvery-white metal had the same density as antimony but very different properties. Because it was difficult to analyze, Müller called it metallum problematicum (meaning “difficult metal”). The name tellurium (from the Latin tellus, meaning “earth”) was coined by another Austrian chemist, Martin Klaproth, who demonstrated in 1798 that Müller’s “difficult metal” was actually a new element. Tellurium is used to color glass and ceramics, in the manufacture of blasting caps, and in thermoelectric devices.

Jöns Jakob Berzelius (1779–1848)

Berzelius was born into a well-educated Swedish family, but both parents died when he was young. He studied medicine at the University of Uppsala, where his experiments with electroshock therapy caused his interests to turn to electrochemistry. Berzelius devised the system of chemical notation that we use today. In addition, he discovered six elements (cerium, thorium, selenium, silicon, titanium, and zirconium).

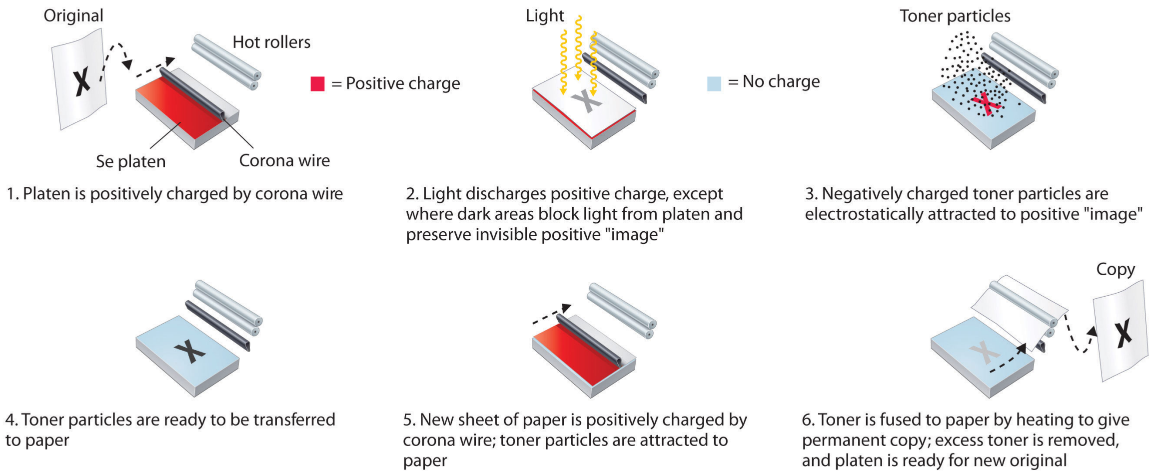


Figure 18.10.1: The Chemistry of Photocopying. Because amorphous selenium is a photosensitive semiconductor, exposing an electrostatically charged Se film to light causes the positive charge on the film to be discharged in all areas that are white in the original. Dark areas in the original block the light and generate an invisible, positively charged image. To produce an image on paper, negatively charged toner particles are attracted to the positive image, transferred to a negatively charged sheet of blank paper, and fused with the paper at high temperature to give a permanent image.

The heaviest chalcogen, polonium, was isolated after an extraordinary effort by Marie Curie. Although she was never able to obtain macroscopic quantities of the element, which she named for her native country of Poland, she demonstrated that its chemistry required it to be assigned to group 16. Marie Curie was awarded a second Nobel Prize in Chemistry in 1911 for the discovery of radium and polonium.

Preparation and General Properties of the Group 16 Elements

Oxygen is by far the most abundant element in Earth’s crust and in the hydrosphere (about 44% and 86% by mass, respectively). The same process that is used to obtain nitrogen from the atmosphere produces pure oxygen. Oxygen can also be obtained by the electrolysis of water, the decomposition of alkali metal or alkaline earth peroxides or superoxides, or the thermal decomposition of simple inorganic salts, such as potassium chlorate in the presence of a catalytic amount of MnO_2:

$$2KClO_3(s) \underset{\Delta}{\overset{MnO_2(s)}{\rightleftharpoons}} 2KCl(s) + 3O_2(g) \tag{18.10.1}$$

Unlike oxygen, sulfur is not very abundant, but it is found as elemental sulfur in rock formations overlying salt domes, which often accompany petroleum deposits (Figure 18.10.1). Sulfur is also recovered from H_2S and organosulfur compounds in crude oil and coal and from metal sulfide ores such as pyrite (FeS_2).

Pyrite (FeS_2). Because of its lustrous golden yellow cubic crystals, FeS_2 is sometimes mistaken for gold, giving rise to its common name “fool’s gold.” Real gold, however, is much denser than FeS_2, and gold is soft and malleable rather than hard and brittle.

Because selenium and tellurium are chemically similar to sulfur, they are usually found as minor contaminants in metal sulfide ores and are typically recovered as by-products. Even so, they are as abundant in Earth’s crust as silver, palladium, and gold. One of the best sources of selenium and tellurium is the “slime” deposited during the electrolytic purification of copper. Both of these elements are notorious for the vile odors of many of their compounds. For example, when the body absorbs even trace amounts of tellurium, dimethyltellurium [$(CH_3)_2Te$] is produced and slowly released in the breath and perspiration, resulting in an intense garlic-like smell that is commonly called “tellurium breath.”

With their ns^{2}np^4 electron configurations, the chalcogens are two electrons short of a filled valence shell. Thus in reactions with metals, they tend to acquire two additional electrons to form compounds in the −2 oxidation state. This tendency is greatest for oxygen, the chalcogen with the highest electronegativity. The heavier, less electronegative chalcogens can lose either four np electrons or four np and two ns electrons to form compounds in the +4 and +6 oxidation state, respectively, as shown in Table Figure 18.10.1 As with the other groups, the lightest member in the group, in this case oxygen, differs greatly from the others in size, ionization energy, electronegativity, and electron affinity, so its chemistry is unique. Also as in the other groups, the second and third members (sulfur and selenium) have similar properties because of shielding effects. Only polonium is metallic, forming either the hydrated Po^{2+} or Po^{4+} ion in aqueous solution, depending on conditions.

Table 18.10.1: Selected Properties of the Group 16 Elements

Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
atomic mass (amu)	16.00	32.07	78.96	127.60	209
atomic number	8	16	34	52	84
atomic radius (pm)	48	88	103	123	135
atomic symbol	O	S	Se	Te	Po
density (g/cm^3) at 25°C	1.31 (g/L)	2.07	4.81	6.24	9.20
electron affinity (kJ/mol)	−141	−200	−195	−190	−180
electronegativity	3.4	2.6	2.6	2.1	2.0
first ionization energy (kJ/mol)	1314	1000	941	869	812
ionic radius (pm)†	140 (−2)	184 (−2), 29 (+6)	198 (−2), 42 (+6)	221 (−2), 56 (+6)	230 (−2), 97 (+4)
melting point/boiling point (°C)	−219/−183	115/445	221/685	450/988	254/962
normal oxidation state(s)	−2	+6, +4, −2	+6, +4, −2	+6, +4, −2	+2 (+4)
product of reaction with H_2	H_2O	H_2S	H_2Se	none	none
product of reaction with N_2	NO, NO_2	none	none	none	none
product of reaction with O_2	—	SO_2	SeO_2	TeO_2	PoO_2
product of reaction with X_2	O_2F_2	SF_6, S_2Cl_2, S_2Br_2	SeF_6, SeX_4	TeF_6, TeX_4	PoF_4, $PoCl_2$, $PoBr_2$
standard reduction potential (E°, V) (E^0 → H_2E in acidic solution)	+1.23	+0.14	−0.40	−0.79	−1.00
type of oxide	—	acidic	acidic	amphoteric	basic

*The configuration shown does not include filled d and f subshells.

†The values cited for the hexacations are for six-coordinate ions and are only estimated values.

Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
valence electron configuration*	$2s^2 2p^4$	$3s^2 3p^4$	$4s^2 4p^4$	$5s^2 5p^4$	$6s^2 6p^4$

*The configuration shown does not include filled d and f subshells.

†The values cited for the hexacations are for six-coordinate ions and are only estimated values.

Reactions and Compounds of Oxygen

As in groups 14 and 15, the lightest group 16 member has the greatest tendency to form multiple bonds. Thus elemental oxygen is found in nature as a diatomic gas that contains a net double bond: O=O. As with nitrogen, electrostatic repulsion between lone pairs of electrons on adjacent atoms prevents oxygen from forming stable catenated compounds. In fact, except for O_2, all compounds that contain O–O bonds are potentially explosive. Ozone, peroxides, and superoxides are all potentially dangerous in pure form. Ozone (O_3), one of the most powerful oxidants known, is used to purify drinking water because it does not produce the characteristic taste associated with chlorinated water. Hydrogen peroxide (H_2O_2) is so thermodynamically unstable that it has a tendency to undergo explosive decomposition when impure:

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)} \qquad \Delta G^o = -119\ kJ/mol \tag{18.10.2}$$

> *As in groups 14 and 15, the lightest element in group 16 has the greatest tendency to form multiple bonds.*

Despite the strength of the O=O bond (D_{O_2} = 494 kJ/mol), O_2 is extremely reactive, reacting directly with nearly all other elements except the noble gases. Some properties of O_2 and related species, such as the peroxide and superoxide ions, are in Table 18.10.2 With few exceptions, the chemistry of oxygen is restricted to negative oxidation states because of its high electronegativity (χ = 3.4). Unlike the other chalcogens, oxygen does not form compounds in the +4 or +6 oxidation state. Oxygen is second only to fluorine in its ability to stabilize high oxidation states of metals in both ionic and covalent compounds. For example, AgO is a stable solid that contains silver in the unusual Ag(II) state, whereas OsO_4 is a volatile solid that contains Os(VIII). Because oxygen is so electronegative, the O–H bond is highly polar, creating a large bond dipole moment that makes hydrogen bonding much more important for compounds of oxygen than for similar compounds of the other chalcogens.

Table 18.10.2: Some Properties of O_2 and Related Diatomic Species

Species	Bond Order	Number of Unpaired e^-	O–O Distance (pm)*
O_2^+	2.5	1	112
O_2	2	2	121
O_2^-	1.5	1	133
O_2^{2-}	1	0	149

*Source of data: Lauri Vaska, “Dioxygen-Metal Complexes: Toward a Unified View,” Accounts of Chemical Research 9 (1976): 175.

Metal oxides are usually basic, and nonmetal oxides are acidic, whereas oxides of elements that lie on or near the diagonal band of semimetals are generally amphoteric. A few oxides, such as CO and PbO_2, are neutral and do not react with water, aqueous acid, or aqueous base. Nonmetal oxides are typically covalent compounds in which the bonds between oxygen and the nonmetal are polarized ($E^{\delta+}$–$O^{\delta-}$). Consequently, a lone pair of electrons on a water molecule can attack the partially positively charged E atom to eventually form an oxoacid. An example is reacting sulfur trioxide with water to form sulfuric acid:

$$H_2O_{(l)} + SO_{3(g)} \rightarrow H_2SO_{4(aq)} \tag{18.10.3}$$

The oxides of the semimetals and of elements such as Al that lie near the metal/nonmetal dividing line are amphoteric, as we expect:

$$Al_2O_{3(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)} \tag{18.10.4}$$

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} \tag{18.10.5}$$

> *Oxides of metals tend to be basic, oxides of nonmetals tend to be acidic, and oxides of elements in or near the diagonal band of semimetals are generally amphoteric.*

✓ Example 18.10.1

For each reaction, explain why the given products form.

a. $Ga_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Ga(OH)_4^-(aq)$
b. $3H_2O_2(aq) + 2MnO_4^-(aq) + 2H^+(aq) \rightarrow 3O_2(g) + 2MnO_2(s) + 4H_2O(l)$
c. $KNO_3(s) \xrightarrow{\Delta} KNO(s) + O_2(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. Gallium is a metal. We expect the oxides of metallic elements to be basic and therefore not to react with aqueous base. A close look at the periodic table, however, shows that gallium is close to the diagonal line of semimetals. Moreover, aluminum, the element immediately above gallium in group 13, is amphoteric. Consequently, we predict that gallium will behave like aluminum (Equation 18.10.5).
b. Hydrogen peroxide is an oxidant that can accept two electrons per molecule to give two molecules of water. With a strong oxidant, however, H_2O_2 can also act as a reductant, losing two electrons (and two protons) to produce O_2. Because the other reactant is permanganate, which is a potent oxidant, the only possible reaction is a redox reaction in which permanganate is the oxidant and hydrogen peroxide is the reductant. Recall that reducing permanganate often gives MnO_2, an insoluble brown solid. Reducing MnO_4^- to MnO_2 is a three-electron reduction, whereas the oxidation of H_2O_2 to O_2 is a two-electron oxidation.
c. This is a thermal decomposition reaction. Because KNO_3 contains nitrogen in its highest oxidation state (+5) and oxygen in its lowest oxidation state (−2), a redox reaction is likely. Oxidation of the oxygen in nitrate to atomic oxygen is a two-electron process per oxygen atom. Nitrogen is likely to accept two electrons because oxoanions of nitrogen are known only in the +5 (NO_3^-) and +3 (NO_2^-) oxidation states.

? Exercise 18.10.2

Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $SiO_2(s) + H^+(aq) \rightarrow$
b. $NO(g) + O_2(g) \rightarrow$
c. $SO_3(g) + H_2O(l) \rightarrow$
d. $H_2O_2(aq) + I^-(aq) \rightarrow$

Answer

a. $SiO_2(s) + H^+(aq) \rightarrow$ no reaction
b. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
c. $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
d. $H_2O_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2OH^-(aq)$

Reactions and Compounds of the Heavier Chalcogens

Because most of the heavier chalcogens (group 16) and pnicogens (group 15) are nonmetals, they often form similar compounds. For example, both third-period elements of these groups (phosphorus and sulfur) form catenated compounds and form multiple allotropes. Consistent with periodic trends, the tendency to catenate decreases as we go down the column.

Sulfur and selenium both form a fairly extensive series of catenated species. For example, elemental sulfur forms S_8 rings packed together in a complex “crankshaft” arrangement (Figure 18.10.2), and molten sulfur contains long chains of sulfur atoms connected by S–S bonds. Moreover, both sulfur and selenium form polysulfides (S_n^{2-}) and polyselenides (Se_n^{2-}), with $n \le 6$. The only stable allotrope of tellurium is a silvery white substance whose properties and structure are similar to those of one of the selenium allotropes. Polonium, in contrast, shows no tendency to form catenated compounds. The striking decrease in structural complexity from sulfur to polonium is consistent with the decrease in the strength of single bonds and the increase in metallic character as we go down the group.

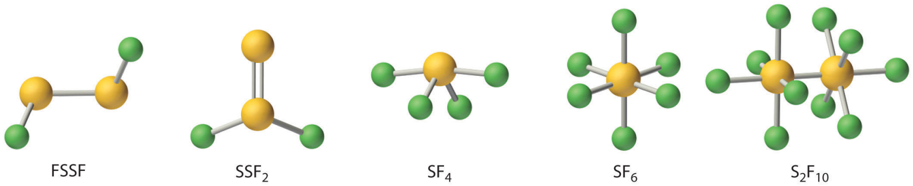


Figure 18.10.2: The Structures of the Known Fluorides of Sulfur. Five stable sulfur fluorides are known, containing sulfur in oxidation states ranging from +1 to +6. All are volatile molecular compounds that vary tremendously in stability and toxicity. Although both SF_6 and S_2F_{10} are very stable, S_2F_{10} is toxic and SF_6 is not. The other three are highly reactive substances.

As in group 15, the reactivity of elements in group 16 decreases from lightest to heaviest. For example, selenium and tellurium react with most elements but not as readily as sulfur does. As expected for nonmetals, sulfur, selenium, and tellurium do not react with water, aqueous acid, or aqueous base, but all dissolve in strongly oxidizing acids such as HNO_3 to form oxoacids such as H_2SO_4. In contrast to the other chalcogens, polonium behaves like a metal, dissolving in dilute HCl to form solutions that contain the Po^{2+} ion.

> *Just as with the other groups, the tendency to catenate, the strength of single bonds, and reactivity decrease down the group.*

Fluorine reacts directly with all chalcogens except oxygen to produce the hexafluorides (YF_6), which are extraordinarily stable and unreactive compounds. Four additional stable fluorides of sulfur are known; thus sulfur oxidation states range from +1 to +6 (Figure 18.10.2). In contrast, only four fluorides of selenium (SeF_6, SeF_4, FSeSeF, and $SeSeF_2$) and only three of tellurium (TeF_4, TeF_6, and Te_2F_{10}) are known.

Direct reaction of the heavier chalcogens with oxygen at elevated temperatures gives the dioxides (YO_2), which exhibit a dramatic range of structures and properties. The dioxides become increasingly metallic in character down the group, as expected, and the coordination number of the chalcogen steadily increases. Thus SO_2 is a gas that contains V-shaped molecules (as predicted by the valence-shell electron-pair repulsion model), SeO_2 is a white solid with an infinite chain structure (each Se is three coordinate), TeO_2 is a light yellow solid with a network structure in which each Te atom is four coordinate, and PoO_2 is a yellow ionic solid in which each Po^{4+} ion is eight coordinate.

The dioxides of sulfur, selenium, and tellurium react with water to produce the weak, diprotic oxoacids (H_2YO_3—sulfurous, selenous, and tellurous acid, respectively). Both sulfuric acid and selenic acid (H_2SeO_4) are strong acids, but telluric acid [$Te(OH)_6$] is quite different. Because tellurium is larger than either sulfur or selenium, it forms weaker π bonds to oxygen. As a result, the most stable structure for telluric acid is $Te(OH)_6$, with six Te–OH bonds rather than Te=O bonds. Telluric acid therefore behaves like a weak triprotic acid in aqueous solution, successively losing the hydrogen atoms bound to three of the oxygen atoms. As expected for compounds that contain elements in their highest accessible oxidation state (+6 in this case), sulfuric, selenic, and telluric acids are oxidants. Because the stability of the highest oxidation state decreases with increasing atomic number, telluric acid is a stronger oxidant than sulfuric acid.

> *The stability of the highest oxidation state of the chalcogens decreases down the column.*

Sulfur and, to a lesser extent, selenium react with carbon to form an extensive series of compounds that are structurally similar to their oxygen analogues. For example, CS_2 and CSe_2 are both volatile liquids that contain C=S or C=Se bonds and have the same linear structure as CO_2. Because these double bonds are significantly weaker than the C=O bond, however, CS_2, CSe_2, and related compounds are less stable and more reactive than their oxygen analogues. The chalcogens also react directly with nearly all metals to form compounds with a wide range of stoichiometries and a variety of structures. Metal chalcogenides can contain either the simple chalcogenide ion (Y^{2-}), as in Na_2S and FeS, or polychalcogenide ions (Y_n^{2-}), as in FeS_2 and Na_2S_5.

> *The dioxides of the group 16 elements become increasingly basic, and the coordination number of the chalcogen steadily increases down the group.*

Ionic chalcogenides like Na_2S react with aqueous acid to produce binary hydrides such as hydrogen sulfide (H_2S). Because the strength of the Y–H bond decreases with increasing atomic radius, the stability of the binary hydrides decreases rapidly down the group. It is perhaps surprising that hydrogen sulfide, with its familiar rotten-egg smell, is much more toxic than hydrogen cyanide (HCN), the gas used to execute prisoners in the “gas chamber.” Hydrogen sulfide at relatively low concentrations deadens the olfactory receptors in the nose, which allows it to reach toxic levels without detection and makes it especially dangerous.

✓ Example 18.10.2

For each reaction, explain why the given product forms or no reaction occurs.

a. $SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$
b. $SF_6(g) + H_2O(l) \rightarrow$ no reaction
c. $2Se(s) + Cl_2(g) \rightarrow Se_2Cl_2(l)$

Given: balanced chemical equations

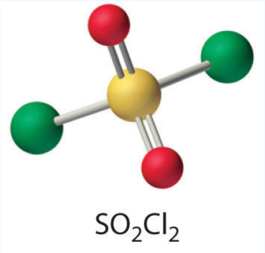
Asked for: why the given products (or no products) form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form or why no reaction occurs.

Solution

a. One of the reactants (Cl_2) is an oxidant. If the other reactant can be oxidized, then a redox reaction is likely. Sulfur dioxide contains sulfur in the +4 oxidation state, which is 2 less than its maximum oxidation state. Sulfur dioxide is also known to be a mild reducing agent in aqueous solution, producing sulfuric acid as the oxidation product. Hence a redox reaction is probable. The simplest reaction is the formation of SO_2Cl_2 (sulfuryl chloride), which is a tetrahedral species with two S–Cl and two S=O bonds.



b. Sulfur hexafluoride is a nonmetallic halide. Such compounds normally react vigorously with water to produce an oxoacid of the nonmetal and the corresponding hydrohalic acid. In this case, however, we have a highly stable species, presumably because all of sulfur’s available orbitals are bonding orbitals. Thus SF_6 is not likely to react with water.
c. Here we have the reaction of a chalcogen with a halogen. The halogen is a good oxidant, so we can anticipate that a redox reaction will occur. Only fluorine is capable of oxidizing the chalcogens to a +6 oxidation state, so we must decide between $SeCl_4$ and Se_2Cl_2 as the product. The stoichiometry of the reaction determines which of the two is obtained: $SeCl_4$ or Se_2Cl_2.

? Exercise 18.10.2

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $Te(s) + Na(s) \xrightarrow{\Delta}$
b. $SF_4(g) + H_2O(l) \rightarrow$
c. $CH_3SeSeCH_3(soln) + K(s) \rightarrow$
d. $Li_2Se(s) + H^+(aq) \rightarrow$

Answer

a. $Te(s) + 2Na(s) \rightarrow Na_2Te(s)$
b. $SF_4(g) + 3H_2O(l) \rightarrow H_2SO_3(aq) + 4HF(aq)$
c. $CH_3SeSeCH_3(soln) + 2K(s) \rightarrow 2KCH_3Se(soln)$
d. $Li_2Se(s) + 2H^+(aq) \rightarrow H_2Se(g) + 2Li^+(aq)$

Summary

The chalcogens have no stable metallic elements. The tendency to catenate, the strength of single bonds, and the reactivity all decrease moving down the group. Because the electronegativity of the chalcogens decreases down the group, so does their tendency to acquire two electrons to form compounds in the −2 oxidation state. The lightest member, oxygen, has the greatest tendency to form multiple bonds with other elements. It does not form stable catenated compounds, however, due to repulsions between lone pairs of electrons on adjacent atoms. Because of its high electronegativity, the chemistry of oxygen is generally restricted to compounds in which it has a negative oxidation state, and its bonds to other elements tend to be highly polar. Metal oxides are usually basic, and nonmetal oxides are acidic, whereas oxides of elements along the dividing line between metals and nonmetals are amphoteric. The reactivity, the strength of multiple bonds to oxygen, and the tendency to form catenated compounds all decrease down the group, whereas the maximum coordination numbers increase. Because Te=O bonds are comparatively weak, the most stable oxoacid of tellurium contains six Te–OH bonds. The stability of the highest oxidation state (+6) decreases down the group. Double bonds between S or Se and second-row atoms are weaker than the analogous C=O bonds because of reduced orbital overlap. The stability of the binary hydrides decreases down the group.

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18.11: The Chemistry of Oxygen

Oxygen is an element that is widely known by the general public because of the large role it plays in sustaining life. Without oxygen, animals would be unable to breathe and would consequently die. Oxygen not only is important to supporting life, but also plays an important role in many other chemical reactions. Oxygen is the most common element in the earth's crust and makes up about 20% of the air we breathe. Historically the discovery of oxygen as an element essential for combustion stands at the heart of the phlogiston controversy (see below).

The Origin and History

Oxygen is found in the group 16 elements and is considered a chalcogen. Named from the Greek oxys + genes, "acid-former", oxygen was discovered in 1772 by Scheele and independently by Priestly in 1774. Oxygen was given its name by the French scientist, Antoine Lavoisier.

Scheele discovered oxygen through an experiment which involved burning manganese oxide. Scheele came to find that the hot manganese oxide produced a gas which he called "fire air". He also came to find that when this gas was able to come into contact with charcoal, it produced beautiful bright sparks. All of the other elements produced the same gas. Although Scheele discovered oxygen, he did not publish his work until three years after another chemist, Joseph Priestly, discovered oxygen. Joseph Priestly, an English chemist, repeated Scheele's experiment in 1774 using a slightly different setup. Priestly used a 12 in burning glass and aimed the sunlight directly towards the compound that he was testing, mercuric oxide. As a result, he was able to "discover better air" that was shown to expand a mouse's lifetime to four times as long and caused a flame to burn with higher intensity. Despite these experiments, both chemists were not able to pinpoint exactly what this element was. It was not until 1775 that Antoine Lavoisier, a French chemist, was able to recognize this unknown gas as an element.

Our atmosphere currently contains about 21% of free oxygen. Oxygen is produced in various ways. The process of photochemical dissociation in which water molecules are broken up by ultraviolet rays produces about 1-2% of our oxygen. Another process that produces oxygen is photosynthesis which is performed by plants and photosynthetic bacteria. Photosynthesis occurs through the following general reaction:

$$\mathrm{CO_2 + H_2O + h\nu \rightarrow organic\ compounds + O_2}$$

The Dangers of Phlogiston

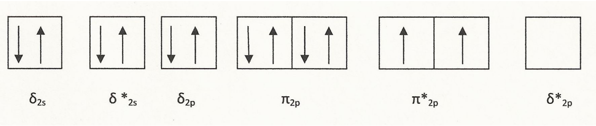
Phlogiston theory is the outdated belief that a fire-like element called phlogiston is contained within combustible bodies and released during combustion. The name comes from the Ancient Greek φλογιστόν phlogistón (burning up), from φλόξ phlóx (flame). It was first stated in 1667 by Johann Joachim Becher, and then put together more formally by Georg Ernst Stahl. The theory attempted to explain burning processes such as combustion and rusting, which are now collectively known as oxidation.

Properties

- Element number: 8
- Atomic weight 15.9994
- Color: gas form- colorless, liquid- pale blue
- Melting point: 54.36K
- Boiling point: 90.2 K
- Density: .001429
- 21% of earth's atmosphere
- Third most abundant element in the universe
- Most abundant element in Earth's crust at 45.4%
- 3 Stable isotopes
- Ionization energy: 13.618 eV
- Oxygen is easily reduced and is a great oxidizing agent making it readily reactive with other elements

Magnetic Properties of Oxygen

Oxygen (O_2) is paramagnetic. An oxygen molecule has six valence electrons, so the O_2 molecule has 12 valence electrons with the electron configuration shown below:



As shown, there are two unpaired electrons, which causes O_2 to be paramagnetic. There are also eight valence electrons in the bonding orbitals and four in antibonding orbitals, which makes the bond order 2. This accounts for the double covalent bond that is present in O_2.

Video* 18.11.1*: A chemical demonstration of the paramagnetism of molecular oxygen, as shown by the attraction of liquid oxygen to magnets.

As shown in Video 18.11.1, since molecular oxygen (O_2) has unpaired electrons, it is paramagnetic and is attracted to the magnet. In contrast, molecular nitrogen (N_2) has no unpaired electrons and is not attracted to the magnet.

General Chemistry of Oxygen

Oxygen normally has an oxidation state of -2, but is capable of having oxidation states of -2, -1, -1/2, 0, +1, and +2. The oxidation states of oxides, peroxides and superoxides are as follows:

- Oxides: O^{-2} ,
- peroxides: O_2^{-2} ,

- superoxide: O_2^{-1}.

Oxygen does not react with itself, nitrogen, or water under normal conditions. Oxygen does, however, dissolve in water at 20 degrees Celsius and 1 atmosphere. Oxygen also does not normally react with bases or acids. Group 1 metals (alkaline metals) are very reactive with oxygen and must be stored away from oxygen in order to prevent them from becoming oxidized. The metals at the bottom of the group are more reactive than those at the top. The reactions of a few of these metals are explored in more detail below.

Lithium: Reacts with oxygen to form white lithium oxide in the reaction below.

$$4\,\mathrm{Li} + \mathrm{O_2} \rightarrow 2\,\mathrm{Li_2O} \tag{18.11.1}$$

Sodium: Reacts with oxygen to form a white mixture of sodium oxide and sodium peroxide. The reactions are shown below.

- Sodium oxide:

$$4\,\mathrm{Na} + \mathrm{O_2} \rightarrow 2\,\mathrm{Na_2O} \tag{18.11.2}$$

- Sodium peroxide:

$$2\,\mathrm{Na} + \mathrm{O_2} \rightarrow \mathrm{Na_2O_2} \tag{18.11.3}$$

Potassium: Reacts with oxygen to form a mixture of potassium peroxide and potassium superoxide. The reactions are shown below.

- Potassium peroxide:

$$2\,\mathrm{K} + \mathrm{O_2} \rightarrow 2\,\mathrm{K_2O_2} \tag{18.11.4}$$

- Potassium superoxide:

$$\mathrm{K} + \mathrm{O_2} \rightarrow \mathrm{KO_2} \tag{18.11.5}$$

Rubidium and Cesium: Both metals react to produce superoxides through the same process as that of the potassium superoxide reaction.

> *The oxides of these metals form metal hydroxides when they react with water. These metal hydroxides make the solution basic or alkaline, hence the name alkaline metals.*

Group 2 metals (alkaline earth metals) react with oxygen through the process of burning to form metal oxides but there are a few exceptions.

Beryllium is very difficult to burn because it has a layer of beryllium oxide on its surface which prevents further interaction with oxygen. Strontium and barium react with oxygen to form peroxides. The reaction of barium and oxygen is shown below, and the reaction with strontium would be the same.

$$\mathrm{Ba(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{BaO_2(s)} \tag{18.11.6}$$

Group 13 reacts with oxygen in order to form oxides and hydroxides that are of the form X_2O_3 and $X(OH)_3$. The variable X represents the various group 13 elements. As you go down the group, the oxides and hydroxides get increasingly basic.

Group 14 elements react with oxygen to form oxides. The oxides formed at the top of the group are more acidic than those at the bottom of the group. Oxygen reacts with silicon and carbon to form silicon dioxide and carbon dioxide. Carbon is also able to react with oxygen to form carbon monoxide, which is slightly acidic. Germanium, tin, and lead react with oxygen to form monoxides and dioxides that are amphoteric, which means that they react with both acids and bases.

Group 15 elements react with oxygen to form oxides. The most important are listed below.

- Nitrogen: N_2O, NO, N_2O_3, N_2O_4, N_2O_5
- Phosphorus: P_4O_6, P_4O_8, P_2O_5
- Arsenic: As_2O_3, As_2O_5
- Antimony: Sb_2O_3, Sb_2O_5
- Bismuth: Bi_2O_3, Bi_2O_5

Group 16 elements react with oxygen to form various oxides. Some of the oxides are listed below.

- Sulfur: SO, SO_2, SO_3, S_2O_7
- Selenium: SeO_2, SeO_3
- Tellurium: TeO, TeO_2, TeO_3
- Polonium: PoO, PoO_2, PoO_3

Group 17 elements (halogens) fluorine, chlorine, bromine, and iodine react with oxygen to form oxides. Fluorine forms two oxides with oxygen: F_2O and F_2O_2. Both fluorine oxides are called oxygen fluorides because fluorine is the more electronegative element. One of the fluorine reactions is shown below.

$$\mathrm{O_2(g) + F_2(g) \rightarrow F_2O_2(g)} \tag{18.11.7}$$

Group 18: Some would assume that the Noble Gases would not react with oxygen. However, xenon does react with oxygen to form $\mathrm{XeO_3}$ and $\mathrm{XeO_4}$. The ionization energy of xenon is low enough for the electronegative oxygen atom to "steal away" electrons. Unfortunately, $\mathrm{XeO_3}$ is HIGHLY unstable, and it has been known to spontaneously detonate in a clean, dry environment.

Transition metals react with oxygen to form metal oxides. However, gold, silver, and platinum do not react with oxygen. A few reactions involving transition metals are shown below:

$$2Sn_{(s)} + O_{2(g)} \rightarrow 2SnO_{(s)} \tag{18.11.8}$$

$$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)} \tag{18.11.9}$$

$$4Al_{(s)} + 3O_{2(g)} \rightarrow 2Al_2O_{3(s)} \tag{18.11.10}$$

Reaction of Oxides

We will be discussing metal oxides of the form X_2O. The variable X represents any metal that is able to bond to oxygen to form an oxide.

- **Reaction with water:** The oxides react with water to form a metal hydroxide.

$$X_2O + H_2O \rightarrow 2XOH$$

- **Reaction with dilute acids:** The oxides react with dilute acids to form a salt and water.

$$X_2O + 2HCl \rightarrow 2XCl + H_2O$$

Reactions of Peroxides

The peroxides we will be discussing are of the form X_2O_2. The variable X represents any metal that can form a peroxide with oxygen.

Reaction with water: If the temperature of the reaction is kept constant despite the fact that the reaction is exothermic, then the reaction proceeds as follows:

$$X_2O_2 + 2H_2O \rightarrow 2XOH + H_2O_2$$

If the reaction is not carried out at a constant temperature, then the reaction of the peroxide and water will result in decomposition of the hydrogen peroxide that is produced into water and oxygen.

Reaction with dilute acid: This reaction is more exothermic than that with water. The heat produced causes the hydrogen peroxide to decompose to water and oxygen. The reaction is shown below.

$$X_2O_2 + 2HCl \rightarrow 2XCl + H_2O_2$$

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Reaction of Superoxides

The superoxides we will be talking about are of the form XO_2, with X representing any metal that forms a superoxide when reacting with oxygen.

Reaction with water: The superoxide and water react in a very exothermic reaction that is shown below. The heat that is produced in forming the hydrogen peroxide will cause the hydrogen peroxide to decompose to water and oxygen.

$$2XO_2 + 2H_2O \rightarrow 2XOH + H_2O_2 + O_2$$

Reaction with dilute acids: The superoxide and dilute acid react in a very exothermic reaction that is shown below. The heat produced will cause the hydrogen peroxide to decompose to water and oxygen.

$$2XO_2 + 2HCl \rightarrow 2XCl + H_2O_2 + O_2$$

Allotropes of Oxygen

There are two allotropes of oxygen; dioxygen (O_2) and trioxygen (O_3) which is called ozone. The reaction of converting dioxygen into ozone is very endothermic, causing it to occur rarely and only in the lower atmosphere. The reaction is shown below:

$$3O_{2(g)} \rightarrow 2O_{3(g)} \quad \Delta H^o = +285\ kJ$$

Ozone is unstable and quickly decomposes back to oxygen but is a great oxidizing agent.

Miscellaneous Reactions

Reaction with Alkanes: The most common reactions that involve alkanes occur with oxygen. Alkanes are able to burn and it is the process of oxidizing the hydrocarbons that makes them important as fuels. An example of an alkane reaction is the reaction of octane with oxygen as shown below.

$$C_8H_{18}(l) + 25/2\ O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)\ \Delta H_o = -5.48 \text{ X } 10^3 \text{ kJ}$$

Reaction with ammonia: Oxygen is able to react with ammonia to produce dinitrogen (N_2) and water (H_2O) through the reaction shown below.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Reaction with Nitrogen Oxide: Oxygen is able to react with nitrogen oxide in order to produce nitrogen dioxide through the reaction shown below.

$$NO + O_2 \rightarrow NO_2$$

Problems

1. Is oxygen reactive with noble gases?
2. Which transition metals does oxygen not react with?
3. What is produced when an oxide reacts with water?
4. Is oxygen reactive with alkali metals? Why are the alkali metals named that way?
5. If oxygen is reactive with alkali metals, are oxides, peroxides or superoxides produced?

Solutions

1. No, noble gases are unreactive with oxygen.
2. Oxygen is mostly unreactive with gold and platinum.
3. When an oxide reacts with water, a metal hydroxide is produced.
4. Oxygen is very reactive with alkali metals. Alkali metals are given the name alkali because the oxides of these metals react with water to form a metal hydroxide that is basic or alkaline.
5. Lithium produces an oxide, sodium produces a peroxide, and potassium, cesium, and rubidium produce superoxides.

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18.12: The Chemistry of Sulfur

Learning Objectives

- Describe the properties, preparation, and uses of sulfur

Sulfur exists in nature as elemental deposits as well as sulfides of iron, zinc, lead, and copper, and sulfates of sodium, calcium, barium, and magnesium. Hydrogen sulfide is often a component of natural gas and occurs in many volcanic gases, like those shown in Figure 18.12.1 Sulfur is a constituent of many proteins and is essential for life.

Figure 18.12.1: Volcanic gases contain hydrogen sulfide. (credit: Daniel Julie/Wikimedia Commons)

The Frasch process, illustrated in Figure 18.12.2, is important in the mining of free sulfur from enormous underground deposits in Texas and Louisiana. Superheated water (170 °C and 10 atm pressure) is forced down the outermost of three concentric pipes to the underground deposit. The hot water melts the sulfur. The innermost pipe conducts compressed air into the liquid sulfur. The air forces the liquid sulfur, mixed with air, to flow up through the outlet pipe. Transferring the mixture to large settling vats allows the solid sulfur to separate upon cooling. This sulfur is 99.5% to 99.9% pure and requires no purification for most uses.

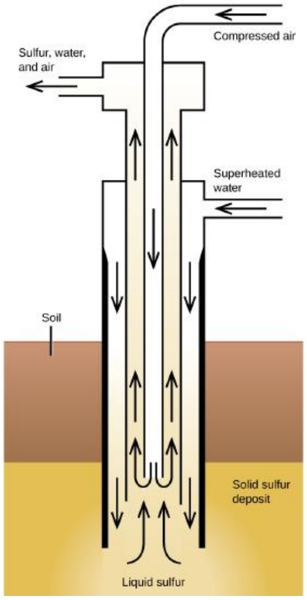

Figure 18.12.2: The Frasch process is used to mine sulfur from underground deposits.

Larger amounts of sulfur also come from hydrogen sulfide recovered during the purification of natural gas.

Sulfur exists in several allotropic forms. The stable form at room temperature contains eight-membered rings, and so the true formula is S_8. However, chemists commonly use S to simplify the coefficients in chemical equations; we will follow this practice in this book.

Like oxygen, which is also a member of group 16, sulfur exhibits a distinctly nonmetallic behavior. It oxidizes metals, giving a variety of binary sulfides in which sulfur exhibits a negative oxidation state (2−). Elemental sulfur oxidizes less electronegative nonmetals, and more electronegative nonmetals, such as oxygen and the halogens, will oxidize it. Other strong oxidizing agents also oxidize sulfur. For example, concentrated nitric acid oxidizes sulfur to the sulfate ion, with the concurrent formation of nitrogen(IV) oxide:

$$\mathrm{S}(s) + 6\,\mathrm{HNO_3}(aq) \longrightarrow 2\,\mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) + 6\,\mathrm{NO_2}(g)$$

The chemistry of sulfur with an oxidation state of 2− is similar to that of oxygen. Unlike oxygen, however, sulfur forms many compounds in which it exhibits positive oxidation states.

Summary

Sulfur (group 16) reacts with almost all metals and readily forms the sulfide ion, S^{2-}, in which it has as oxidation state of 2−. Sulfur reacts with most nonmetals.

Glossary

Frasch process

important in the mining of free sulfur from enormous underground deposits

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18.13: The Group 7A Elements

Learning Objectives

- To understand the periodic trends and reactivity of the group 17 elements: the halogens.

Because the halogens are highly reactive, none is found in nature as the free element. Hydrochloric acid, which is a component of aqua regia (a mixture of HCl and HNO_3 that dissolves gold), and the mineral fluorspar (CaF_2) were well known to alchemists, who used them in their quest for gold. Despite their presence in familiar substances, none of the halogens was even recognized as an element until the 19th century.

> *Because the halogens are highly reactive, none is found in nature as the free element.*

Chlorine was the first halogen to be obtained in pure form. In 1774, Carl Wilhelm Scheele (the codiscoverer of oxygen) produced chlorine by reacting hydrochloric acid with manganese dioxide. Scheele was convinced, however, that the pale green gas he collected over water was a compound of oxygen and hydrochloric acid. In 1811, Scheele's "compound" was identified as a new element, named from the Greek chloros, meaning "yellowish green" (the same stem as in chlorophyll, the green pigment in plants). That same year, a French industrial chemist, Bernard Courtois, accidentally added too much sulfuric acid to the residue obtained from burned seaweed. A deep purple vapor was released, which had a biting aroma similar to that of Scheele's "compound." The purple substance was identified as a new element, named iodine from the Greek iodes, meaning "violet." Bromine was discovered soon after by a young French chemist, Antoine Jérôme Balard, who isolated a deep red liquid with a strong chlorine-like odor from brine from the salt marshes near Montpellier in southern France. Because many of its properties were intermediate between those of chlorine and iodine, Balard initially thought he had isolated a compound of the two (perhaps ICl). He soon realized, however, that he had discovered a new element, which he named bromine from the Greek bromos, meaning "stench." Currently, organic chlorine compounds, such as PVC (polyvinylchloride), consume about 70% of the Cl_2 produced annually; organobromine compounds are used in much smaller quantities, primarily as fire retardants.

A crystal of the mineral fluorite (CaF_2). The purple color of some fluorite crystals is due to small inclusions of highly oxidizing impurities, which generate detectable amounts of ozone when the crystals are crushed.

Because of the unique properties of its compounds, fluorine was believed to exist long before it was actually isolated. The mineral fluorspar (now called fluorite [CaF_2]) had been used since the 16th century as a "flux," a low-melting-point substance that could dissolve other minerals and ores. In 1670, a German glass cutter discovered that heating fluorspar with strong acid produced a solution that could etch glass. The solution was later recognized to contain the acid of a new element, which was named fluorine in 1812. Elemental fluorine proved to be very difficult to isolate, however, because both HF and F_2 are extraordinarily reactive and toxic. After being poisoned three times while trying to isolate the element, the French chemist Henri Moissan succeeded in 1886 in electrolyzing a sample of KF in anhydrous HF to produce a pale green gas (Figure $18.13.1$). For this achievement, among others, Moissan narrowly defeated Mendeleev for the Nobel Prize in Chemistry in 1906. Large amounts of fluorine are now consumed in the production of cryolite (Na_3AlF_6), a key intermediate in the production of aluminum metal. Fluorine is also found in teeth as fluoroapatite [$Ca_5(PO_4)_3F$], which is formed by reacting hydroxyapatite [$Ca_5(PO_4)_3OH$] in tooth enamel with fluoride ions in toothpastes, rinses, and drinking water.

Figure 18.13.1 Isolation of Elemental Fluorine. The French chemist Henri Moissan was the first person to isolate elemental fluorine. A reproduction of the U-shaped electrolysis cell with which Moissan first isolated elemental fluorine in 1866 is shown with samples of cryolite (left) and fluorspar (right). Fluorspar is the raw material from which anhydrous hydrofluoric acid (HF) is prepared. Cryolite is a rare mineral that contains the fluoride ion.

The heaviest halogen is astatine (At), which is continuously produced by natural radioactive decay. All its isotopes are highly radioactive, and the most stable has a half-life of only about 8 h. Consequently, astatine is the least abundant naturally occurring element on Earth, with less than 30 g estimated to be present in Earth's crust at any one time.

Preparation and General Properties of the Group 17 Elements

All the halogens except iodine are found in nature as salts of the halide ions (X^-), so the methods used for preparing F_2, Cl_2, and Br_2 all involve oxidizing the halide. Reacting CaF_2 with concentrated sulfuric acid produces gaseous hydrogen fluoride:

$$CaF_{2(s)} + H_2SO_{4(l)} \rightarrow CaSO_{4(s)} + 2HF_{(g)} \tag{18.13.1}$$

Fluorine is produced by the electrolysis of a 1:1 mixture of HF and $K^+HF_2^-$ at 60–300°C in an apparatus made of Monel, a highly corrosion-resistant nickel–copper alloy:

$$KHF_2 \cdot HF(l) \xrightarrow{electrolysis} F_2(g) + H_2(g) \tag{18.13.2}$$

Fluorine is one of the most powerful oxidants known, and both F_2 and HF are highly corrosive. Consequently, the production, storage, shipping, and handling of these gases pose major technical challenges.

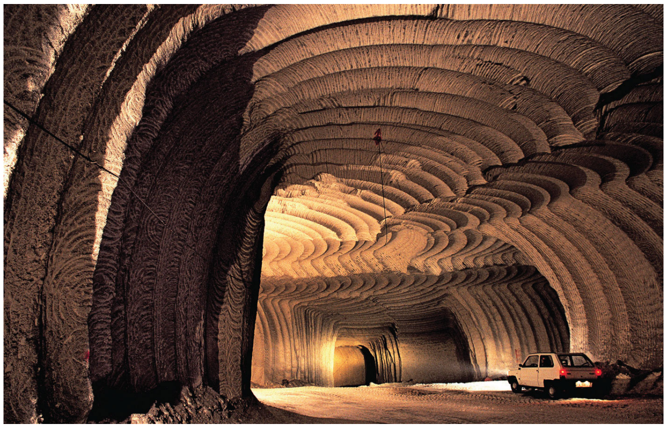

Figure 18.13.2: A Subterranean Salt Mine. Subterranean deposits of rock salt are located worldwide, such as this one at Petralia in Sicily.

Although chlorine is significantly less abundant than fluorine, elemental chlorine is produced on an enormous scale. Fortunately, large subterranean deposits of rock salt (NaCl) are found around the world (Figure 18.13.2), and seawater consists of about 2% NaCl by mass, providing an almost inexhaustible reserve. Inland salt lakes such as the Dead Sea and the Great Salt Lake are even richer sources, containing about 23% and 8% NaCl by mass, respectively. Chlorine is prepared industrially by the chloralkali process, which uses the following reaction:

$$2NaCl_{(aq)} + 2H_2O_{(l)} \xrightarrow{electrolysis} 2NaOH(aq) + Cl_{2(g)} + H_{2(g)} \tag{18.13.3}$$

Bromine is much less abundant than fluorine or chlorine, but it is easily recovered from seawater, which contains about 65 mg of Br^- per liter. Salt lakes and underground brines are even richer sources; for example, the Dead Sea contains 4 g of Br^- per liter.

Iodine is the least abundant of the nonradioactive halogens, and it is a relatively rare element. Because of its low electronegativity, iodine tends to occur in nature in an oxidized form. Hence most commercially important deposits of iodine, such as those in the Chilean desert, are iodate salts such as $Ca(IO_3)_2$. The production of iodine from such deposits therefore requires reduction rather than oxidation. The process is typically carried out in two steps: reduction of iodate to iodide with sodium hydrogen sulfite, followed by reaction of iodide with additional iodate:

$$2IO^-_{3(aq)} + 6HSO^-_{3(aq)} \rightarrow 2I^-_{(aq)} + 6SO^2 -_{4(aq)} + 6H^+_{(aq)} \tag{18.13.4}$$

$$5I^-_{(aq)} + IO^-_{3(aq)} + 6H^+_{(aq)} \rightarrow 3I_{2(s)} + 3H_2O_{(l)} \tag{18.13.5}$$

Because the halogens all have ns^2np^5 electron configurations, their chemistry is dominated by a tendency to accept an additional electron to form the closed-shell ion (X^-). Only the electron affinity and the bond dissociation energy of fluorine differ significantly from the expected periodic trends shown in Table 18.13.1. Electron–electron repulsion is important in fluorine because of its small atomic volume, making the electron affinity of fluorine less than that of chlorine. Similarly, repulsions between electron pairs on adjacent atoms are responsible for the unexpectedly low F–F bond dissociation energy. (As discussed earlier, this effect is also responsible for the weakness of O–O, N–N, and N–O bonds.)

> *Electrostatic repulsions between lone pairs of electrons on adjacent atoms cause single bonds between N, O, and F to be weaker than expected.*

Table 18.13.1: Selected Properties of the Group 17 Elements

Property	Fluorine	Chlorine	Bromine	Iodine	Astatine
atomic symbol	F	Cl	Br	I	At
atomic number	9	17	35	53	85
atomic mass (amu)	19.00	35.45	79.90	126.90	210
valence electron configuration*	$2s^22p^5$	$3s^23p^5$	$4s^24p^5$	$5s^25p^5$	$6s^26p^5$
melting point/boiling point (°C)	−220/−188	−102/−34.0	−7.2/58.8	114/184	302/—
density (g/cm^3) at 25°C	1.55 (g/L)	2.90 (g/L)	3.10	4.93	—
atomic radius (pm)	42	79	94	115	127
first ionization energy (kJ/mol)	1681	1251	1140	1008	926
normal oxidation state(s)	−1	−1 (+1, +3, +5, +7)	−1 (+1, +3, +5, +7)	−1 (+1, +3, +5, +7)	−1, +1
ionic radius (pm)†	133	181	196	220	—
electron affinity (kJ/mol)	−328	−349	−325	−295	−270
electronegativity	4.0	3.2	3.0	2.7	2.2
standard reduction potential (E°, V) ($X_2 \rightarrow X^-$ in basic solution)	+2.87	+1.36	+1.07	+0.54	+0.30

*The configuration shown does not include filled d and f subshells. †The values cited are for the six-coordinate anion (X−).

Property	Fluorine	Chlorine	Bromine	Iodine	Astatine
dissociation energy of $X_2(g)$ (kJ/mol)	158.8	243.6	192.8	151.1	~80
product of reaction with O_2	O_2F_2	none	none	none	none
type of oxide	acidic	acidic	acidic	acidic	acidic
product of reaction with N_2	none	none	none	none	none
product of reaction with H_2	HF	HCl	HBr	HI	HAt

*The configuration shown does not include filled d and f subshells. †The values cited are for the six-coordinate anion (X−).

Because it is the most electronegative element in the periodic table, fluorine forms compounds in only the −1 oxidation state. Notice, however, that all the halogens except astatine have electronegativities greater than 2.5, making their chemistry exclusively that of nonmetals. The halogens all have relatively high ionization energies, but the energy required to remove electrons decreases substantially as we go down the column. Hence the heavier halogens also form compounds in positive oxidation states (+1, +3, +5, and +7), derived by the formal loss of ns and np electrons.

> *Because ionization energies decrease down the group, the heavier halogens form compounds in positive oxidation states (+1, +3, +5, and +7).*

Reactions and Compounds of the Halogens

Fluorine is the most reactive element in the periodic table, forming compounds with every other element except helium, neon, and argon. The reactions of fluorine with most other elements range from vigorous to explosive; only O_2, N_2, and Kr react slowly. There are three reasons for the high reactivity of fluorine:

1. Because fluorine is so electronegative, it is able to remove or at least share the valence electrons of virtually any other element.
2. Because of its small size, fluorine tends to form very strong bonds with other elements, making its compounds thermodynamically stable.
3. The F–F bond is weak due to repulsion between lone pairs of electrons on adjacent atoms, reducing both the thermodynamic and kinetic barriers to reaction.

With highly electropositive elements, fluorine forms ionic compounds that contain the closed-shell F^- ion. In contrast, with less electropositive elements (or with metals in very high oxidation states), fluorine forms covalent compounds that contain terminal F atoms, such as SF_6. Because of its high electronegativity and $2s^22p^5$ valence electron configuration, fluorine normally participates in only one electron-pair bond. Only a very strong Lewis acid, such as AlF_3, can share a lone pair of electrons with a fluoride ion, forming AlF_6^{3-}.

> *Oxidative strength decreases down group 17.*

The halogens (X_2) react with metals (M) according to the general equation

$$M_{(s,l)} + nX_{2(s,l,g)} \rightarrow MX_{n(s,l)} \tag{18.13.6}$$

For elements that exhibit multiple oxidation states fluorine tends to produce the highest possible oxidation state and iodine the lowest. For example, vanadium reacts with the halogens to give VF_5, VCl_4, VBr_4, and VI_3.

Metal halides in the +1 or +2 oxidation state, such as CaF_2, are typically ionic halides, which have high melting points and are often soluble in water. As the oxidation state of the metal increases, so does the covalent character of the halide due to polarization of the M–X bond. With its high electronegativity, fluoride is the least polarizable, and iodide, with the lowest electronegativity, is the most polarizable of the halogens. Halides of small trivalent metal ions such as Al^{3+} tend to be relatively covalent. For example, $AlBr_3$ is a volatile solid that contains bromide-bridged Al_2Br_6 molecules. In contrast, the halides of larger trivalent metals, such as the lanthanides, are essentially ionic. For example, indium tribromide ($InBr_3$) and lanthanide tribromide ($LnBr_3$) are all high-melting-point solids that are quite soluble in water.

> *As the oxidation state of the metal increases, the covalent character of the corresponding metal halides also increases due to polarization of the M–X bond.*

All halogens react vigorously with hydrogen to give the hydrogen halides (HX). Because the H–F bond in HF is highly polarized ($H^{\delta+}$–$F^{\delta-}$), liquid HF has extensive hydrogen bonds, giving it an unusually high boiling point and a high dielectric constant. As a result, liquid HF is a polar solvent that is similar in some ways to water and liquid ammonia; after a reaction, the products can be recovered simply by evaporating the HF solvent. (Hydrogen fluoride must be handled with extreme caution, however, because contact of HF with skin causes extraordinarily painful burns that are slow to heal.) Because fluoride has a high affinity for silicon, aqueous hydrofluoric acid is used to etch glass, dissolving SiO_2 to give solutions of the stable SiF_6^{2-} ion.

Glass etched with hydrogen flouride.*© Thinkstock*

Except for fluorine, all the halogens react with water in a disproportionation reaction, where X is Cl, Br, or I:

$$X_{2(g,l,s)} + H_2O_{(l)} \rightarrow H^+_{(aq)} + X^-_{(aq)} + HOX_{(aq)} \tag{18.13.7}$$

The most stable oxoacids are the perhalic acids, which contain the halogens in their highest oxidation state (+7). The acid strengths of the oxoacids of the halogens increase with increasing oxidation state, whereas their stability and acid strength decrease down the group. Thus perchloric acid ($HOClO_3$, usually written as $HClO_4$) is a more potent acid and stronger oxidant than perbromic acid. Although all the oxoacids are strong oxidants, some, such as $HClO_4$, react rather slowly at low temperatures. Consequently, mixtures of the halogen oxoacids or oxoanions with organic compounds are potentially explosive if they are heated or even agitated mechanically to initiate the reaction. Because of the danger of explosions, oxoacids and oxoanions of the halogens should never be allowed to come into contact with organic compounds.

> *Both the acid strength and the oxidizing power of the halogen oxoacids decrease down the group.*

The halogens react with one another to produce interhalogen compounds, such as ICl_3, BrF_5, and IF_7. In all cases, the heavier halogen, which has the lower electronegativity, is the central atom. The maximum oxidation state and the number of terminal halogens increase smoothly as the ionization energy of the central halogen decreases and the electronegativity of the terminal halogen increases. Thus depending on conditions, iodine reacts with the other halogens to form IF_n (n = 1–7), ICl or ICl_3, or IBr, whereas bromine reacts with fluorine to form only BrF, BrF_3, and BrF_5 but not BrF_7. The interhalogen compounds are among the most powerful Lewis acids known, with a strong tendency to react with halide ions to give complexes with higher coordination numbers, such as the IF_8^- ion:

$$IF_{7(l)} + KF_{(s)} \rightarrow KIF_{8(s)} \tag{18.13.8}$$

All group 17 elements form compounds in odd oxidation states (−1, +1, +3, +5, +7). The interhalogen compounds are also potent oxidants and strong fluorinating agents; contact with organic materials or water can result in an explosion.

> *All group 17 elements form compounds in odd oxidation states (−1, +1, +3, +5, +7), but the importance of the higher oxidation states generally decreases down the group.*

Example 18.13.1

For each reaction, explain why the given products form.

a. $ClF_3(g) + Cl_2(g) \rightarrow 3ClF(g)$
b. $2KI(s) + 3H_2SO_4(aq) \rightarrow I_2(aq) + SO_2(g) + 2KHSO_4(aq) + 2H_2O(l)$
c. $Pb(s) + 2BrF_3(l) \rightarrow PbF_4(s) + 2BrF(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. When the reactants have the same element in two different oxidation states, we expect the product to have that element in an intermediate oxidation state. We have Cl^{3+} and Cl^0 as reactants, so a possible product would have Cl in either the +1 or +2 oxidation state. From our discussion, we know that +1 is much more likely. In this case, Cl_2 is behaving like a reductant rather than an oxidant.
b. At first glance, this appears to be a simple acid–base reaction, in which sulfuric acid transfers a proton to I^- to form HI. Recall, however, that I^- can be oxidized to I_2. Sulfuric acid contains sulfur in its highest oxidation state (+6), so it is a good oxidant. In this case, the redox reaction predominates.
c. This is the reaction of a metallic element with a very strong oxidant. Consequently, a redox reaction will occur. The only question is whether lead will be oxidized to Pb(II) or Pb(IV). Because BrF_3 is a powerful oxidant and fluorine is able to stabilize high oxidation states of other elements, it is likely that PbF_4 will be the product. The two possible reduction products for BrF_3 are BrF and Br_2. The actual product will likely depend on the ratio of the reactants used. With excess BrF_3, we expect the more oxidized product (BrF). With lower ratios of oxidant to lead, we would probably obtain Br_2 as the product.

Exercise 18.13.1

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $CaCl_2(s) + H_3PO_4(l) \rightarrow$
b. $GeO_2(s) + HF(aq) \rightarrow$
c. $Fe_2O_3(s) + HCl(g) \xrightarrow{\Delta}$
d. $NaClO_2(aq) + Cl_2(g) \rightarrow$

Answer

a. $CaCl_2(s) + H_3PO_4(l) \rightarrow 2HCl(g) + Ca(HPO_4)(soln)$
b. $GeO_2(s) + 6HF(aq) \rightarrow GeF_6{}^{2-}(aq) + 2H_2O(l) + 2H^+(aq)$
c. $Fe_2O_3(s) + 6HCl(g) \xrightarrow{\Delta} 2FeCl_3(s) + 3H_2O(g)$
d. $2NaClO_2(aq) + Cl_2(g) \rightarrow 2ClO_2(g) + 2NaCl(aq)$

Summary

The halogens are highly reactive. All halogens have relatively high ionization energies, and the acid strength and oxidizing power of their oxoacids decreases down the group. The halogens are so reactive that none is found in nature as the free element; instead, all but iodine are found as halide salts with the X^- ion. Their chemistry is exclusively that of nonmetals. Consistent with periodic trends, ionization energies decrease down the group. Fluorine, the most reactive element in the periodic table, has a low F–F bond dissociation energy due to repulsions between lone pairs of electrons on adjacent atoms. Fluorine forms ionic compounds with electropositive elements and covalent compounds with less electropositive elements and metals in high oxidation states. All the halogens react with hydrogen to produce hydrogen halides. Except for F_2, all react with water to form oxoacids, including the perhalic acids, which contain the halogens in their highest oxidation state. Halogens also form interhalogen compounds; the heavier halogen, with the lower electronegativity, is the central atom.

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18.14: The Group 8A Elements

Learning Objectives

- To understand the trends in properties and reactivity of the group 18 elements: the noble gases.

The noble gases were all isolated for the first time within a period of only five years at the end of the 19th century. Their very existence was not suspected until the 18th century, when early work on the composition of air suggested that it contained small amounts of gases in addition to oxygen, nitrogen, carbon dioxide, and water vapor. Helium was the first of the noble gases to be identified, when the existence of this previously unknown element on the sun was demonstrated by new spectral lines seen during a solar eclipse in 1868. Actual samples of helium were not obtained until almost 30 years later, however. In the 1890s, the English physicist J. W. Strutt (Lord Rayleigh) carefully measured the density of the gas that remained after he had removed all O_2, CO_2, and water vapor from air and showed that this residual gas was slightly denser than pure N_2 obtained by the thermal decomposition of ammonium nitrite. In 1894, he and the Scottish chemist William Ramsay announced the isolation of a new “substance” (not necessarily a new element) from the residual nitrogen gas. Because they could not force this substance to decompose or react with anything, they named it argon (Ar), from the Greek argos, meaning “lazy.” Because the measured molar mass of argon was 39.9 g/mol, Ramsay speculated that it was a member of a new group of elements located on the right side of the periodic table between the halogens and the alkali metals. He also suggested that these elements should have a preferred valence of 0, intermediate between the +1 of the alkali metals and the −1 of the halogens.

J. W. Strutt (Lord Rayleigh) (1842–1919)

Lord Rayleigh was one of the few members of British higher nobility to be recognized as an outstanding scientist. Throughout his youth, his education was repeatedly interrupted by his frail health, and he was not expected to reach maturity. In 1861 he entered Trinity College, Cambridge, where he excelled at mathematics. A severe attack of rheumatic fever took him abroad, but in 1873 he succeeded to the barony and was compelled to devote his time to the management of his estates. After leaving the entire management to his younger brother, Lord Rayleigh was able to devote his time to science. He was a recipient of honorary science and law degrees from Cambridge University.

Sir William Ramsay (1852–1916)

Born and educated in Glasgow, Scotland, Ramsay was expected to study for the Calvanist ministry. Instead, he became interested in chemistry while reading about the manufacture of gunpowder. Ramsay earned his PhD in organic chemistry at the University of Tübingen in Germany in 1872. When he returned to England, his interests turned first to physical chemistry and then to inorganic chemistry. He is best known for his work on the oxides of nitrogen and for the discovery of the noble gases with Lord Rayleigh.

In 1895, Ramsey was able to obtain a terrestrial sample of helium for the first time. Then, in a single year (1898), he discovered the next three noble gases: krypton (Kr), from the Greek kryptos, meaning “hidden,” was identified by its orange and green emission lines; neon (Ne), from the Greek neos, meaning “new,” had bright red emission lines; and xenon (Xe), from the Greek xenos, meaning “strange,” had deep blue emission lines. The last noble gas was discovered in 1900 by the German chemist Friedrich Dorn, who was investigating radioactivity in the air around the newly discovered radioactive elements radium and polonium. The element was named radon (Rn), and Ramsay succeeded in obtaining enough radon in 1908 to measure its density (and thus its atomic mass). For their discovery of the noble gases, Rayleigh was awarded the Nobel Prize in Physics and Ramsay the Nobel Prize in Chemistry in 1904. Because helium has the lowest boiling point of any substance known (4.2 K), it is used primarily as a cryogenic liquid. Helium and argon are both much less soluble in water (and therefore in blood) than N_2, so scuba divers often use gas mixtures that contain these gases, rather than N_2, to minimize the likelihood of the “bends,” the painful and potentially fatal formation of bubbles of $N_2(g)$ that can occur when a diver returns to the surface too rapidly.

Preparation and General Properties of the Group 18 Elements

Fractional distillation of liquid air is the only source of all the noble gases except helium. Although helium is the second most abundant element in the universe (after hydrogen), the helium originally present in Earth’s atmosphere was lost into space long ago because of its low molecular mass and resulting high mean velocity. Natural gas often contains relatively high concentrations of helium (up to 7%), however, and it is the only practical terrestrial source.

The elements of group 18 all have closed-shell valence electron configurations, either ns^2np^6 or $1s^2$ for He. Consistent with periodic trends in atomic properties, these elements have high ionization energies that decrease smoothly down the group. From their electron affinities, the data in Table 18.14.1 indicate that the noble gases are unlikely to form compounds in negative oxidation states. A potent oxidant is needed to oxidize noble gases and form compounds in positive oxidation states. Like the heavier halogens, xenon and perhaps krypton should form covalent compounds with F, O, and possibly Cl, in which they have even formal oxidation states (+2, +4, +6, and possibly +8). These predictions actually summarize the chemistry observed for these elements.

Table 18.14.1: Selected Properties of the Group 18 Elements

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
atomic symbol	He	Ne	Ar	Kr	Xe	Rn
atomic number	2	10	18	36	54	86
atomic mass (amu)	4.00	20.18	39.95	83.80	131.29	222
valence electron configuration*	$1s^2$	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$
triple point/boiling point (°C)	—/−269[†]	−249 (at 43 kPa)/−246	−189 (at 69 kPa)/−189	−157/−153	−112 (at 81.6 kPa)/−108	−71/−62
density (g/L) at 25°C	0.16	0.83	1.63	3.43	5.37	9.07
atomic radius (pm)	31	38	71	88	108	120
first ionization energy (kJ/mol)	2372	2081	1521	1351	1170	1037
normal oxidation state(s)	0	0	0	0 (+2)	0 (+2, +4, +6, +8)	0 (+2)
electron affinity (kJ/mol)	> 0	> 0	> 0	> 0	> 0	> 0
electronegativity	—	—	—	—	2.6	—
product of reaction with O_2	none	none	none	none	not directly with oxygen, but XeO_3 can be formed by Equation 18.14.5.	none
type of oxide	—	—	—	—	acidic	—
product of reaction with N_2	none	none	none	none	none	none
product of reaction with X_2	none	none	none	KrF_2	XeF_2, XeF_4, XeF_6	RnF_2

*The configuration shown does not include filled d and f subshells. [†]This is the normal boiling point of He. Solid He does not exist at 1 atm pressure, so no melting point can be given.

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
product of reaction with H_2	none	none	none	none	none	none
*The configuration shown does not include filled d and f subshells. †This is the normal boiling point of He. Solid He does not exist at 1 atm pressure, so no melting point can be given.						

Reactions and Compounds of the Noble Gases

For many years, it was thought that the only compounds the noble gases could form were clathrates. Clathrates are solid compounds in which a gas, the guest, occupies holes in a lattice formed by a less volatile, chemically dissimilar substance, the host (Figure 18.14.1).

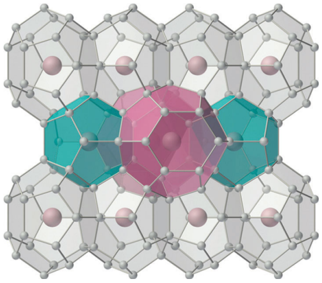


Figure 18.14.1: The Structure of Xenon Hydrate, a Clathrate. Small gaseous atoms or molecules such as Xe or CH_4 can occupy cavities in a lattice of hydrogen-bonded water molecules to produce a stable structure with a fixed stoichiometry (in this case, $Xe{\cdot}5.75H_2O$). (The hydrogen atoms of the water molecules have been omitted for clarity.) Warming the solid hydrate or decreasing the pressure of the gas causes it to collapse, with the evolution of gas and the formation of liquid water.

Because clathrate formation does not involve the formation of chemical bonds between the guest (Xe) and the host molecules (H_2O, in the case of xenon hydrate), the guest molecules are immediately released when the clathrate is melted or dissolved.

Methane Clathrates

In addition to the noble gases, many other species form stable clathrates. One of the most interesting is methane hydrate, large deposits of which occur naturally at the bottom of the oceans. It is estimated that the amount of methane in such deposits could have a major impact on the world’s energy needs later in this century.

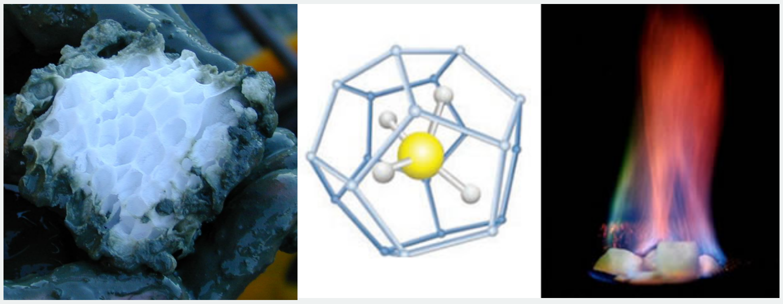


Figure 18.14.2: “Burning snowballs.” Like xenon, methane (CH_4) forms a crystalline clathrate with water: methane hydrate. When the solid is warmed, methane is released and can be ignited to give what appears to be burning snow. (left) Structure of a gas hydrate (methane clathrate) block embedded in the sediment of hydrate ridge, off Oregon, USA (CC-SA-BY-3.0 Wusel007) (middle) A ball-and-stick model of methane hydrate showing the central methane molecule surrounded by a "cage" of water molecules. Other hydrocarbon molecules such as pentane and ethane can occupy the central position in this structure. (United States Department of Energy image). (Right): A burning specimen of methane hydrate ice (United States Geological Survey image).

The widely held belief in the intrinsic lack of reactivity of the noble gases was challenged when Neil Bartlett, a British professor of chemistry at the University of British Columbia, showed that PtF_6, a compound used in the Manhattan Project, could oxidize O_2. Because the ionization energy of xenon (1170 kJ/mol) is actually lower than that of O_2, Bartlett recognized that PtF_6 should also be able to oxidize xenon. When he mixed colorless xenon gas with deep red PtF_6 vapor, yellow-orange crystals immediately formed

(Figure 18.14.3). Although Bartlett initially postulated that they were $Xe^+PtF_6^-$, it is now generally agreed that the reaction also involves the transfer of a fluorine atom to xenon to give the XeF^+ ion:

$$Xe(g) + PtF_6(g) \longrightarrow [XeF^+][PtF_5^-](s) \tag{18.14.1}$$

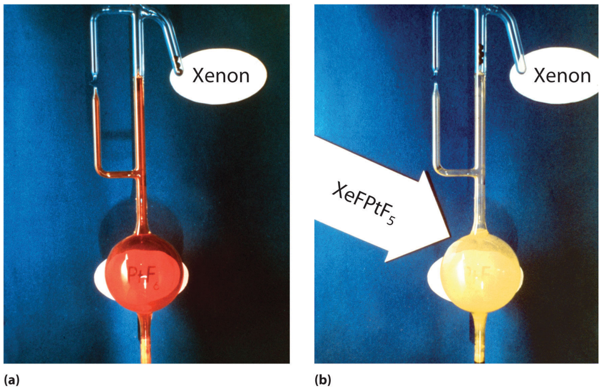


Figure 18.14.3: The Synthesis of the First Chemical Compound of Xenon. (a) An apparatus containing platinum hexafluoride, the red vapor at the bottom left, and xenon, the colorless gas in the small tube at the upper right. (b) When the glass seal separating the two gases is broken and the gases are allowed to mix, a bright yellow solid is formed, which is best described as $XeF^+PtF_5^-$.

Subsequent work showed that xenon reacts directly with fluorine under relatively mild conditions to give XeF_2, XeF_4, or XeF_6, depending on conditions; one such reaction is as follows:

$$Xe(g) + 2\,F_2(g) \longrightarrow XeF_4(s) \tag{18.14.2}$$

The ionization energies of helium, neon, and argon are so high (Table 18.14.1) that no stable compounds of these elements are known. The ionization energies of krypton and xenon are lower but still very high; consequently only highly electronegative elements (F, O, and Cl) can form stable compounds with xenon and krypton without being oxidized themselves. Xenon reacts directly with only two elements: F_2 and Cl_2. Although $XeCl_2$ and KrF_2 can be prepared directly from the elements, they are substantially less stable than the xenon fluorides.

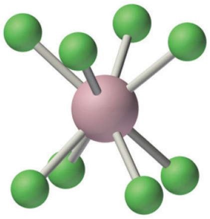
> *The ionization energies of helium, neon, and argon are so high that no stable compounds of these elements are known.*

Because halides of the noble gases are powerful oxidants and fluorinating agents, they decompose rapidly after contact with trace amounts of water, and they react violently with organic compounds or other reductants. The xenon fluorides are also Lewis acids; they react with the fluoride ion, the only Lewis base that is not oxidized immediately on contact, to form anionic complexes. For example, reacting cesium fluoride with XeF_6 produces $CsXeF_7$, which gives Cs_2XeF_8 when heated:

$$XeF_6(s) + CsF(s) \longrightarrow CsXeF_7(s) \tag{18.14.3}$$

$$2\,CsXeF_7(s) \xrightarrow{\Delta} Cs_2XeF_8(s) + XeF_6(g) \tag{18.14.4}$$

The XeF_8^{2-} ion contains eight-coordinate xenon and has the square antiprismatic structure, which is essentially identical to that of the IF_8^- ion. Cs_2XeF_8 is surprisingly stable for a polyatomic ion that contains xenon in the +6 oxidation state, decomposing only at temperatures greater than 300°C. Major factors in the stability of Cs_2XeF_8 are almost certainly the formation of a stable ionic lattice and the **high coordination number** of xenon, which protects the central atom from attack by other species. (Recall from that this latter effect is responsible for the extreme stability of SF_6.)



XeF_8^{2-}

For a previously "inert" gas, xenon has a surprisingly high affinity for oxygen, presumably because of π bonding between O and Xe. Consequently, xenon forms an extensive series of oxides and oxoanion salts. For example, hydrolysis of either XeF_4 or XeF_6 produces XeO_3, an explosive white solid:

$$\mathrm{XeF_6(aq) + 3\,H_2O(l) \longrightarrow XeO_3(aq) + 6\,HF(aq)} \tag{18.14.5}$$

Treating a solution of XeO_3 with ozone, a strong oxidant, results in further oxidation of xenon to give either XeO_4, a colorless, explosive gas, or the surprisingly stable perxenate ion ($XeO_6{}^{4-}$), both of which contain xenon in its highest possible oxidation state (+8). The chemistry of the xenon halides and oxides is best understood by analogy to the corresponding compounds of iodine. For example, XeO_3 is isoelectronic with the iodate ion ($IO_3{}^{-}$), and $XeF_8{}^{2-}$ is isoelectronic with the $IF_8{}^{-}$ ion.

> *Xenon has a high affinity for both fluorine and oxygen.*

Because the ionization energy of radon is less than that of xenon, in principle radon should be able to form an even greater variety of chemical compounds than xenon. Unfortunately, however, radon is so radioactive that its chemistry has not been extensively explored.

✓ Example 18.14.1

On a virtual planet similar to Earth, at least one isotope of radon is not radioactive. A scientist explored its chemistry and presented her major conclusions in a trailblazing paper on radon compounds, focusing on the kinds of compounds formed and their stoichiometries. Based on periodic trends, how did she summarize the chemistry of radon?

Given: nonradioactive isotope of radon

Asked for: summary of its chemistry

Strategy:

Based on the position of radon in the periodic table and periodic trends in atomic properties, thermodynamics, and kinetics, predict the most likely reactions and compounds of radon.

Solution

We expect radon to be significantly easier to oxidize than xenon. Based on its position in the periodic table, however, we also expect its bonds to other atoms to be weaker than those formed by xenon. Radon should be more difficult to oxidize to its highest possible oxidation state (+8) than xenon because of the inert-pair effect. Consequently, radon should form an extensive series of fluorides, including RnF_2, RnF_4, RnF_6, and possibly RnF_8 (due to its large radius). The ion $RnF_8{}^{2-}$ should also exist. We expect radon to form a series of oxides similar to those of xenon, including RnO_3 and possibly RnO_4. The biggest surprise in radon chemistry is likely to be the existence of stable chlorides, such as $RnCl_2$ and possibly even $RnCl_4$.

? Exercise 18.14.1

Predict the stoichiometry of the product formed by reacting XeF_6 with a 1:1 stoichiometric amount of KF and propose a reasonable structure for the anion.

Answer

$KXeF_7$; the xenon atom in $XeF_7{}^{-}$ has 16 valence electrons, which according to the valence-shell electron-pair repulsion model could give either a square antiprismatic structure with one fluorine atom missing or a pentagonal bipyramid if the $5s^2$ electrons behave like an inert pair that does not participate in bonding.

Summary

The noble gases are characterized by their high ionization energies and low electron affinities. Potent oxidants are needed to oxidize the noble gases to form compounds in positive oxidation states. The noble gases have a closed-shell valence electron configuration. The ionization energies of the noble gases decrease with increasing atomic number. Only highly electronegative elements can form stable compounds with the noble gases in positive oxidation states without being oxidized themselves. Xenon has a high affinity for both fluorine and oxygen, which form stable compounds that contain xenon in even oxidation states up to +8.

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CHAPTER OVERVIEW

19: Transition Metals and Coordination Chemistry

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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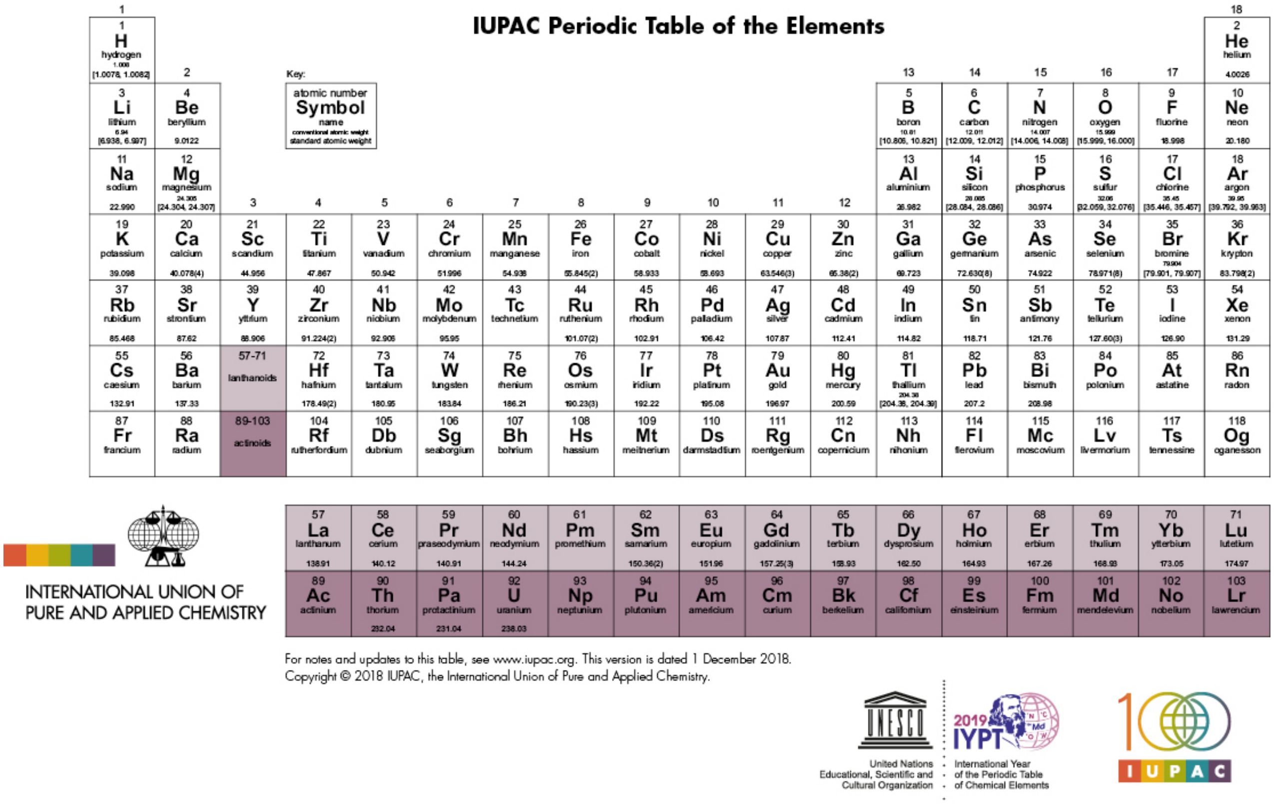
19.1: The Transition Metals: A Survey

We have daily contact with many transition metals. Iron occurs everywhere—from the rings in your spiral notebook and the cutlery in your kitchen to automobiles, ships, buildings, and in the hemoglobin in your blood. Titanium is useful in the manufacture of lightweight, durable products such as bicycle frames, artificial hips, and jewelry. Chromium is useful as a protective plating on plumbing fixtures and automotive detailing.

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. As shown in Figure 19.1.2, the *d*-block elements in groups 3–11 are transition elements. The *f*-block elements, also called *inner transition metals* (the lanthanides and actinides), also meet this criterion because the *d* orbital is partially occupied before the *f* orbitals. The *d* orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.

Figure 19.1.1: Transition metals often form vibrantly colored complexes. The minerals malachite (green), azurite (blue), and proustite (red) are some examples. (credit left: modification of work by James St. John; credit middle: modification of work by Stephanie Clifford; credit right: modification of work by Terry Wallace)

The *d*-block elements are divided into the first transition series (the elements Sc through Cu), the second transition series (the elements Y through Ag), and the third transition series (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the fourth transition series, which also includes Rf through Rg.



IUPAC Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H hydrogen 1.008 [1.0078, 1.0082]																	2 He helium 4.0026
3 Li lithium 6.94 [6.938, 6.997]	4 Be beryllium 9.0122		Key: atomic number Symbol name conventional atomic weight standard atomic weight									5 B boron 10.81 [10.806, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999 [15.999, 16.000]	9 F fluorine 18.998	10 Ne neon 20.180
11 Na sodium 22.990	12 Mg magnesium 24.305 [24.304, 24.307]											13 Al aluminium 26.982	14 Si silicon 28.085 [28.084, 28.086]	15 P phosphorus 30.974	16 S sulfur 32.06 [32.059, 32.076]	17 Cl chlorine 35.45 [35.446, 35.457]	18 Ar argon 39.95 [39.792, 39.963]
19 K potassium 39.098	20 Ca calcium 40.078(4)	21 Sc scandium 44.956	22 Ti titanium 47.867	23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845(2)	27 Co cobalt 58.933	28 Ni nickel 58.693	29 Cu copper 63.546(3)	30 Zn zinc 65.38(2)	31 Ga gallium 69.723	32 Ge germanium 72.630(8)	33 As arsenic 74.922	34 Se selenium 78.971(8)	35 Br bromine 79.904 [79.901, 79.907]	36 Kr krypton 83.798(2)
37 Rb rubidium 85.468	38 Sr strontium 87.62	39 Y yttrium 88.906	40 Zr zirconium 91.224(2)	41 Nb niobium 92.906	42 Mo molybdenum 95.95	43 Tc technetium	44 Ru ruthenium 101.07(2)	45 Rh rhodium 102.91	46 Pd palladium 106.42	47 Ag silver 107.87	48 Cd cadmium 112.41	49 In indium 114.82	50 Sn tin 118.71	51 Sb antimony 121.76	52 Te tellurium 127.60(3)	53 I iodine 126.90	54 Xe xenon 131.29
55 Cs caesium 132.91	56 Ba barium 137.33	57-71 lanthanoids	72 Hf hafnium 178.49(2)	73 Ta tantalum 180.95	74 W tungsten 183.84	75 Re rhenium 186.21	76 Os osmium 190.23(3)	77 Ir iridium 192.22	78 Pt platinum 195.08	79 Au gold 196.97	80 Hg mercury 200.59	81 Tl thallium 204.38 [204.38, 204.39]	82 Pb lead 207.2	83 Bi bismuth 208.98	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganesson

57 La lanthanum 138.91	58 Ce cerium 140.12	59 Pr praseodymium 140.91	60 Nd neodymium 144.24	61 Pm promethium	62 Sm samarium 150.36(2)	63 Eu europium 151.96	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.93	66 Dy dysprosium 162.50	67 Ho holmium 164.93	68 Er erbium 167.26	69 Tm thulium 168.93	70 Yb ytterbium 173.05	71 Lu lutetium 174.97
89 Ac actinium	90 Th thorium 232.04	91 Pa protactinium 231.04	92 U uranium 238.03	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

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United Nations
Educational, Scientific and
Cultural Organization

International Year
of the Periodic Table
of Chemical Elements

Figure 19.1.2: The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

The *f*-block elements are the elements Ce through Lu, which constitute the lanthanide series (or lanthanoid series), and the elements Th through Lr, which constitute the actinide series (or actinoid series). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series

Properties and Trends in Transition Metals

The elements of the second and third rows of the Periodic Table show gradual changes in properties across the table from left to right as expected. Electrons in the outer shells of the atoms of these elements have little shielding effects resulting in an increase in effective nuclear charge due to the addition of protons in the nucleus. Consequently, the effects on atomic properties are: smaller atomic radius, increased first ionization energy, enhanced electronegativity and more nonmetallic character. This trend continues until one reaches calcium (Z=20). There is an abrupt break at this point. The next ten elements called the first transition series are remarkably similar in their physical and chemical properties. This general similarity in properties has been explained in terms of their relatively small difference in effective nuclear charge over the series. This occurs because each additional electron enters the penultimate 3d shell providing an effective shield between the nucleus and the outer 4s shell.

What is a Transition Metal?

Thus, the transition elements can be defined as those in which the d electron shells are being filled and so we generally ignore Sc and Zn where Sc(III) is d^0 and Zn(II) is d^{10}.

It is useful, at the beginning, to identify the physical and chemical properties of transition elements which differ from main group elements (s-block). Properties of transition elements include:

- have large charge/radius ratio;
- are hard and have high densities;
- have high melting and boiling points;
- form compounds which are often paramagnetic;
- show variable oxidation states;
- form coloured ions and compounds;
- form compounds with profound catalytic activity;
- form stable complexes.

Table 19.1.1 : Summary of select physical properties of transition elements:

Element	Group	density /g cm^{-3}	m. p. / °C	b.p. / °C	radius / pm	free atom configuration	ionization energy / kJ mol^{-1}	Uses
Sc	3	2.99	1541	2831	164	[Ar] $3d^14s^2$	631	
Ti	4	4.50	1660	3287	147	[Ar]$3d^24s^2$	658	- engines/aircraft industry- density is 60% of iron
V	5	5.96	1890	3380	135	[Ar]$3d^34s^2$	650	-stainless steel, 19% Cr, 9% Ni the rest Fe
Cr	6	7.20	1857	2670	129	[Ar]$3d^54s^1$	653	-alloys eg with C steel, the most significant use

Element	**Group**	**density /g cm^{-3}**	**m. p. / °C**	**b.p. / °C**	**radius / pm**	**free atom configuration**	**ionization energy / kJ mol^{-1}**	**Uses**
Mn	7	7.20	1244	1962	137	$[Ar]3d^5 4s^2$	717	-alloys eg with Cu
Fe	8	7.86	1535	2750	126	$[Ar]3d^6 4s^2$	759	-alloys eg with C steel, the most significant use
Co	9	8.90	1495	2870	125	$[Ar]3d^7 4s^2$	758	-alloys eg with Cr and W for hardened drill bits
Ni	10	8.90	1455	2730	125	$[Ar]3d^8 4s^2$	737	-alloys Fe/Ni armor plating, resists corrosion
Cu	11	8.92	1083	2567	128	$[Ar]3d^{10} 4s^1$	746	-high electrical conductivity (2nd to Ag), wiring
Zn	12	7.14	420	907	137	$[Ar]3d^{10} 4s^2$	906	

Densities and Metallic Radii

The transition elements are much denser than the s-block elements and show a gradual increase in density from scandium to copper. This trend in density can be explained by the small and irregular decrease in metallic radii coupled with the relative increase in atomic mass.

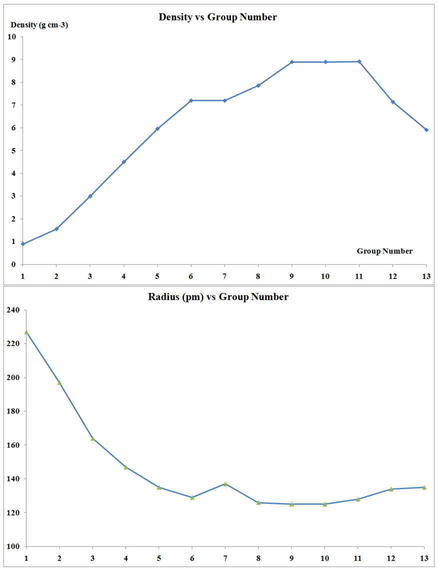


Figure 19.1.3: Variations of the density (leff) and metallic radius (right) in the first row transition metals.

Melting and Boiling points

The melting points and the molar enthalpies of fusion of the transition metals are both high in comparison to main group elements. This arises from strong metallic bonding in transition metals which occurs due to delocalization of electrons facilitated by the availability of both d and s electrons.

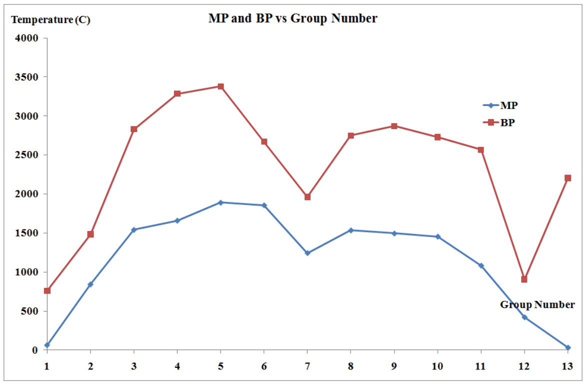


Figure 19.1.4: Variations of the melting point (blue curve) and boiling points (red) in the first row transition metals.

Ionization Energies

In moving across the series of metals from scandium to zinc a small change in the values of the first and second ionization energies is observed. This is due to the build-up of electrons in the immediately underlying d-sub-shells that efficiently shields the 4s electrons from the nucleus and minimizing the increase in effective nuclear charge Z_{eff} from element to element. The increases in third and fourth ionization energy values are more rapid. However, the trends in these values show the usual discontinuity half way along the series. The reason is that the five d electrons are all unpaired, in singly occupied orbitals. When the sixth and subsequent electrons enter, the electrons have to share the already occupied orbitals resulting in inter-electron repulsions, which would require less energy to remove an electron. Hence, the third ionization energy curve for the last five elements is identical in shape to the curve for the first five elements, but displaced upwards by 580 kJ mol^{-1}.

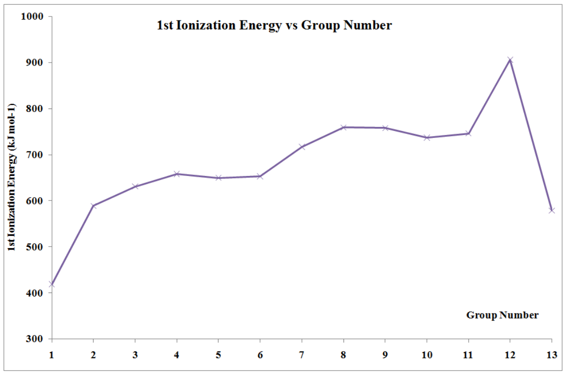
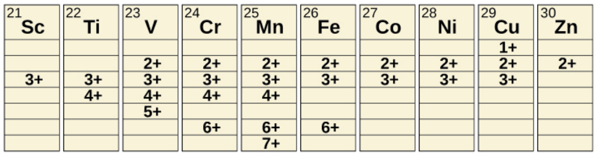


Figure 19.1.4: Variations of the first ionization energy in the first row transition metals.

Oxidation States

Transition metals can form compounds with a wide range of oxidation states. Some of the observed oxidation states of the elements of the first transition series are shown in Figure 19.1.5. As we move from left to right across the first transition series, we see that the number of common oxidation states increases at first to a maximum towards the middle of the table, then decreases. The values in the table are typical values; there are other known values, and it is possible to synthesize new additions. For example, in 2014, researchers were successful in synthesizing a new oxidation state of iridium (9+).



21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
								1+	
		2+	2+	2+	2+	2+	2+	2+	2+
3+	3+	3+	3+	3+	3+	3+	3+	3+	
	4+	4+	4+	4+					
		5+							
			6+	6+	6+				
				7+					

Figure 19.1.5:Transition metals of the first transition series can form compounds with varying oxidation states.

For the elements scandium through manganese (the first half of the first transition series), the highest oxidation state corresponds to the loss of all of the electrons in both the *s* and *d* orbitals of their valence shells. The titanium(IV) ion, for example, is formed when the titanium atom loses its two 3*d* and two 4*s* electrons. These highest oxidation states are the most stable forms of scandium, titanium, and vanadium. However, it is not possible to continue to remove all of the valence electrons from metals as we continue through the series. Iron is known to form oxidation states from 2+ to 6+, with iron(II) and iron(III) being the most common. Most of the elements of the first transition series form ions with a charge of 2+ or 3+ that are stable in water, although those of the early members of the series can be readily oxidized by air.

The elements of the second and third transition series generally are more stable in higher oxidation states than are the elements of the first series. In general, the atomic radius increases down a group, which leads to the ions of the second and third series being larger than are those in the first series. Removing electrons from orbitals that are located farther from the nucleus is easier than removing electrons close to the nucleus. For example, molybdenum and tungsten, members of group 6, are limited mostly to an oxidation state of 6+ in aqueous solution. Chromium, the lightest member of the group, forms stable Cr^{3+} ions in water and, in the absence of air, less stable Cr^{2+} ions. The sulfide with the highest oxidation state for chromium is Cr_2S_3, which contains the Cr^{3+} ion. Molybdenum and tungsten form sulfides in which the metals exhibit oxidation states of 4+ and 6+.

Electronic Configurations

The electronic configuration of the atoms of the first row transition elements are basically the same. It can be seen in the Table above that there is a gradual filling of the 3d orbitals across the series starting from scandium. This filling is, however, not regular, since at chromium and copper the population of 3d orbitals increase by the acquisition of an electron from the 4s shell. This illustrates an important generalization about orbital energies of the first row transition series. At chromium, both the 3d and 4s orbitals are occupied, but neither is completely filled in preference to the other. This suggests that the energies of the 3d and 4s orbitals are relatively close for atoms in this row.

In the case of copper, the 3d level is full, but only one electron occupies the 4s orbital. This suggests that in copper the 3d orbital energy is lower than the 4s orbital. Thus the 3d orbital energy has passed from higher to lower as we move across the period from potassium to zinc. However, the whole question of preference of an atom to adopt a particular electronic configuration is not determined by orbital energy alone. In chromium it can be shown that the 4s orbital energy is still below the 3d which suggests a configuration $[Ar]\ 3d^4 4s^2$. However due to the effect of electronic repulsion between the outer electrons the actual configuration becomes $[Ar]3d^5 4s^1$ where all the electrons in the outer orbitals are unpaired. It should be remembered that the factors that determine electronic configuration in this period are indeed delicately balanced.

Redox Couple	**E°/V**
Mn^{2+}(aq.)/Mn(s)	-1.18
H^+(aq.)/H_2(g)	0.00

This shows that elemental Mn is a stronger reductant than molecular hydrogen and hence should be able to displace hydrogen gas from 1 mol dm^{-3} hydrochloric acid.

✓ Valence Electrons in Transition Metals

Review how to write electron configurations, covered in the chapter on electronic structure and periodic properties of elements. Recall that for the transition and inner transition metals, it is necessary to remove the *s* electrons before the *d* or *f* electrons. Then, for each ion, give the electron configuration:

a. cerium(III)
b. lead(II)
c. Ti^{2+}
d. Am^{3+}
e. Pd^{2+}

For the examples that are transition metals, determine to which series they belong.

Solution

For ions, the *s*-valence electrons are lost prior to the *d* or *f* electrons.

a. Ce^{3+}[Xe]4f^1; Ce^{3+} is an inner transition element in the lanthanide series.
b. Pb^{2+}[Xe]6$s^2$5d^{10}4f^{14}; the electrons are lost from the *p* orbital. This is a main group element.
c. titanium(II) [Ar]3d^2; first transition series
d. americium(III) [Rn]5f^6; actinide
e. palladium(II) [Kr]4d^8; second transition series

Exercise 19.1.1

Check Your Learning Give an example of an ion from the first transition series with no *d* electrons.

Answer

V^{5+} is one possibility. Other examples include Sc^{3+}, Ti^{4+}, Cr^{6+}, and Mn^{7+}.

Chemical Reactivity

Transition metals demonstrate a wide range of chemical behaviors. As can be seen from their reduction potentials (Table P1), some transition metals are strong reducing agents, whereas others have very low reactivity. For example, the lanthanides all form stable 3+ aqueous cations. The driving force for such oxidations is similar to that of alkaline earth metals such as Be or Mg, forming Be^{2+} and Mg^{2+}. On the other hand, materials like platinum and gold have much higher reduction potentials. Their ability to resist oxidation makes them useful materials for constructing circuits and jewelry.

Ions of the lighter *d*-block elements, such as Cr^{3+}, Fe^{3+}, and Co^{2+}, form colorful hydrated ions that are stable in water. However, ions in the period just below these (Mo^{3+}, Ru^{3+}, and Ir^{2+}) are unstable and react readily with oxygen from the air. The majority of simple, water-stable ions formed by the heavier *d*-block elements are oxyanions such as $\mathrm{MoO_4^{2-}}$ and $\mathrm{ReO_4^-}$.

Ruthenium, osmium, rhodium, iridium, palladium, and platinum are the *"platinum metals"*. With difficulty, they form simple cations that are stable in water, and, unlike the earlier elements in the second and third transition series, they do not form stable oxyanions.

Both the *d*- and *f*-block elements react with nonmetals to form binary compounds; heating is often required. These elements react with halogens to form a variety of halides ranging in oxidation state from 1+ to 6+. On heating, oxygen reacts with all of the transition elements except palladium, platinum, silver, and gold. The oxides of these latter metals can be formed using other reactants, but they decompose upon heating. The *f*-block elements, the elements of group 3, and the elements of the first transition series except copper react with aqueous solutions of acids, forming hydrogen gas and solutions of the corresponding salts.

✓ Activity of the Transition Metals

Which is the strongest oxidizing agent in acidic solution: dichromate ion, which contains chromium(VI), permanganate ion, which contains manganese(VII), or titanium dioxide, which contains titanium(IV)?

Solution

First, we need to look up the reduction half reactions (Table P1) for each oxide in the specified oxidation state:

$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O} \quad +1.33\text{ V} \tag{19.1.1}$$

$$\mathrm{MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + H_2O} \quad +1.51\text{ V} \tag{19.1.2}$$

$$\mathrm{TiO_2 + 4\,H^+ + 2\,e^- \longrightarrow Ti^{2+} + 2\,H_2O} \quad -0.50\text{ V} \tag{19.1.3}$$

A larger reduction potential means that it is easier to reduce the reactant. Permanganate, with the largest reduction potential, is the strongest oxidizer under these conditions. Dichromate is next, followed by titanium dioxide as the weakest oxidizing agent (the hardest to reduce) of this set.

Exercise 19.1.2

Predict what reaction (if any) will occur between HCl and Co(*s*), and between HBr and Pt(*s*). You will need to use the standard reduction potentials from (Table P1).

Answer

$\mathrm{Co}(s) + 2\,\mathrm{HCl} \longrightarrow \mathrm{H_2} + \mathrm{CoCl_2}(aq)$; no reaction because Pt(*s*) will not be oxidized by H^+

Contributors and Attributions

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19.2: The First-Row Transition Metals

Learning Objectives

- To use periodic trends to understand the chemistry of the transition metals.

As we shall see, the two heaviest members of each group usually exhibit substantial similarities in chemical behavior and are quite different from the lightest member.

Group 3 (Sc, Y, La, and Ac)

As shown in Table $19.2.1$, the observed trends in the properties of the group 3 elements are similar to those of groups 1 and 2. Due to their $ns^2(n-1)d^1$ valence electron configurations, the chemistry of all four elements is dominated by the +3 oxidation state formed by losing all three valence electrons. As expected based on periodic trends, these elements are highly electropositive metals and powerful reductants, with La (and Ac) being the most reactive. In keeping with their highly electropositive character, the group 3 metals react with water to produce the metal hydroxide and hydrogen gas:

$$2M_{(s)}+6H_2O_{(l)}\rightarrow 2M(OH)_{3(s)}+3H_{2(g)} \tag{19.2.1}$$

> *The chemistry of the group 3 metals is almost exclusively that of the M^{3+} ion; the elements are powerful reductants.*

Moreover, all dissolve readily in aqueous acid to produce hydrogen gas and a solution of the hydrated metal ion: $M^{3+}(aq)$.

Table 19.2.1: Some Properties of the Elements of Groups 3, 4, and 5

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
3	Sc	21	$4s^23d^1$	1.36	162	1541	2.99
	Y	39	$5s^24d^1$	1.22	180	1522	4.47
	La	57	$6s^25d^1$	1.10	183	918	6.15
	Ac	89	$7s^26d^1$	1.10	188	1051	10.07
4	Ti	22	$4s^23d^2$	1.54	147	1668	4.51
	Zr	40	$5s^24d^2$	1.33	160	1855	6.52
	Hf	72	$6s^25d^24f^{14}$	1.30	159	2233	13.31
5	V	23	$4s^23d^3$	1.63	134	1910	6.00
	Nb	41	$5s^24d^3$	1.60	146	2477	8.57
	Ta	73	$6s^25d^34f^{14}$	1.50	146	3017	16.65

The group 3 metals react with nonmetals to form compounds that are primarily ionic in character. For example, reacting group 3 metals with the halogens produces the corresponding trihalides: MX_3. The trifluorides are insoluble in water because of their high lattice energies, but the other trihalides are very soluble in water and behave like typical ionic metal halides. All group 3 elements react with air to form an oxide coating, and all burn in oxygen to form the so-called sesquioxides (M_2O_3), which react with H_2O or CO_2 to form the corresponding hydroxides or carbonates, respectively. Commercial uses of the group 3 metals are limited, but “mischmetal,” a mixture of lanthanides containing about 40% La, is used as an additive to improve the properties of steel and make flints for cigarette lighters.

Group 4 (Ti, Zr, and Hf)

Because the elements of group 4 have a high affinity for oxygen, all three metals occur naturally as oxide ores that contain the metal in the +4 oxidation state resulting from losing all four $ns^2(n-1)d^2$ valence electrons. They are isolated by initial conversion to the tetrachlorides, as shown for Ti:

$$2FeTiO_{3(s)} + 6C_{(s)} + 7Cl_{2(g)} \rightarrow 2TiCl_{4(g)} + 2FeCl_{3(g)} + 6CO_{(g)} \tag{19.2.2}$$

followed by reduction of the tetrachlorides with an active metal such as Mg.

> *The chemistry of the group 4 metals is dominated by the +4 oxidation state. Only Ti has an extensive chemistry in lower oxidation states.*

In contrast to the elements of group 3, the group 4 elements have important applications. Titanium (melting point = 1668°C) is often used as a replacement for aluminum (melting point = 660°C) in applications that require high temperatures or corrosion resistance. For example, friction with the air heats the skin of supersonic aircraft operating above Mach 2.2 to temperatures near the melting point of aluminum; consequently, titanium is used instead of aluminum in many aerospace applications. The corrosion resistance of titanium is increasingly exploited in architectural applications, as shown in the chapter-opening photo. Metallic zirconium is used in UO_2-containing fuel rods in nuclear reactors, while hafnium is used in the control rods that modulate the output of high-power nuclear reactors, such as those in nuclear submarines.

Consistent with the periodic trends shown in Figure 23.2, the group 4 metals become denser, higher melting, and more electropositive down the column (Table 19.2.1). Unexpectedly, however, the atomic radius of Hf is slightly smaller than that of Zr due to the lanthanide contraction. Because of their $ns^2(n-1)d^2$ valence electron configurations, the +4 oxidation state is by far the most important for all three metals. Only titanium exhibits a significant chemistry in the +2 and +3 oxidation states, although compounds of Ti^{2+} are usually powerful reductants. In fact, the $Ti^{2+}(aq)$ ion is such a strong reductant that it rapidly reduces water to form hydrogen gas.

Reaction of the group 4 metals with excess halogen forms the corresponding tetrahalides (MX_4), although titanium, the lightest element in the group, also forms dihalides and trihalides (X is not F). The covalent character of the titanium halides increases as the oxidation state of the metal increases because of increasing polarization of the anions by the cation as its charge-to-radius ratio increases. Thus $TiCl_2$ is an ionic salt, whereas $TiCl_4$ is a volatile liquid that contains tetrahedral molecules. All three metals react with excess oxygen or the heavier chalcogens (Y) to form the corresponding dioxides (MO_2) and dichalcogenides (MY_2). Industrially, TiO_2, which is used as a white pigment in paints, is prepared by reacting $TiCl_4$ with oxygen at high temperatures:

$$TiCl_{4(g)} + O_{2(g)} \rightarrow TiO_{2(s)} + 2Cl_{2(g)} \tag{19.2.3}$$

The group 4 dichalcogenides have unusual layered structures with no M–Y bonds holding adjacent sheets together, which makes them similar in some ways to graphite (Figure 19.2.1). The group 4 metals also react with hydrogen, nitrogen, carbon, and boron to form hydrides (such as TiH_2), nitrides (such as TiN), carbides (such as TiC), and borides (such as TiB_2), all of which are hard, high-melting solids. Many of these binary compounds are nonstoichiometric and exhibit metallic conductivity.

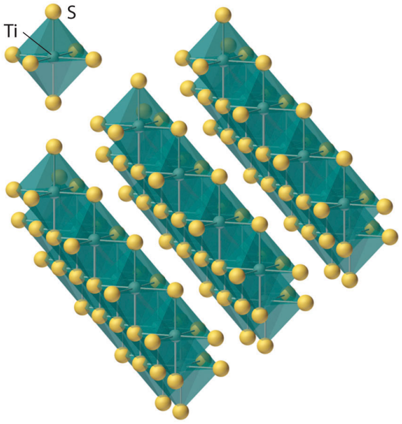


Figure 19.2.1: The Layered Structure of TiS_2. Each titanium atom is surrounded by an octahedral arrangement of six sulfur atoms that are shared to form extended layers of atoms. Because the layers are held together by only van der Waals forces between adjacent sulfur atoms, rather than covalent bonds, the layers slide past one another relatively easily when a mechanical stress is applied.

Group 5 (V, Nb, and Ta)

Like the group 4 elements, all group 5 metals are normally found in nature as oxide ores that contain the metals in their highest oxidation state (+5). Because of the lanthanide contraction, the chemistry of Nb and Ta is so similar that these elements are usually found in the same ores.

Three-fourths of the vanadium produced annually is used in the production of steel alloys for springs and high-speed cutting tools. Adding a small amount of vanadium to steel results in the formation of small grains of V_4C_3, which greatly increase the strength and resilience of the metal, especially at high temperatures. The other major use of vanadium is as V_2O_5, an important catalyst for the industrial conversion of SO_2 to SO_3 in the contact process for the production of sulfuric acid. In contrast, Nb and Ta have only limited applications, and they are therefore produced in relatively small amounts. Although niobium is used as an additive in certain stainless steels, its primary application is in superconducting wires such as Nb_3Zr and Nb_3Ge, which are used in superconducting magnets for the magnetic resonance imaging of soft tissues. Because tantalum is highly resistant to corrosion, it is used as a liner for chemical reactors, in missile parts, and as a biologically compatible material in screws and pins for repairing fractured bones.

> *The chemistry of the two heaviest group 5 metals (Nb and Ta) is dominated by the +5 oxidation state. The chemistry of the lightest element (V) is dominated by lower oxidation states, especially +4.*

As indicated in Table 19.2.1, the trends in properties of the group 5 metals are similar to those of group 4. Only vanadium, the lightest element, has any tendency to form compounds in oxidation states lower than +5. For example, vanadium is the only element in the group that forms stable halides in the lowest oxidation state (+2). All three metals react with excess oxygen, however, to produce the corresponding oxides in the +5 oxidation state (M_2O_5), in which polarization of the oxide ions by the high-oxidation-state metal is so extensive that the compounds are primarily covalent in character. Vanadium–oxygen species provide a classic example of the effect of increasing metal oxidation state on the protonation state of a coordinated water molecule: vanadium(II) in water exists as the violet hydrated ion $[V(H_2O)_6]^{2+}$; the blue-green $[V(H_2O)_6]^{3+}$ ion is acidic, dissociating to form small amounts of the $[V(H_2O)_5(OH)]^{2+}$ ion and a proton; and in water, vanadium(IV) forms the blue vanadyl ion $[(H_2O)_4VO]^{2+}$, which contains a formal V=O bond (Figure 19.2.2). Consistent with its covalent character, V_2O_5 is acidic, dissolving in base to give the vanadate ion ($[VO_4]^{3-}$), whereas both Nb_2O_5 and Ta_2O_5 are comparatively inert. Oxides of these metals in lower oxidation states tend to be nonstoichiometric.

Because vanadium ions with different oxidation states have different numbers of d electrons, aqueous solutions of the ions have different colors: in acid V(V) forms the pale yellow $[VO_2]^+$ ion; V(IV) is the blue vanadyl ion $[VO]^{2+}$; and V(III) and V(II) exist as the hydrated V^{3+} (blue-green) and V^{2+} (violet) ions, respectively.

Although group 5 metals react with the heavier chalcogens to form a complex set of binary chalcogenides, the most important are the dichalcogenides (MY_2), whose layered structures are similar to those of the group 4 dichalcogenides. The elements of group 5 also form binary nitrides, carbides, borides, and hydrides, whose stoichiometries and properties are similar to those of the corresponding group 4 compounds. One such compound, tantalum carbide (TiC), has the highest melting point of any compound known (3738°C); it is used for the cutting edges of high-speed machine tools.

Group 6 (Cr, Mo, and W)

As an illustration of the trend toward increasing polarizability as we go from left to right across the d block, in group 6 we first encounter a metal (Mo) that occurs naturally as a sulfide ore rather than as an oxide. Molybdenite (MoS_2) is a soft black mineral that can be used for writing, like PbS and graphite. Because of this similarity, people long assumed that these substances were all the same. In fact, the name molybdenum is derived from the Greek molybdos, meaning “lead.” More than 90% of the molybdenum produced annually is used to make steels for cutting tools, which retain their sharp edge even when red hot. In addition, molybdenum is the only second- or third-row transition element that is essential for humans. The major chromium ore is chromite ($FeCr_2O_4$), which is oxidized to the soluble $[CrO_4]^{2-}$ ion under basic conditions and reduced successively to Cr_2O_3 and Cr with carbon and aluminum, respectively. Pure chromium can be obtained by dissolving Cr_2O_3 in sulfuric acid followed by electrolytic reduction; a similar process is used for electroplating metal objects to give them a bright, shiny, protective surface layer. Pure tungsten is obtained by first converting tungsten ores to WO_3, which is then reduced with hydrogen to give the metal.

> *The metals become increasing polarizable across the d block.*

Consistent with periodic trends, the group 6 metals are slightly less electropositive than those of the three preceding groups, and the two heaviest metals are essentially the same size because of the lanthanide contraction (Table 19.2.2). All three elements have a total of six valence electrons, resulting in a maximum oxidation state of +6. Due to extensive polarization of the anions, compounds in the +6 oxidation state are highly covalent. As in groups 4 and 5, the lightest element exhibits variable oxidation states, ranging from Cr^{2+}, which is a powerful reductant, to CrO_3, a red solid that is a powerful oxidant. For Mo and W, the highest oxidation state (+6) is by far the most important, although compounds in the +4 and +5 oxidation states are known.

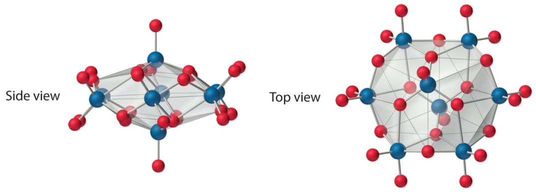
Table 19.2.2: Some Properties of the Elements of Groups 6 and 7

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
6	Cr	24	$4s^13d^5$	1.66	128	1907	7.15
	Mo	42	$5s^14d^5$	2.16	139	2623	10.20
	W	74	$6s^25d^44f^{14}$	1.70	139	3422	19.30
7	Mn	25	$4s^23d^5$	1.55	127	1246	7.30
	Tc	43	$5s^24d^5$	2.10	136	2157	11.50
	Re	75	$6s^25d^54f^{14}$	1.90	137	3186	20.80

> The chemistry of the two heaviest group 6 metals (Mo and W) is dominated by the +6 oxidation state. The chemistry of the lightest element (Cr) is dominated by lower oxidation states.

As observed in previous groups, the group 6 halides become more covalent as the oxidation state of the metal increases: their volatility increases, and their melting points decrease. Recall that as the electronegativity of the halogens decreases from F to I, they are less able to stabilize high oxidation states; consequently, the maximum oxidation state of the corresponding metal halides decreases. Thus all three metals form hexafluorides, but CrF_6 is unstable at temperatures above −100°C, whereas MoF_6 and WF_6 are stable. Consistent with the trend toward increased stability of the highest oxidation state for the second- and third-row elements, the other halogens can oxidize chromium to only the trihalides, CrX_3 (X is Cl, Br, or I), while molybdenum forms $MoCl_5$, $MoBr_4$, and MoI_3, and tungsten gives WCl_6, WBr_5, and WI_4.

Both Mo and W react with oxygen to form the covalent trioxides (MoO_3 and WO_3), but Cr reacts to form only the so-called sesquioxide (Cr_2O_3). Chromium will form CrO_3, which is a highly toxic compound that can react explosively with organic materials. All the trioxides are acidic, dissolving in base to form the corresponding oxoanions ($[MO_4]^{2-}$). Consistent with periodic trends, the sesquioxide of the lightest element in the group (Cr_2O_3) is amphoteric. The aqueous chemistry of molybdate and tungstate is complex, and at low pH they form a series of polymeric anions called isopolymetallates, such as the $[Mo_8O_{26}]^{4-}$ ion, whose structure is as follows:



An isopolymolybdate cluster. The $[Mo_8O_{26}]^{4-}$ ion, shown here in both side and top views, is typical of the oxygen-bridged clusters formed by Mo(VI) and W(VI) in aqueous solution.

Reacting molybdenum or tungsten with heavier chalcogens gives binary chalcogenide phases, most of which are nonstoichiometric and electrically conducting. One of the most stable is MoS_2; it has a layered structure similar to that of TiS_2 (Figure 19.2.1), in which the layers are held together by only weak van der Waals forces, which allows them to slide past one another rather easily. Consequently, both MoS_2 and WS_2 are used as lubricants in a variety of applications, including automobile engines. Because tungsten itself has an extraordinarily high melting point (3380°C), lubricants described as containing “liquid tungsten” actually contain a suspension of very small WS_2 particles.

As in groups 4 and 5, the elements of group 6 form binary nitrides, carbides, and borides whose stoichiometries and properties are similar to those of the preceding groups. Tungsten carbide (WC), one of the hardest compounds known, is used to make the tips of drill bits.

Group 7 (Mn, Tc, and Re)

Continuing across the periodic table, we encounter the group 7 elements (Table 19.2.2). One group 7 metal (Mn) is usually combined with iron in an alloy called ferromanganese, which has been used since 1856 to improve the mechanical properties of steel by scavenging sulfur and oxygen impurities to form MnS and MnO. Technetium is named after the Greek technikos, meaning “artificial,” because all its isotopes are radioactive. One isotope, ^{99m}Tc (m for metastable), has become an important biomedical tool for imaging internal organs. Because of its scarcity, Re is one of the most expensive elements, and its applications are limited. It is, however, used in a bimetallic Pt/Re catalyst for refining high-octane gasoline.

All three group 7 elements have seven valence electrons and can form compounds in the +7 oxidation state. Once again, the lightest element exhibits multiple oxidation states. Compounds of Mn in oxidation states ranging from −3 to +7 are known, with the most common being +2 and +4 (Figure 19.2.3). In contrast, compounds of Tc and Re in the +2 oxidation state are quite rare. Because the electronegativity of Mn is anomalously low, elemental manganese is unusually reactive. In contrast, the chemistry of Tc is similar to that of Re because of their similar size and electronegativity, again a result of the lanthanide contraction. Due to the stability of the half-filled $3d^5$ electron configuration, the aqueous Mn^{3+} ion, with a $3d^4$ valence electron configuration, is a potent oxidant that is able to oxidize water. It is difficult to generalize about other oxidation states for Tc and Re because their stability depends dramatically on the nature of the compound.

Like vanadium, compounds of manganese in different oxidation states have different numbers of d electrons, which leads to compounds with different colors: the Mn^{2+}(aq) ion is pale pink; $Mn(OH)_3$, which contains Mn(III), is a dark brown solid; MnO_2, which contains Mn(IV), is a black solid; and aqueous solutions of Mn(VI) and Mn(VII) contain the green manganate ion $[MnO_4]^{2-}$ and the purple permanganate ion $[MnO_4]^{-}$, respectively.

Consistent with higher oxidation states being more stable for the heavier transition metals, reacting Mn with F_2 gives only MnF_3, a high-melting, red-purple solid, whereas Re reacts with F_2 to give ReF_7, a volatile, low-melting, yellow solid. Again, reaction with the less oxidizing, heavier halogens produces halides in lower oxidation states. Thus reaction with Cl_2, a weaker oxidant than F_2, gives $MnCl_2$ and $ReCl_6$. Reaction of Mn with oxygen forms only Mn_3O_4, a mixed-valent compound that contains two Mn(II) and one Mn(III) per formula unit and is similar in both stoichiometry and structure to magnetite (Fe_3O_4). In contrast, Tc and Re form high-valent oxides, the so-called heptoxides (M_2O_7), consistent with the increased stability of higher oxidation states for the second and third rows of transition metals. Under forced conditions, manganese will form Mn_2O_7, an unstable, explosive, green liquid. Also consistent with this trend, the permanganate ion $[MnO_4]^{2-}$ is a potent oxidant, whereas $[TcO_4]^-$ and $[ReO_4]^-$ are much more stable. Both Tc and Re form disulfides and diselenides with layered structures analogous to that of MoS_2, as well as more complex heptasulfides (M_2S_7). As is typical of the transition metals, the group 7 metals form binary nitrides, carbides, and borides that are generally stable at high temperatures and exhibit metallic properties.

> *The chemistry of the group 7 metals (Mn, Tc, and Re) is dominated by lower oxidation states. Compounds in the maximum possible oxidation state (+7) are readily reduced.*

Groups 8, 9, and 10

In many older versions of the periodic table, groups 8, 9, and 10 were combined in a single group (group VIII) because the elements of these three groups exhibit many horizontal similarities in their chemistry, in addition to the similarities within each column. In part, these horizontal similarities are due to the fact that the ionization potentials of the elements, which increase slowly but steadily across the d block, have now become so large that the oxidation state corresponding to the formal loss of all valence electrons is encountered only rarely (group 8) or not at all (groups 9 and 10). As a result, the chemistry of all three groups is dominated by intermediate oxidation states, especially +2 and +3 for the first-row metals (Fe, Co, and Ni). The heavier elements of these three groups are called precious metals because they are rather rare in nature and mostly chemically inert.

> *The chemistry of groups 8, 9, and 10 is dominated by intermediate oxidation states such as +2 and +3.*

Group 8 (Fe, Ru, and Os)

The chemistry of group 8 is dominated by iron, whose high abundance in Earth's crust is due to the extremely high stability of its nucleus. Ruthenium and osmium, on the other hand, are extremely rare elements, with terrestrial abundances of only about 0.1 ppb and 5 ppb, respectively, and they were not discovered until the 19th century. Because of the high melting point of iron (1538°C), early humans could not use it for tools or weapons. The advanced techniques needed to work iron were first developed by the Hittite civilization in Asia Minor sometime before 2000 BC, and they remained a closely guarded secret that gave the Hittites military supremacy for almost a millennium. With the collapse of the Hittite civilization around 1200 BC, the technology became widely distributed, however, leading to the Iron Age.

Group 9 (Co, Rh, and Ir)

Cobalt is one of the least abundant of the first-row transition metals. Its oxide ores, however, have been used in glass and pottery for thousands of years to produce the brilliant color known as "cobalt blue," and its compounds are consumed in large quantities in the paint and ceramics industries. The heavier elements of group 9 are also rare, with terrestrial abundances of less than 1 ppb; they are generally found in combination with the heavier elements of groups 8 and 10 in Ni–Cu–S ores.

Group 10 (Ni, Pd, and Pt)

Nickel silicates are easily processed; consequently, nickel has been known and used since antiquity. In fact, a 75:25 Cu:Ni alloy was used for more than 2000 years to mint "silver" coins, and the modern US nickel uses the same alloy. In contrast to nickel, palladium and platinum are rare (their terrestrial abundance is about 10–15 ppb), but they are at least an order of magnitude more abundant than the heavier elements of groups 8 and 9. Platinum and palladium are used in jewelry, the former as the pure element and the latter as the Pd/Au alloy known as white gold.

Over 2000 years ago, the Bactrian civilization in Western Asia used a 75:25 alloy of copper and nickel for its coins. A modern US nickel has the same composition, but a modern Canadian nickel is nickel-plated steel and contains only 2.5% nickel by mass.

Trends in Group 8, 9, and 10

Some properties of the elements in groups 8–10 are summarized in Table 19.2.3. As in earlier groups, similarities in size and electronegativity between the two heaviest members of each group result in similarities in chemistry. We are now at the point in the d block where there is no longer a clear correlation between the valence electron configuration and the preferred oxidation state. For example, all the elements of group 8 have eight valence electrons, but only Ru and Os have any tendency to form compounds in the +8 oxidation state, and those compounds are powerful oxidants. The predominant oxidation states for all three group 8 metals are +2 and +3. Although the elements of group 9 possess a total of nine valence electrons, the +9 oxidation state is unknown for these elements, and the most common oxidation states in the group are +3 and +1. Finally, the elements of group 10 all have 10 valence electrons, but all three elements are normally found in the +2 oxidation state formed by losing the ns2 valence electrons. In addition, Pd and Pt form numerous compounds and complexes in the +4 oxidation state.

Table 19.2.3: Some Properties of the Elements of Groups 8, 9, and 10

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
8	Fe	26	$4s^23d^6$	1.83	126	1538	7.87
	Ru	44	$5s^14d^7$	2.20	134	2334	12.10
	Os	76	$6s^25d^64f^{14}$	2.20	135	3033	22.59
9	Co	27	$4s^23d^7$	1.88	125	1495	8.86

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
	Rh	45	$5s^14d^8$	2.28	134	1964	12.40
	Ir	77	$6s^25d^74f^{14}$	2.20	136	2446	22.50
10	Ni	28	$4s^23d^8$	1.91	124	1455	8.90
	Pd	46	$4d^{10}$	2.20	137	1555	12.00
	Pt	78	$6s^25d^84f^{14}$	2.20	139	1768	21.50

We stated that higher oxidation states become less stable as we go across the d-block elements and more stable as we go down a group. Thus Fe and Co form trifluorides, but Ni forms only the difluoride NiF_2. In contrast to Fe, Ru and Os form a series of fluorides up to RuF_6 and OsF_7. The hexafluorides of Rh and Ir are extraordinarily powerful oxidants, and Pt is the only element in group 10 that forms a hexafluoride. Similar trends are observed among the oxides. For example, Fe forms only FeO, Fe_2O_3, and the mixed-valent Fe_3O_4 (magnetite), all of which are nonstoichiometric. In contrast, Ru and Os form the dioxides (MO_2) and the highly toxic, volatile, yellow tetroxides, which contain formal M=O bonds. As expected for compounds of metals in such high oxidation states, the latter are potent oxidants. The tendency of the metals to form the higher oxides decreases rapidly as we go farther across the d block.

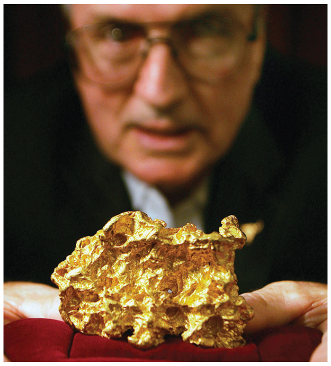
> *Higher oxidation states become less stable across the d-block, but more stable down a group.*

Reactivity with the heavier chalcogens is rather complex. Thus the oxidation state of Fe, Ru, Os, Co, and Ni in their disulfides is +2 because of the presence of the disulfide ion (S_2^{2-}), but the disulfides of Rh, Ir, Pd, and Pt contain the metal in the +4 oxidation state together with sulfide ions (S^{2-}). This combination of highly charged cations and easily polarized anions results in substances that are not simple ionic compounds and have significant covalent character.

The groups 8–10 metals form a range of binary nitrides, carbides, and borides. By far the most important of these is cementite (Fe_3C), which is used to strengthen steel. At high temperatures, Fe_3C is soluble in iron, but slow cooling causes the phases to separate and form particles of cementite, which gives a metal that retains much of its strength but is significantly less brittle than pure iron. Palladium is unusual in that it forms a binary hydride with the approximate composition $PdH_{0.5}$. Because the H atoms in the metal lattice are highly mobile, thin sheets of Pd are highly permeable to H_2 but essentially impermeable to all other gases, including He. Consequently, diffusion of H_2 through Pd is an effective method for separating hydrogen from other gases.

Group 11 (Cu, Ag, and Au)

The coinage metals—copper, silver, and gold—occur naturally (like the gold nugget shown here); consequently, these were probably the first metals used by ancient humans. For example, decorative gold artifacts dating from the late Stone Age are known, and some gold Egyptian coins are more than 5000 yr old. Copper is almost as ancient, with objects dating to about 5000 BC. Bronze, an alloy of copper and tin that is harder than either of its constituent metals, was used before 3000 BC, giving rise to the Bronze Age. Deposits of silver are much less common than deposits of gold or copper, yet by 3000 BC, methods had been developed for recovering silver from its ores, which allowed silver coins to be widely used in ancient times.



This 1 kg gold nugget was found in Australia; in 2005, it was for sale in Hong Kong at an asking price of more than US$64,000.

Deposits of gold and copper are widespread and numerous, and for many centuries it was relatively easy to obtain large amounts of the pure elements. For example, a single gold nugget discovered in Australia in 1869 weighed more than 150 lb. Because the demand for these elements has outstripped their availability, methods have been developed to recover them economically from even very low-grade ores (as low as 1% Cu content for copper) by operating on a vast scale, as shown in the photo of an open-pit copper mine. Copper is used primarily to manufacture electric wires, but large quantities are also used to produce bronze, brass, and alloys for coins. Much of the silver made today is obtained as a by-product of the manufacture of other metals, especially Cu, Pb, and Zn. In addition to its use in jewelry and silverware, silver is used in Ag/Zn and Ag/Cd button batteries. Gold is typically found either as tiny particles of the pure metal or as gold telluride ($AuTe_2$). It is used as a currency reserve, in jewelry, in the electronics industry for corrosion-free contacts, and, in very thin layers, as a reflective window coating that minimizes heat transfer.

The Chuquicamata copper mine in northern Chile, the world's largest open-pit copper mine, is 4.3 km long, 3 km wide, and 825 m deep. Each gigantic truck in the foreground (and barely visible in the lower right center) can hold 330 metric tn (330,000 kg) of copper ore.

Some properties of the coinage metals are listed in Table 19.2.4. The electronegativity of gold (χ = 2.40) is close to that of the nonmetals sulfur and iodine, which suggests that the chemistry of gold should be somewhat unusual for a metal. The coinage metals have the highest electrical and thermal conductivities of all the metals, and they are also the most ductile and malleable. With an $ns^1(n-1)d^{10}$ valence electron configuration, the chemistry of these three elements is dominated by the +1 oxidation state due to losing the single ns electron. Higher oxidation states are also known, however: +2 is common for Cu and, to a lesser extent, Ag, and +3 for Au because of the relatively low values of the second and (for Au) third ionization energies. All three elements have significant electron affinities due to the half-filled ns orbital in the neutral atoms. As a result, gold reacts with powerful reductants like Cs and solutions of the alkali metals in liquid ammonia to produce the gold anion Au^- with a $6s^25d^{10}$ valence electron configuration.

Table 19.2.4: Some Properties of the Elements of Groups 11 and 12

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
11	Cu	29	$4s^13d^{10}$	1.90	128	1085	8.96

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
	Ag	47	$5s^1 4d^{10}$	1.93	144	962	10.50
	Au	79	$6s^1 5d^{10} 4f^{14}$	2.40	144	1064	19.30
12	Zn	30	$4s^2 3d^{10}$	1.65	134	420	7.13
	Cd	48	$5s^2 4d^{10}$	1.69	149	321	8.69
	Hg	80	$6s^2 5d^{10} 4f^{14}$	1.90	151	−38.8	13.53

All group 11 elements are relatively unreactive, and their reactivity decreases from Cu to Au. Hence they are noble metals that are particularly well suited for use in coins and jewelry. Copper reacts with O_2 at high temperatures to produce Cu_2O and with sulfur to form Cu_2S. Neither silver nor gold reacts directly with oxygen, although oxides of these elements can be prepared by other routes. Silver reacts with sulfur compounds to form the black Ag_2S coating known as tarnish. Gold is the only metal that does not react with sulfur; it also does not react with nitrogen, carbon, or boron. All the coinage metals do, however, react with oxidizing acids. Thus both Cu and Ag dissolve in HNO_3 and in hot concentrated H_2SO_4, while Au dissolves in the 3:1 HCl:HNO_3 mixture known as aqua regia. Furthermore, all three metals dissolve in basic cyanide solutions in the presence of oxygen to form very stable $[M(CN)_2]^-$ ions, a reaction that is used to separate gold from its ores.

> *Although the most important oxidation state for group 11 is +1, the elements are relatively unreactive, with reactivity decreasing from Cu to Au.*

All the monohalides except CuF and AuF are known (including AgF). Once again, iodine is unable to stabilize the higher oxidation states (Au^{3+} and Cu^{2+}). Thus all the copper(II) halides except the iodide are known, but the only dihalide of silver is AgF_2. In contrast, all the gold trihalides (AuX_3) are known, again except the triiodide. No binary nitrides, borides, or carbides are known for the group 11 elements.

Group 12 (Zn, Cd, and Hg)

We next encounter the group 12 elements. Because none of the elements in group 12 has a partially filled (n − 1)d subshell, they are not, strictly speaking, transition metals. Nonetheless, much of their chemistry is similar to that of the elements that immediately precede them in the d block. The group 12 metals are similar in abundance to those of group 11, and they are almost always found in combination with sulfur. Because zinc and cadmium are chemically similar, virtually all zinc ores contain significant amounts of cadmium. All three metals are commercially important, although the use of Cd is restricted because of its toxicity. Zinc is used for corrosion protection, in batteries, to make brass, and, in the form of ZnO, in the production of rubber and paints. Cadmium is used as the cathode in rechargeable NiCad batteries. Large amounts of mercury are used in the production of chlorine and NaOH by the chloralkali process, while smaller amounts are consumed in mercury-vapor streetlights and mercury batteries.

As shown in Table 19.2.4, the group 12 metals are significantly more electropositive than the elements of group 11, and they therefore have less noble character. They also have much lower melting and boiling points than the preceding transition metals. In contrast to trends in the preceding groups, Zn and Cd are similar to each other, but very different from the heaviest element (Hg). In particular, Zn and Cd are rather active metals, whereas mercury is not. Because mercury, the only metal that is a liquid at room temperature, can dissolve many metals by forming amalgams, medieval alchemists especially valued it when trying to transmute base metals to gold and silver. All three elements in group 12 have $ns^2(n-1)d^{10}$ valence electron configurations; consequently, the +2 oxidation state, corresponding to losing the two ns electrons, dominates their chemistry. In addition, mercury forms a series of compounds in the +1 oxidation state that contain the diatomic mercurous ion $Hg_2{}^{2+}$.

> *The most important oxidation state for group 12 is +2; the metals are significantly more electropositive than the group 11 elements, so they are less noble.*

All the possible group 12 dihalides (MX_2) are known, and they range from ionic (the fluorides) to highly covalent (such as $HgCl_2$). The highly covalent character of many mercuric and mercurous halides is surprising given the large size of the cations, and this has been attributed to the existence of an easily distorted $5d^{10}$ subshell. Zinc and cadmium react with oxygen to form amphoteric MO, whereas mercury forms HgO only within a narrow temperature range (350–400°C). Whereas zinc and cadmium dissolve in mineral acids such as HCl with the evolution of hydrogen, mercury dissolves only in oxidizing acids such as HNO_3 and H_2SO_4. All three metals react with sulfur and the other chalcogens to form the binary chalcogenides; mercury also has an extraordinarily high affinity for sulfur.

✓ Example 19.2.1

For each reaction, explain why the indicated products form.

a. $TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(aq)$
b. $WO_3(s) + 3C(s) + 3Cl_2(g) \xrightarrow{\Delta} WCl_6(s) + 3CO(g)$
c. $Sc_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Sc(OH)_4]^-(aq)$
d. $2KMnO_4(aq) + 2H_2SO_4(l) \rightarrow Mn_2O_7(l) + 2KHSO_4(soln) + H_2O(soln)$
e. $4CrCl_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Cr^{3+}(aq) + 8Cl^-(aq) + 2H_2O(l)$

Given: balanced chemical equation

Asked for: why the indicated products form

Strategy:

Refer to the periodic trends in this section.

Solution:

a. The most stable oxidation state for Ti is +4, and neither reactant is a particularly strong oxidant or reductant; hence a redox reaction is unlikely. Similarly, neither reactant is a particularly strong acid or base, so an acid–base reaction is unlikely. Because $TiCl_4$ contains Ti in a relatively high oxidation state (+4), however, it is likely to be rather covalent in character, with reactivity similar to that of a semimetal halide such as $SiCl_4$. Covalent halides tend to hydrolyze in water to produce the hydrohalic acid and either the oxide of the other element or a species analogous to an oxoacid.
b. This reaction involves the oxide of a group 6 metal in its highest oxidation state (WO_3) and two elements, one of which is a reductant (C) and the other an oxidant (Cl_2). Consequently, some sort of redox reaction will occur. Carbon can certainly react with chlorine to form CCl_4, and WO_3 is a potential source of oxygen atoms that can react with carbon to produce CO, which is very stable. If CO is one of the products, then it seems likely that the other product will contain the metal and chlorine. The most likely combination is WCl_6 (leaving the oxidation state of the metal unchanged).
c. One of the reactants is a strong base (OH^-), so an acid–base reaction is likely if the other reactant is acidic. Because oxides like Sc_2O_3, in which the metal is in an intermediate oxidation state, are often amphoteric, we expect Sc_2O_3 to dissolve in base to form a soluble hydroxide complex.
d. Concentrated sulfuric acid is both an oxidant and a strong acid that tends to protonate and dehydrate other substances. The permanganate ion already contains manganese in its highest possible oxidation state (+7), so it cannot be oxidized further. A redox reaction is impossible, which leaves an acid–base reaction as the most likely alternative. Sulfuric acid is likely to protonate the terminal oxygen atoms of permanganate, allowing them to be lost as water.
e. Molecular oxygen is an oxidant, so a redox reaction is likely if the other reactant can be oxidized. Because chromous chloride contains chromium in its lowest accessible oxidation state, a redox reaction will occur in which Cr^{2+} ions are oxidized and O_2 is reduced. In the presence of protons, the reduction product of O_2 is water, so we need to determine only the identity of the oxidation product of Cr^{2+}. Chromium forms compounds in two common higher oxidation states: the Cr^{3+} ion, which is the most stable, and the $[Cr_2O_7]^{2-}$ ion, which is a more powerful oxidant than O_2. We therefore predict that the reaction will form $Cr^{3+}(aq)$ and water.

? Exercise 19.2.1

Predict the products of each reactions and then balance each chemical equation.

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \xrightarrow{H^+}$
b. $Na_2Cr_2O_7(aq) + H_2SO_4(l) \rightarrow$
c. $FeBr_2(aq) + O_2(g) \xrightarrow{H^+}$
d. $VBr_4(l) + H_2O(l) \rightarrow$

e. $ZrO_2(s) + C(s) + Cl_2(g) \xrightarrow{\Delta}$

Answer

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \xrightarrow{H^+} Cr^{3+}(aq) + Fe^{2+}(aq)$
b. $Na_2Cr_2O_7(aq) + 2H_2SO_4(l) \rightarrow 2NaHSO_4(soln) + H_2O(soln) + 2CrO_3(s)$
c. $4FeBr_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) + 8Br^-(aq)$
d. $VBr_4(l) + H_2O(l) \rightarrow VO^{2+}(aq) + 4Br^-(aq) + 2H^+(aq)$
e. $ZrO_2(s) + 2C(s) + 2Cl_2(g) \xrightarrow{\Delta} ZrCl_4(s) + 2CO(g)$

Summary

The elements tend to become more polarizable going across the d block and higher oxidation states become less stable; higher oxidation states become more stable going down a group. The group 3 transition metals are highly electropositive metals and powerful reductants. They react with nonmetals to form compounds that are largely ionic and with oxygen to form sesquioxides (M_2O_3). The group 4 metals also have a high affinity for oxygen. In their reactions with halogens, the covalent character of the halides increases as the oxidation state of the metal increases because the high charge-to-radius ratio causes extensive polarization of the anions. The dichalcogenides have layered structures similar to graphite, and the hydrides, nitrides, carbides, and borides are all hard, high-melting-point solids with metallic conductivity. The group 5 metals also have a high affinity for oxygen. Consistent with periodic trends, only the lightest (vanadium) has any tendency to form compounds in oxidation states lower than +5. The oxides are sufficiently polarized to make them covalent in character. These elements also form layered chalcogenides, as well as nitrides, carbides, borides, and hydrides that are similar to those of the group 4 elements. As the metals become more polarizable across the row, their affinity for oxygen decreases. The group 6 metals are less electropositive and have a maximum oxidation state of +6, making their compounds in high oxidation states largely covalent in character. As the oxidizing strength of the halogen decreases, the maximum oxidation state of the metal also decreases. All three trioxides are acidic, but Cr_2O_3 is amphoteric. The chalcogenides of the group 6 metals are generally nonstoichiometric and electrically conducting, and these elements also form nitrides, carbides, and borides that are similar to those in the preceding groups. The metals of group 7 have a maximum oxidation state of +7, but the lightest element, manganese, exhibits an extensive chemistry in lower oxidation states. As with the group 6 metals, reaction with less oxidizing halogens produces metals in lower oxidation states, and disulfides and diselenides of Tc and Re have layered structures. The group 7 metals also form nitrides, carbides, and borides that are stable at high temperatures and have metallic properties. In groups 8, 9, and 10, the ionization potentials of the elements are so high that the oxidation state corresponding to the formal loss of all valence electrons is encountered rarely (group 8) or not at all (groups 9 and 10). Compounds of group 8 metals in their highest oxidation state are powerful oxidants. The reaction of metals in groups 8, 9, and 10 with the chalcogens is complex, and these elements form a range of binary nitrides, carbides, and borides. The coinage metals (group 11) have the highest electrical and thermal conductivities and are the most ductile and malleable of the metals. Although they are relatively unreactive, they form halides but not nitrides, borides, or carbides. The group 12 elements, whose chemistry is dominated by the +2 oxidation state, are almost always found in nature combined with sulfur. Mercury is the only metal that is a liquid at room temperature, and it dissolves many metals to form amalgams. The group 12 halides range from ionic to covalent. These elements form chalcogenides and have a high affinity for soft ligands.

Contributors and Attributions

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19.3: Coordination Compounds

Learning Objectives

- To know the most common structures observed for metal complexes.
- To predict the relative stabilities of metal complexes with different ligands

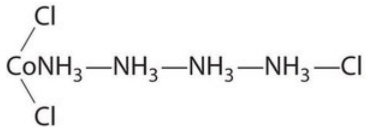
One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands (from the Latin ligare, meaning "to bind"), which are ions or molecules that contain one or more pairs of electrons that can be shared with the metal. Metal complexes can be neutral, such as $Co(NH_3)_3Cl_3$; positively charged, such as $[Nd(H_2O)_9]^{3+}$; or negatively charged, such as $[UF_8]^{4-}$. Electrically charged metal complexes are sometimes called *complex ions*. A *coordination compound* contains one or more metal complexes.

Coordination compounds are important for at least three reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene "plastic" items we use every day. Finally, transition-metal complexes are essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions.

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue: $KFe_2(CN)_6$. The chemical nature of these substances, however, was unclear for a number of reasons. For example, many compounds called "double salts" were known, such as $AlF_3 \cdot 3\,KF$, $Fe(CN)_2 \cdot 4\,KCN$, and $ZnCl_2 \cdot 2\,CsCl$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $AlF_3 \cdot 3\,KF$ exist but not $AlF_3 \cdot 4\,KF$ or $AlF_3 \cdot 2\,KF$? And why should a 3:1 KF:AlF3 mixture have different chemical and physical properties than either of its components? Similarly, adducts of metal salts with neutral molecules such as ammonia were also known—for example, $CoCl_3 \cdot 6\,NH_3$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $CoCl_3 \cdot 6\,NH_3$, $CoCl_3 \cdot 5\,NH_3$, $CoCl_3 \cdot 4\,NH_3$, and $CoCl_3 \cdot 3\,NH_3$ were all known and had very different properties, but despite all attempts, chemists could not prepare $CoCl_3 \cdot 2\,NH_3$ or $CoCl_3 \cdot NH_3$.

Although the chemical composition of such compounds was readily established by existing analytical methods, their chemical nature was puzzling and highly controversial. The major problem was that what we now call valence (i.e., the oxidation state) and coordination number were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds, including the "Chattanooga choo-choo" model for $CoCl_3{\cdot}4NH_3$ shown here.



$CoCl_3 \cdot 4NH_3$

The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different "adducts" of ammonia with $PtCl_4$ were known at the time: $PtCl_4{\cdot}nNH_3$ (n = 2–6). Some of Werner's original data on these compounds are shown in Table 19.3.1. The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding Ag^+(aq) was a measure of the number of "free" chloride ions present. For example, Werner's data on $PtCl_4{\cdot}6NH_3$ in Table 19.3.1 showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4{\cdot}2NH_3$ was a neutral molecule that contained no free chloride ions.

Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table 19.3.1: Werner’s Data on Complexes of Ammonia with $PtCl_4$

Complex	Conductivity (ohm^{-1})	Number of Ions per Formula Unit	Number of Cl^- Ions Precipitated by Ag^+
$PtCl_4·6NH_3$	523	5	4
$PtCl_4·5NH_3$	404	4	3
$PtCl_4·4NH_3$	299	3	2
$PtCl_4·3NH_3$	97	2	1
$PtCl_4·2NH_3$	0	0	0

These data led Werner to postulate that metal ions have two different kinds of valence: (1) a primary valence (**oxidation state**) that corresponds to the positive charge on the metal ion and (2) a secondary valence (**coordination number**) that is the total number of ligand-metal bonds bound to the metal ion. If Pt had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $\mathrm{PtCl_4 \cdot NH_3}$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

$$[\mathrm{Pt(NH_3)_6]Cl_4} \rightarrow [\mathrm{Pt(NH_3)_6}]^{4+}(\mathrm{aq}) + 4\mathrm{Cl}^-(\mathrm{aq})$$

$$[\mathrm{Pt(NH_3)_5Cl]Cl_3} \rightarrow [\mathrm{Pt(NH_3)_5Cl}]^{3+}(\mathrm{aq}) + 3\mathrm{Cl}^-(\mathrm{aq})$$

$$[\mathrm{Pt(NH_3)_4Cl_2]Cl_2} \rightarrow [\mathrm{Pt(NH_3)_4Cl_2}]^{2+}(\mathrm{aq}) + 2\mathrm{Cl}^-(\mathrm{aq})$$

$$[\mathrm{Pt(NH_3)_3Cl_3]Cl} \rightarrow [\mathrm{Pt(NH_3)_3Cl_3}]^{+}(\mathrm{aq}) + \mathrm{Cl}^-(\mathrm{aq})$$

$$[\mathrm{Pt(NH_3)_2Cl_4}] \rightarrow [\mathrm{Pt(NH_3)_2Cl_4}]^{0}(\mathrm{aq})$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for Co^{3+} and Cr^{3+} and 4 for Pt^{2+} and Pd^{2+}.

Werner’s studies on the analogous Co^{3+} complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (Figure $19.3.1a$). Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the metal ion. Werner’s key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (Figure $19.3.1b$ His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.

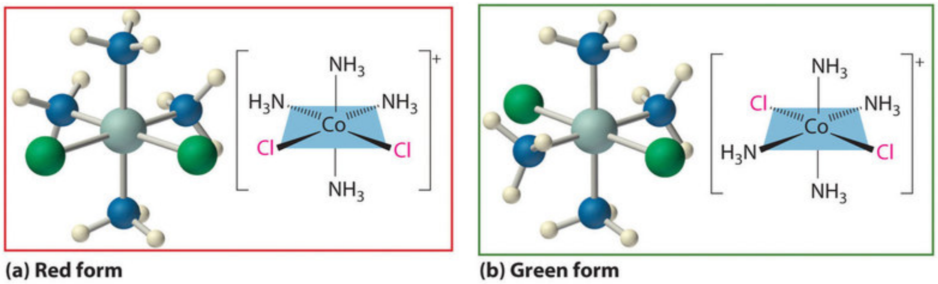


Figure 19.3.1: Complexes with Different Arrangements of the Same Ligands Have Different Properties. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).

✓ Example 19.3.1

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning, calculate the maximum number of different structures that are possible for six-coordinate MA_4B_2 complexes with each of the three most symmetrical possible structures: a hexagon, a trigonal prism, and an octahedron. What does the fact that no more than two forms of any MA_4B_2 complex were known tell you about the three-dimensional structures of these complexes?

Given: three possible structures and the number of different forms known for MA_4B_2 complexes

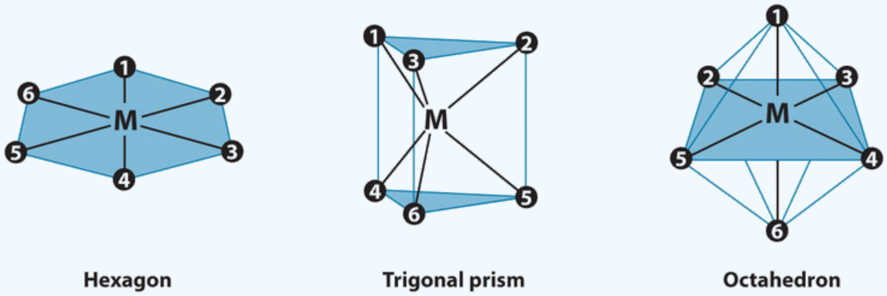
Asked for: number of different arrangements of ligands for MA_4B_2 complex for each structure

Strategy:

Sketch each structure, place a B ligand at one vertex, and see how many different positions are available for the second B ligand.

Solution

The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical MA_6 complex and simply replace two of the A ligands in each structure to give an MA_4B_2 complex:



For the hexagon, we place the first B ligand at position 1. There are now three possible places for the second B ligand: at position 2 (or 6), position 3 (or 5), or position 4. These are the only possible arrangements. The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand: at position 2 or 3 on the same triangular face, position 4 (on the other triangular face but adjacent to 1), or position 5 or 6 (on the other triangular face but not adjacent to 1). The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., MA_3B_3), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

? Exercise 19.3.1

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer

square planar, 2; tetrahedral, 1

Structures of Metal Complexes

The coordination numbers of metal ions in metal complexes can range from 2 to at least 9. In general, the differences in energy between different arrangements of ligands are greatest for complexes with low coordination numbers and decrease as the coordination number increases. Usually only one or two structures are possible for complexes with low coordination numbers, whereas several different energetically equivalent structures are possible for complexes with high coordination numbers ($n > 6$). The following presents the most commonly encountered structures for coordination numbers 2–9. Many of these structures should be familiar to you from our discussion of the valence-shell electron-pair repulsion (VSEPR) model because they correspond to the lowest-energy arrangements of n electron pairs around a central atom.

> *Compounds with low coordination numbers exhibit the greatest differences in energy between different arrangements of ligands.*

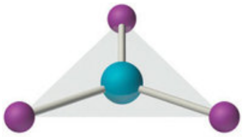
Coordination Number 2

Although it is rare for most metals, this coordination number is surprisingly common for d^{10} metal ions, especially Cu^+, Ag^+, Au^+, and Hg^{2+}. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores. As expected based on VSEPR considerations, these complexes have the linear L–M–L structure shown here.

Linear ML_2

Coordination Number 3

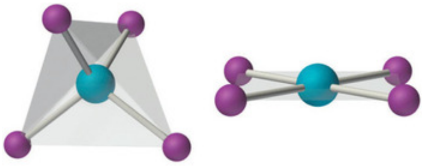
Although it is also rare, this coordination number is encountered with d^{10} metal ions such as Cu^+ and Hg^{2+}. Among the few known examples is the HgI_3^- ion. Three-coordinate complexes almost always have the trigonal planar structure expected from the VSEPR model.



Trigonal planar ML_3

Coordination Number 4

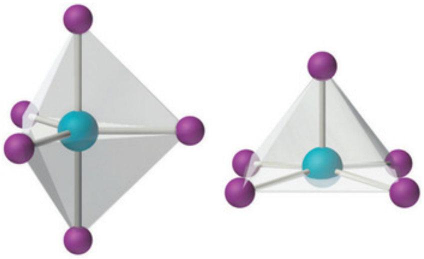
Two common structures are observed for four-coordinate metal complexes: tetrahedral and square planar. The tetrahedral structure is observed for all four-coordinate complexes of nontransition metals, such as $[BeF_4]^{2-}$, and d^{10} ions, such as $[ZnCl_4]^{2-}$. It is also found for four-coordinate complexes of the first-row transition metals, especially those with halide ligands (e.g., $[FeCl_4]^-$ and $[FeCl_4]^{2-}$). In contrast, square planar structures are routinely observed for four-coordinate complexes of second- and third-row transition metals with d^8 electron configurations, such as Rh^+ and Pd^{2+}, and they are also encountered in some complexes of Ni^{2+} and Cu^{2+}.



Tetrahedral and square planar ML_4

Coordination Number 5

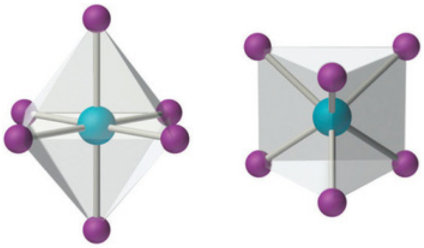
This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures that lie somewhere between the two extremes.



Trigonal bipyramidal and square pyramidal ML_5

Coordination Number 6

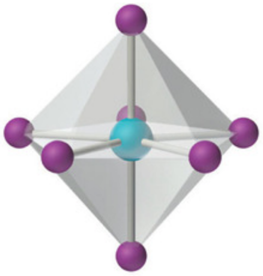
This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.



Octahedral and trigonal prismatic ML_6

Coordination Number 7

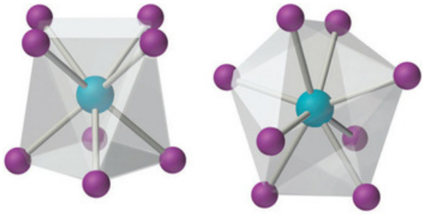
This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand to one face of the polyhedron to give a “capped” octahedron or trigonal prism. By far the most common, however, is the pentagonal bipyramid.



Pentagonal bipyramidal ML_7

Coordination Number 8

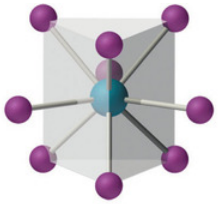
This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.



Square antiprismatic and
trigonal dodecahedral ML_8

Coordination Number 9

This coordination number is found in larger metal ions, and the most common structure is the tricapped trigonal prism, as in $[Nd(H_2O)_9]^{3+}$.



Tricapped trigonal prismatic ML_9

Key Takeaways

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

Summary

Transition metals form metal complexes, polyatomic species in which a metal ion is bound to one or more ligands, which are groups bound to a metal ion. Complex ions are electrically charged metal complexes, and a coordination compound contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures. Coordination numbers of two and three are common for d^{10} metal ions. Tetrahedral and square planar complexes have a coordination number of four; trigonal bipyramidal and square pyramidal complexes have a coordination number of five; and octahedral complexes have a coordination number of six. At least three structures are known for a coordination number of seven, which is generally found for only large metal ions. Coordination numbers of eight and nine are also found for larger metal ions.

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19.4: Isomerism

Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $(NH_3)_2PtCl_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

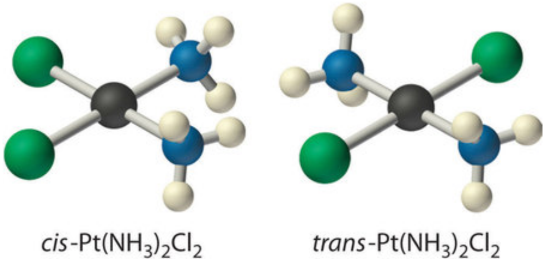


Figure 19.4.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of coordination compounds bond together is discussed in the chapter of Lewis acids and bases. For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by MIT chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two ammines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced, and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

? Exercise 19.4.1

Draw the cis and trans isomers of the following compounds:

a. $(NH_3)_2IrCl(CO)$
b. $(H_3P)_2PtHBr$
c. $(AsH_3)_2PtH(CO)$

? Exercise 19.4.2

Only one isomer of (tmeda)$PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

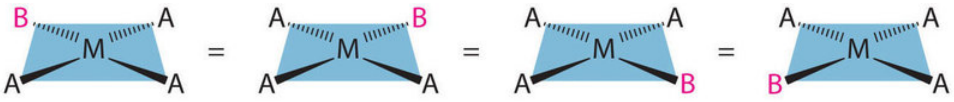
Geometric Isomers

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

Planar Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

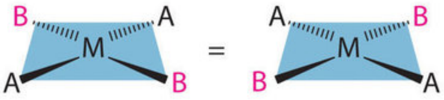
Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



MA_3B square planar complex

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (cis), in which case the B ligands must also be cis, or the A ligands can be across from one another (trans), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:

MA_2B_2 square planar complex, *cis* isomer

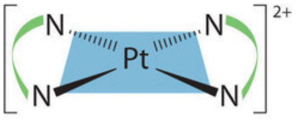


MA_2B_2 square planar complex, *trans* isomer

Figure 19.4.1).

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

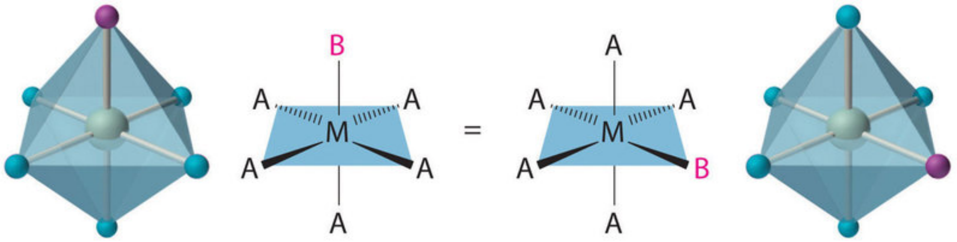
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



$[Pt(en)_2]^{2+}$

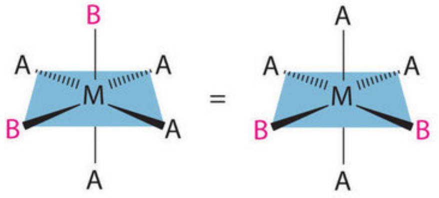
Octahedral Isomers

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:

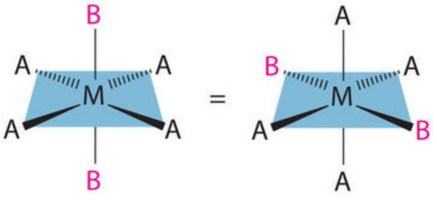


MA_5B octahedral complex

If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:

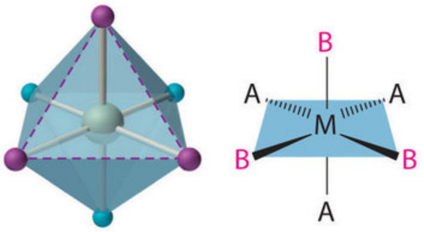


MA_4B_2 octahedral complex, *cis* isomer

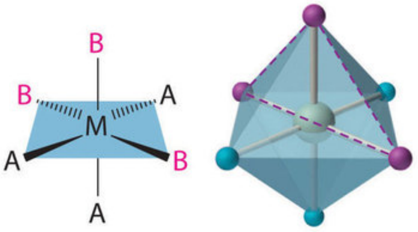


MA_4B_2 octahedral complex, *trans* isomer

Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



MA_3B_3 octahedral complex, *fac* isomer



MA_3B_3 octahedral complex, *mer* isomer

Example 19.4.1

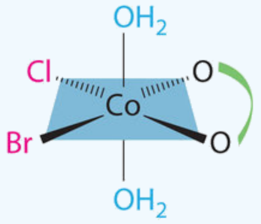
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Given: formula of complex

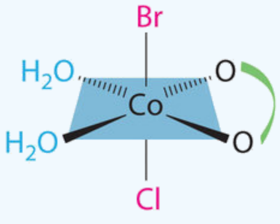
Asked for: structures of geometrical isomers

Solution

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:

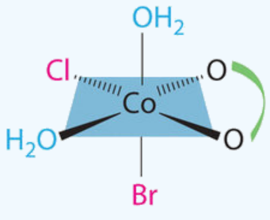


H_2O's *trans*

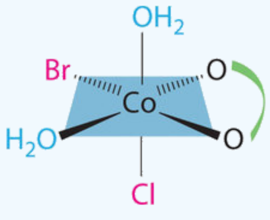


Br, Cl *trans*

In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:



H_2O's *cis*; Br, Cl *cis*;
Cl *trans* to O



H_2O's *cis*; Br, Cl *cis*;
Br *trans* to O

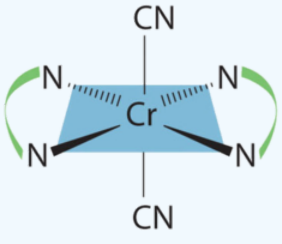
This complex can therefore exist as four different geometrical isomers.

Exercise 19.4.1

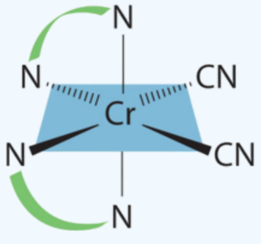
Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer

Two geometrical isomers are possible: trans and cis.



trans



cis

Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

Contributors and Attributions

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19.5: Bonding in Complex Ions

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19.6: The Crystal Field Model

Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

d-Orbital Splittings

CFT focuses on the interaction of the five (n − 1)d orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure $19.6.1a$). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure $19.6.1b$, the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the e_g orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (d_{xy}, d_{xz}, and d_{yz}, collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

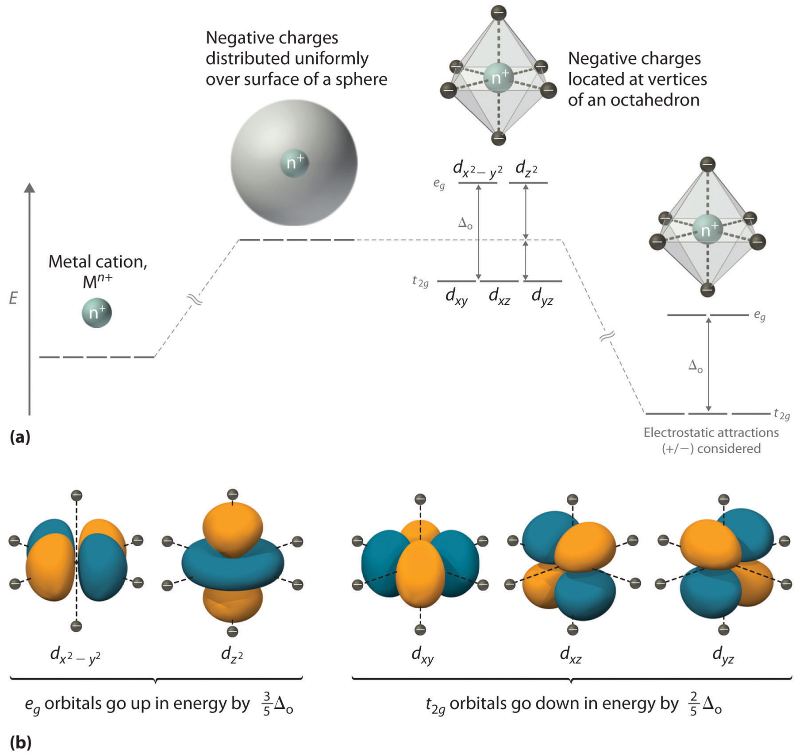

Figure 19.6.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the, d_{xy}, d_{xz}, and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two e_g orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: Δ_t.) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two e_g orbitals increase in energy by $0.6\Delta_o$, whereas the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0.$$

> *Crystal field splitting does not change the total energy of the d orbitals.*

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 19.6.1*a*).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 19.6.1 to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 24.6.2, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

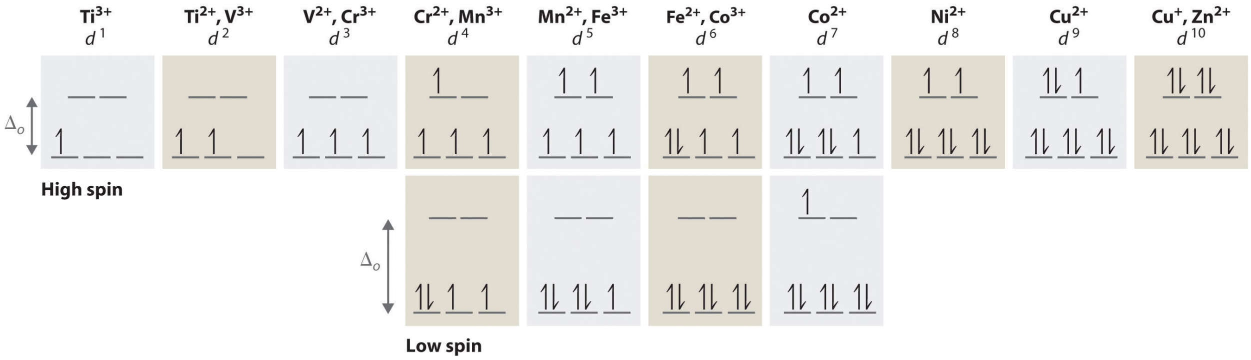

Figure 19.6.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed.

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupied t_{2g} orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e_g orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of d electrons is possible for metal ions with d^8–d^{10} electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

> *If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.*

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table 19.6.1.

Table 19.6.1: Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes

Octahedral Complexes	**Δ_o (cm^{-1})**	**Octahedral Complexes**	**Δ_o (cm^{-1})**	**Tetrahedral Complexes**	**Δ_t (cm^{-1})**
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}: \Delta_o = 22{,}900 \text{ cm}^{-1}$$

$$[Rh(NH_3)_6]^{3+}: \Delta_o = 34{,}100 \text{ cm}^{-1}$$

$$[Ir(NH_3)_6]^{3+}: \Delta_o = 40{,}000 \text{ cm}^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order $F^- > Cl^- > Br^- >$ I− because smaller, more localized charges, such as we see for F^-, interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$\underset{\text{strong-field ligands}}{\mathrm{CO}\approx \mathrm{CN}^-} > \mathrm{NO}_2^- > \mathrm{en} > \mathrm{NH}_3 > \underset{\text{intermediate-field ligands}}{\mathrm{SCN}^- > \mathrm{H}_2\mathrm{O} > \mathrm{oxalate}^{2-}} > \mathrm{OH}^- > \mathrm{F} > \mathrm{acetate}^- > \underset{\text{weak-field ligands}}{\mathrm{Cl}^- > \mathrm{Br}^- > \mathrm{I}^-}$$

The values of Δ_o listed in Table 19.6.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

> *The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a d–d transition (Figure 24.6.3). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o.

Figure 19.6.3: A d–d Transition. In a d–d transition, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o. Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.

Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of Cr^{3+} impurities in octahedral sites in an otherwise colorless metal oxide lattice.

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 19.6.2 gives CFSE values for octahedral complexes with different d electron configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table 19.6.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
d^0			0			
d^1	↿		0.4			
d^2	↿ ↿		0.8			
d^3	↿ ↿ ↿		1.2			
d^4	↿ ↿ ↿	↿	0.6	↿⇂ ↿ ↿		1.6
d^5	↿ ↿ ↿	↿ ↿	0.0	↿⇂ ↿⇂ ↿		2.0
d^6	↿⇂ ↿ ↿	↿ ↿	0.4	↿⇂ ↿⇂ ↿⇂		2.4
d^7	↿⇂ ↿⇂ ↿	↿ ↿	0.8	↿⇂ ↿⇂ ↿⇂	↿	1.8
d^8	↿⇂ ↿⇂ ↿⇂	↿ ↿	1.2			
d^9	↿⇂ ↿⇂ ↿⇂	↿⇂ ↿	0.6			
d^{10}	↿⇂ ↿⇂ ↿⇂	↿⇂ ↿⇂	0.0			

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

> *Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.*

✓ Example 19.6.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[CoF_6]^{3-}$
b. $[Rh(CO)_2Cl_2]^-$

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

a. From the number of ligands, determine the coordination number of the compound.
b. Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.
c. Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.
d. Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

Solution

a. A With six ligands, we expect this complex to be octahedral.

B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

C Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

B C Because rhodium is a second-row transition metal ion with a d^8 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order $d_{z^2}d_{yz}$, and d_{xz} (these are degenerate); d_{xy}; and $d_{x^2-y^2}$.

D The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2-y^2}$. orbital empty. Thus there are no unpaired electrons.

Exercise 19.6.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[Mn(H_2O)_6]^{2+}$
b. $[PtCl_4]^{2-}$

Answers

a. octahedral; high spin; five
b. square planar; low spin; no unpaired electrons

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

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19.7: Molecular Orbital Model

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19.8: The Biologic Importance of Coordination Complexes

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CHAPTER OVERVIEW

20: The Nucleus A Chemists View

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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20.1: Nuclear Stability and Radioactive Decay

Learning Objectives

- Write and balance nuclear equations
- To know the different kinds of radioactive decay.
- To balance a nuclear reaction.

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of ${}^{1}_{1}\text{H}$, neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term nuclide and identify it by the notation:

$$ {}^{\text{A}}_{\text{Z}}\text{X} \tag{20.1.1}$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, ${}^{14}_{6}\text{C}$ is called “carbon-14.”

Protons and neutrons, collectively called nucleons, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth’s density were equal to the average nuclear density, the earth’s radius would be only about 200 meters (earth’s actual radius is approximately 6.4×10^6 meters, 30,000 times larger).

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Nuclear Equations

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that ${}^{17}_{8}\text{O}$ is a product of the nuclear reaction of ${}^{14}_{7}\text{N}$ and ${}^{4}_{2}\text{He}$ if we knew that a proton, ${}^{1}_{1}\text{H}$, was one of the two products. Example $20.1.1$ shows how we can identify a nuclide by balancing the nuclear reaction.

Example 20.1.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 $({}^{25}_{12}\text{Mg})$ produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$^{25}_{12}\text{Mg} + ^{4}_{2}\text{He} \rightarrow ^{1}_{1}\text{H} + ^{\text{A}}_{\text{Z}}\text{X}$$

where

- A is the mass number and
- Z is the atomic number of the new nuclide, X.

Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = \text{A} + 1$$

so

$$\text{A} = 28$$

Similarly, the charges must balance, so:

$$12 + 2 = \text{Z} + 1$$

so

$$\text{Z} = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is $^{28}_{13}\text{Al}$.

? Exercise 20.1.1

The nuclide $^{125}_{53}\text{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer

$$^{125}_{53}\text{I} + ^{0}_{-1}\text{e} \rightarrow ^{125}_{52}\text{Te}$$

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.*

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 $^{A}_{Z}\text{X}$ notation for nuclides to include radioactive emissions. Table $20.1.1$ 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.

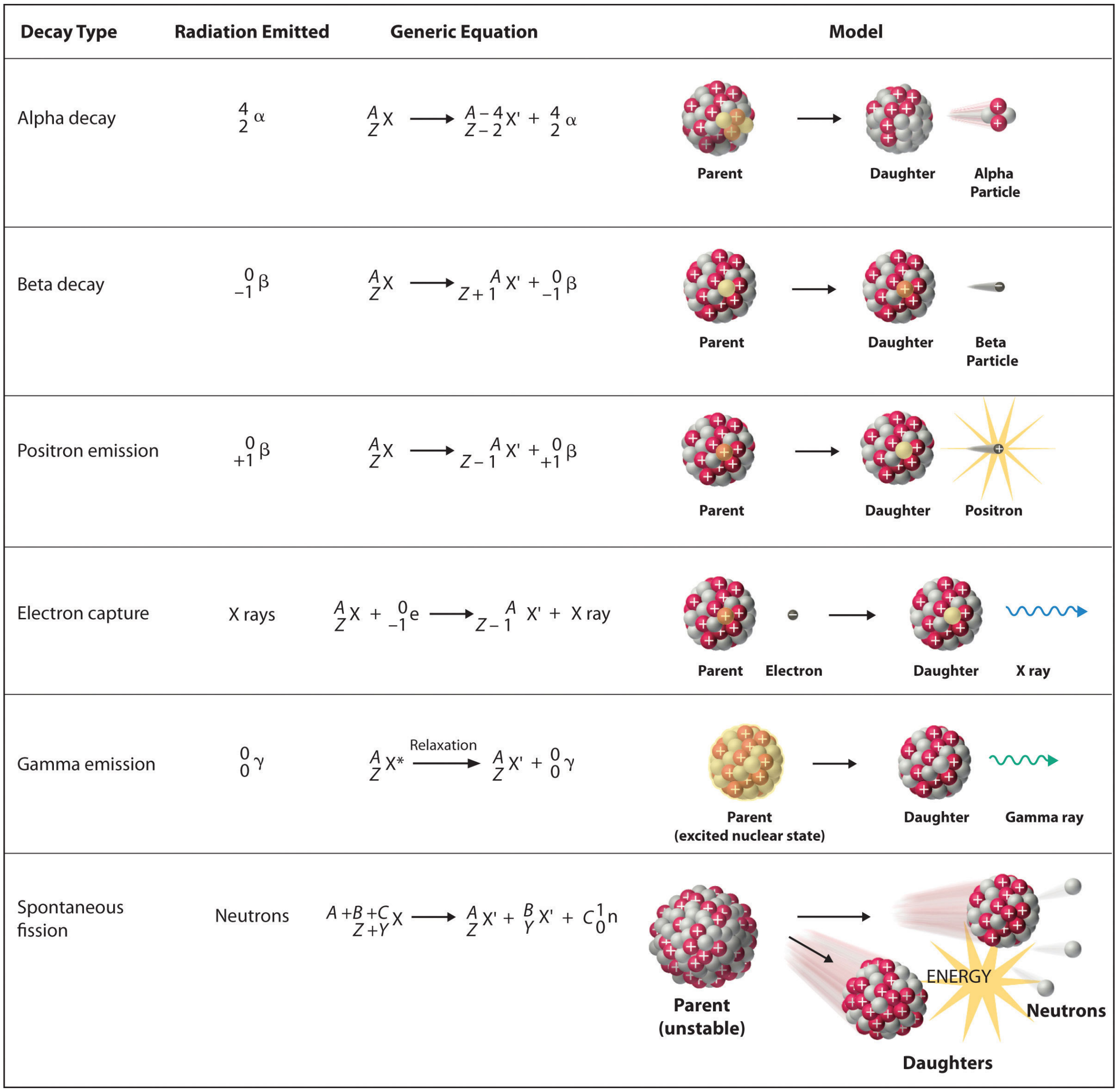
Table 20.1.1: Nuclear Decay Emissions and Their Symbols

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 20.1.1. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.



Decay Type	Radiation Emitted	Generic Equation	Model
Alpha decay	$^{4}_{2}\alpha$	$^{A}_{Z}\text{X} \longrightarrow {}^{A-4}_{Z-2}\text{X}' + {}^{4}_{2}\alpha$	Parent → Daughter, Alpha Particle
Beta decay	$^{0}_{-1}\beta$	$^{A}_{Z}\text{X} \longrightarrow {}_{Z+1}^{A}\text{X}' + {}^{0}_{-1}\beta$	Parent → Daughter, Beta Particle
Positron emission	$^{0}_{+1}\beta$	$^{A}_{Z}\text{X} \longrightarrow {}_{Z-1}^{A}\text{X}' + {}^{0}_{+1}\beta$	Parent → Daughter, Positron
Electron capture	X rays	$^{A}_{Z}\text{X} + {}^{0}_{-1}\text{e} \longrightarrow {}_{Z-1}^{A}\text{X}' + \text{X ray}$	Parent, Electron → Daughter, X ray
Gamma emission	$^{0}_{0}\gamma$	$^{A}_{Z}\text{X}^{*} \xrightarrow{\text{Relaxation}} {}^{A}_{Z}\text{X}' + {}^{0}_{0}\gamma$	Parent (excited nuclear state) → Daughter, Gamma ray
Spontaneous fission	Neutrons	$^{A+B+C}_{Z+Y}\text{X} \longrightarrow {}^{A}_{Z}\text{X}' + {}^{B}_{Y}\text{X}' + \text{C}^{1}_{0}\text{n}$	Parent (unstable) → Daughters, ENERGY, Neutrons

Figure 20.1.1: Common Modes of Nuclear Decay
The different types of decay are alpha, beta, positron emission, electron capture, gamma emission, and spontaneous fission.

Alpha α 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:

$$\underset{\text{parent}}{^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{^{A-4}_{Z-2}\text{X}'} + \underset{\substack{\text{alpha}\\ \text{particle}}}{^{4}_{2}\alpha} \tag{20.1.2}$$

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:

$$^{226}_{88}\text{Ra} \rightarrow ^{222}_{86}\text{Rn} + ^{4}_{2}\alpha \tag{20.1.3}$$

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 β^- 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:

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^1_0\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^1_1\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^0_{-1}\beta} \tag{20.1.4}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^A_Z\text{X}} \rightarrow \underset{\text{daughter}}{{}^A_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^0_{-1}\beta} \tag{20.1.5}$$

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:

$${}^{14}_6\text{C} \rightarrow {}^{14}_7\text{N} + {}^0_{-1}\beta$$

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 β^+ 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:

$${}^1_1\text{p}^+ \rightarrow {}^1_0\text{n} + {}^0_{+1}\beta^+ \tag{20.1.6}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{{}^A_Z\text{X}} \rightarrow \underset{\text{daughter}}{{}^A_{Z-1}\text{X}'} + \underset{\text{positron}}{{}^0_{+1}\beta^+}$$

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:

$${}^{11}_6\text{C} \rightarrow {}^{11}_5\text{B} + {}^0_{+1}\beta^+$$

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:

$${}^1_1\text{p} + {}^0_{-1}\text{e} \rightarrow {}^1_0\text{n} \tag{20.1.7}$$

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

$$\underset{\text{parent}}{{}^A_Z\text{X}} + \underset{\text{electron}}{{}^0_{-1}\text{e}} \rightarrow \underset{\text{daughter}}{{}^A_{Z-1}\text{X}'} + \text{x-ray}$$

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:

$${}^{55}_{26}\text{Fe} \overset{\text{EC}}{\rightarrow} {}^{55}_{25}\text{Mn} + \text{x-ray}$$

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:

$${}^{55}_{26}\text{Fe} + {}^{0}_{-1}\text{e} \rightarrow {}^{55}_{25}\text{Mn} + \text{x-ray}$$

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 γ 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:

$${}^{238}_{92}\text{U} \rightarrow \underset{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}}{{}^{234}_{90}\text{Th*}} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\text{Th} + {}^{0}_{0}\gamma$$

If we disregard the decay event that created the excited nucleus, then

$${}^{234}_{88}\text{Th*} \rightarrow {}^{234}_{88}\text{Th} + {}^{0}_{0}\gamma$$

or more generally,

$${}^{A}_{Z}\text{X*} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{0}\gamma$$

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 ${}^{254}_{98}\text{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$${}^{254}_{98}\text{Cf} \rightarrow {}^{118}_{46}\text{Pd} + {}^{132}_{52}\text{Te} + 4{}^{1}_{0}\text{n}$$

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 20.1.2

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of ${}^{35}_{16}\text{S}$

b. the decay of ${}^{201}_{80}\text{Hg}$ by electron capture
c. the decay of ${}^{30}_{15}\text{P}$ 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 ${}^{A}_{Z}\text{X}$:

$${}^{35}_{16}\text{S} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{-1}\beta$$

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:

$${}^{35}_{16}\text{S} \rightarrow {}^{35}_{17}\text{Cl} + {}^{0}_{-1}\beta$$

b.

A We know the identities of both reactants: ${}^{201}_{80}\text{Hg}$ and an inner electron, ${}^{0}_{-1}\text{e}$. The reaction is as follows:

$${}^{201}_{80}\text{Hg} + {}^{0}_{-1}\text{e} \rightarrow {}^{A}_{Z}\text{X}$$

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

$${}^{201}_{80}\text{Hg} + {}^{0}_{-1}\text{e} \rightarrow {}^{201}_{79}\text{Au}$$

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

$${}^{30}_{15}\text{P} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{+1}\beta$$

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:

$${}^{30}_{15}\text{P} \rightarrow {}^{30}_{14}\text{Si} + {}^{0}_{+1}\beta$$

? Exercise 20.1.2

Write a balanced nuclear equation to describe each reaction.

a. ${}^{11}_{6}\text{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from ${}^{185}_{74}\text{W}$

Answer a

$${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta$$

Answer d

$${}^{99}_{42}\text{Mo} \rightarrow {}^{99m}_{43}\text{Tc} + {}^{0}_{-1}\beta$$

Answer c

$$^{185}_{74}\text{W} \rightarrow {}^{181}_{72}\text{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$$

✓ Example 20.1.3

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{45}_{22}\text{Ti}$
b. $^{242}_{94}\text{Pu}$
c. $^{12}_{5}\text{B}$
d. $^{256}_{100}\text{Fm}$

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 $^{242}_{94}\text{Pu}$ 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 $^{12}_{5}\text{B}$ 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 $^{256}_{100}\text{Fm}$ 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 20.1.3

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{32}_{14}\text{Si}$
b. $^{43}_{21}\text{Sc}$
c. $^{231}_{91}\text{Pa}$

Answer a

beta decay

Answer d

positron emission or electron capture

Answer 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 20.1.2). 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.

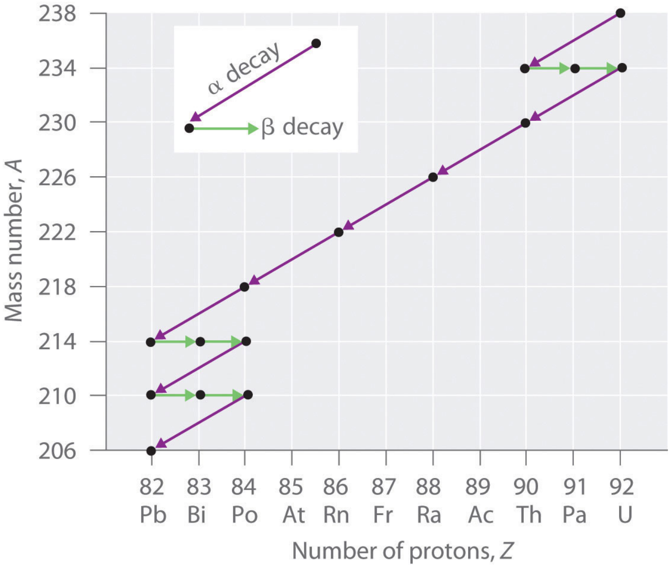


Figure 20.1.2 A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

Graph of mass number against number of protons. The purple lines are alpha decay which are linear while the green lines are beta decay and are horizontal and parallel to the x axis.

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:

$$^{4}_{2}\alpha + {}^{14}_{7}\text{N} \rightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{p}$$

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:

$$^{4}_{2}\alpha + ^{9}_{4}\text{Be} \rightarrow ^{12}_{6}\text{C} + ^{1}_{0}\text{n} \tag{20.1.8}$$

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 20.1.3). 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:

$$^{1}_{0}\text{n} + ^{14}_{7}\text{N} \rightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{p} \tag{20.1.9}$$

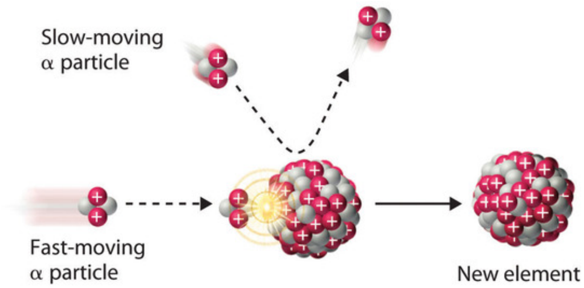


Figure 20.1.3: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively 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 20.1.4

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, $^{30}_{15}\text{P}$.

B The balanced nuclear equation for the reaction is as follows:

$$^{27}_{13}\mathrm{Al} + ^{4}_{2}\alpha \rightarrow ^{30}_{15}\mathrm{P} + ^{1}_{0}\mathrm{n}$$

? Exercise 20.1.4

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 20.1.4:

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \rightarrow ^{236}_{92}\mathrm{U} \rightarrow ^{141}_{56}\mathrm{Ba} + ^{92}_{36}\mathrm{Kr} + 3^{1}_{0}\mathrm{n} \tag{20.1.10}$$

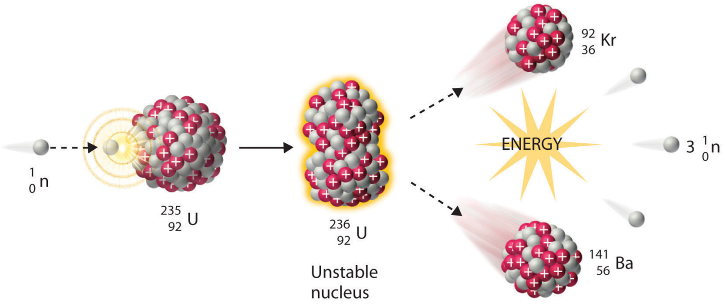


Figure 20.1.4 Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

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 20.1.4. 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 20.1.5, 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.

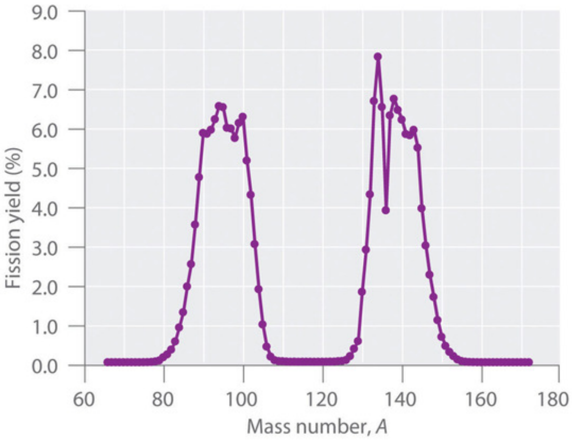


Figure 20.1.5: Mass Distribution of Nuclear Fission Products of ^{235}U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for ^{235}U. 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 20.1.2). 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 20.1.2: 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 20.1.6), 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.

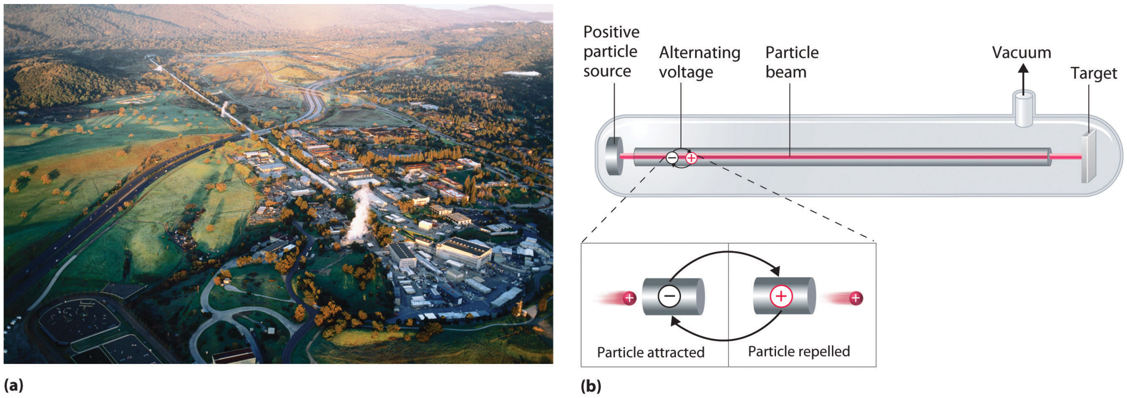


Figure 20.1.6: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as 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 and 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.

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 Equations

alpha decay

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^{4}_{2}\alpha $$

beta decay

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z+1}\mathrm{X}' + {}^{0}_{-1}\beta $$

positron emission

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + {}^{0}_{+1}\beta $$

electron capture

$$ {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + \text{x-ray} $$

gamma emission

$$ {}^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma $$

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20.2: Radioactive Kinetics

Learning Objectives

- To know how to use half-lives to describe the rates of first-order reactions

Another approach to describing reaction rates is based on the time required for the concentration of a reactant to decrease to one-half its initial value. This period of time is called the **half-life** of the reaction, written as $t_{1/2}$. Thus the half-life of a reaction is the time required for the reactant concentration to decrease from $[A]_0$ to $[A]_{0/2}$. If two reactions have the same order, the faster reaction will have a shorter half-life, and the slower reaction will have a longer half-life.

The half-life of a first-order reaction under a given set of reaction conditions is a constant. This is not true for zeroth- and second-order reactions. The half-life of a first-order reaction is independent of the concentration of the reactants. This becomes evident when we rearrange the integrated rate law for a first-order reaction to produce the following equation:

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]} = kt \tag{20.2.1}$$

Substituting $[A]_{0/2}$ for [A] and $t_{1/2}$ for t (to indicate a half-life) into Equation 20.2.1 gives

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_0/2} = \ln 2 = kt_{1/2} \tag{20.2.2}$$

Substituting $\ln 2 \approx 0.693$ into the equation results in the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \tag{20.2.3}$$

Thus, for a first-order reaction, each successive half-life is the same length of time, as shown in Figure $20.2.1$, and is *independent* of [A].

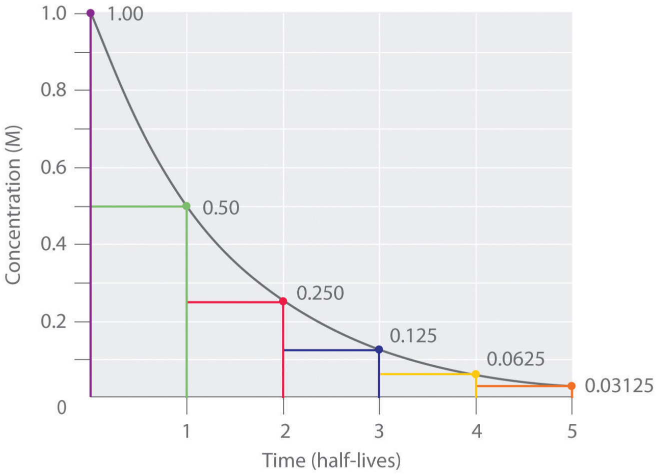

Figure 20.2.1: The Half-Life of a First-Order Reaction. This plot shows the concentration of the reactant in a first-order reaction as a function of time and identifies a series of half-lives, intervals in which the reactant concentration decreases by a factor of 2. In a first-order reaction, every half-life is the same length of time.

If we know the rate constant for a first-order reaction, then we can use half-lives to predict how much time is needed for the reaction to reach a certain percent completion.

Number of Half-Lives	Percentage of Reactant Remaining	
1	$\frac{100\%}{2} = 50\%$	$\frac{1}{2}(100\%) = 50\%$
2	$\frac{50\%}{2} = 25\%$	$\frac{1}{2}\left(\frac{1}{2}\right)(100\%) = 25\%$

Number of Half-Lives	Percentage of Reactant Remaining	
3	$\frac{25\%}{2} = 12.5\%$	$\frac{1}{2}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(100\%) = 12.5\%$
n	$\frac{100\%}{2^n}$	$\left(\frac{1}{2}\right)^n(100\%) = \left(\frac{1}{2}\right)^n\%$

As you can see from this table, the amount of reactant left after n half-lives of a first-order reaction is $(1/2)^n$ times the initial concentration.

> *For a first-order reaction, the concentration of the reactant decreases by a constant with each half-life and is independent of [A].*

Example 20.2.1

The anticancer drug cis-platin hydrolyzes in water with a rate constant of $1.5 \times 10^{-3}\ \text{min}^{-1}$ at pH 7.0 and 25°C. Calculate the half-life for the hydrolysis reaction under these conditions. If a freshly prepared solution of cis-platin has a concentration of 0.053 M, what will be the concentration of cis-platin after 5 half-lives? after 10 half-lives? What is the percent completion of the reaction after 5 half-lives? after 10 half-lives?

Given: rate constant, initial concentration, and number of half-lives

Asked for: half-life, final concentrations, and percent completion

Strategy:

A. Use Equation 20.2.3 to calculate the half-life of the reaction.
B. Multiply the initial concentration by 1/2 to the power corresponding to the number of half-lives to obtain the remaining concentrations after those half-lives.
C. Subtract the remaining concentration from the initial concentration. Then divide by the initial concentration, multiplying the fraction by 100 to obtain the percent completion.

Solution

A We can calculate the half-life of the reaction using Equation 20.2.3:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-3}\ \text{min}^{-1}} = 4.6 \times 10^{2}\ \text{min}$$

Thus it takes almost 8 h for half of the cis-platin to hydrolyze.

B After 5 half-lives (about 38 h), the remaining concentration of cis-platin will be as follows:

$$\frac{0.053\ \text{M}}{2^5} = \frac{0.053\ \text{M}}{32} = 0.0017\ \text{M}$$

After 10 half-lives (77 h), the remaining concentration of cis-platin will be as follows:

$$\frac{0.053\ \text{M}}{2^{10}} = \frac{0.053\ \text{M}}{1024} = 5.2 \times 10^{-5}\ \text{M}$$

C The percent completion after 5 half-lives will be as follows:

$$\text{percent completion} = \frac{(0.053\ \text{M} - 0.0017\ \text{M})(100)}{0.053} = 97\%$$

The percent completion after 10 half-lives will be as follows:

$$\text{percent completion} = \frac{(0.053\ \text{M} - 5.2 \times 10^{-5}\ \text{M})(100)}{0.053\ \text{M}} = 100\%$$

Thus a first-order chemical reaction is 97% complete after 5 half-lives and 100% complete after 10 half-lives.

Exercise 20.2.1

Ethyl chloride decomposes to ethylene and HCl in a first-order reaction that has a rate constant of $1.6 \times 10^{-6}\ s^{-1}$ at 650°C.

a. What is the half-life for the reaction under these conditions?
b. If a flask that originally contains 0.077 M ethyl chloride is heated at 650°C, what is the concentration of ethyl chloride after 4 half-lives?

Answer a

4.3×10^{5} s = 120 h = 5.0 days;

Answer b

4.8×10^{-3} M

Radioactive Decay Rates

Radioactivity, or radioactive decay, is the emission of a particle or a photon that results from the spontaneous decomposition of the unstable nucleus of an atom. The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. In this section, we will describe radioactive decay rates and how half-lives can be used to monitor radioactive decay processes.

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using N to represent the number of atoms of the radioactive isotope, we can define the **rate of decay** of the sample, which is also called its **activity (*A*)** as the decrease in the number of the radioisotope’s nuclei per unit time:

$$A = -\frac{\Delta N}{\Delta t} \tag{20.2.4}$$

Activity is usually measured in disintegrations per second (dps) or disintegrations per minute (dpm).

The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = kN \tag{20.2.5}$$

Here, the symbol k is the radioactive decay constant, which has units of inverse time (e.g., s^{-1}, yr^{-1}) and a characteristic value for each radioactive isotope. If we combine Equation 20.2.4 and Equation 20.2.5, we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{\Delta N}{\Delta t} = kN \tag{20.2.6}$$

Equation 20.2.6 is the same as the equation for the reaction rate of a first-order reaction, except that it uses numbers of atoms instead of concentrations. In fact, radioactive decay is a first-order process and can be described in terms of either the differential rate law (Equation 20.2.6) or the integrated rate law:

$$N = N_0 e^{-kt} \tag{20.2.7}$$

$$\ln \frac{N}{N_0} = -kt \tag{20.2.8}$$

Because radioactive decay is a first-order process, the time required for half of the nuclei in any sample of a radioactive isotope to decay is a constant, called the half-life of the isotope. The half-life tells us how radioactive an isotope is (the number of decays per unit time); thus it is the most commonly cited property of any radioisotope. For a given number of atoms, isotopes with shorter half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table 14.6, along with some of their applications.

Table 20.2.2: Half-Lives and Applications of Some Radioactive Isotopes

Radioactive Isotope	Half-Life	Typical Uses

*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

Radioactive Isotope	Half-Life	Typical Uses
hydrogen-3 (tritium)	12.32 yr	biochemical tracer
carbon-11	20.33 min	positron emission tomography (biomedical imaging)
carbon-14	5.70×10^3 yr	dating of artifacts
sodium-24	14.951 h	cardiovascular system tracer
phosphorus-32	14.26 days	biochemical tracer
potassium-40	1.248×10^9 yr	dating of rocks
iron-59	44.495 days	red blood cell lifetime tracer
cobalt-60	5.2712 yr	radiation therapy for cancer
technetium-99*m**	6.006 h	biomedical imaging
iodine-131	8.0207 days	thyroid studies tracer
radium-226	1.600×10^3 yr	radiation therapy for cancer
uranium-238	4.468×10^9 yr	dating of rocks and Earth's crust
americium-241	432.2 yr	smoke detectors

*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

Note

Radioactive decay is a first-order process.

Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as radioisotope dating techniques.

The most common method for measuring the age of ancient objects is carbon-14 dating. The carbon-14 isotope, created continuously in the upper regions of Earth's atmosphere, reacts with atmospheric oxygen or ozone to form $^{14}CO_2$. As a result, the CO_2 that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}CO_2$ molecules as well as nonradioactive $^{12}CO_2$ and $^{13}CO_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as beta decay, which releases low-energy electrons (β particles) that can be detected and measured:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + \beta^- \tag{20.2.9}$$

The half-life for this reaction is 5700 ± 30 yr.

The $^{14}C/^{12}C$ ratio in living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g of carbon (Figure $20.2.2$). Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables scientists to estimate the age of the artifact, as illustrated in Example 11.Using this method implicitly assumes that the $^{14}CO_2/^{12}CO_2$ ratio in the atmosphere is constant, which is not strictly correct. Other methods, such as tree-ring dating, have been used to calibrate the dates obtained by radiocarbon dating, and all radiocarbon dates reported are now corrected for minor changes in the $^{14}CO_2/^{12}CO_2$ ratio over time.

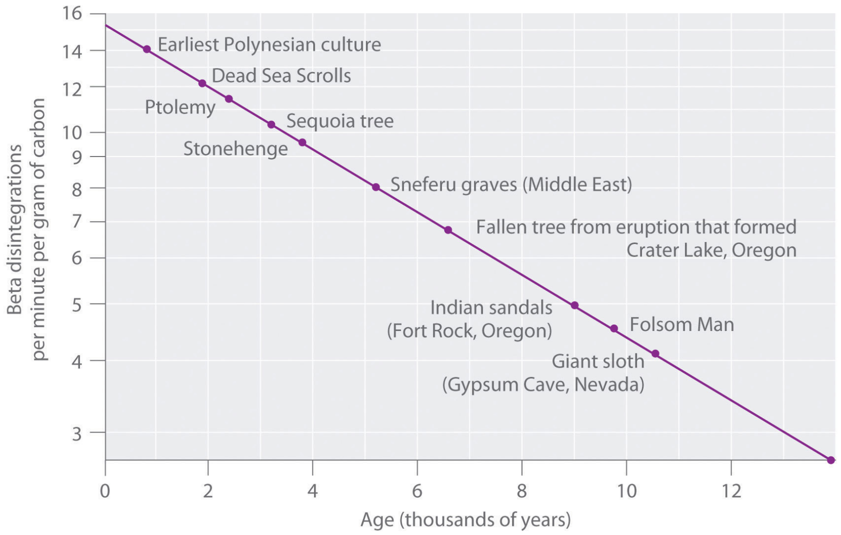

Figure 20.2.2: Radiocarbon Dating. A plot of the specific activity of ^{14}C versus age for a number of archaeological samples shows an inverse linear relationship between ^{14}C content (a log scale) and age (a linear scale).

✓ Example 20.2.2

In 1990, the remains of an apparently prehistoric man were found in a melting glacier in the Italian Alps. Analysis of the ^{14}C content of samples of wood from his tools gave a decay rate of 8.0 dpm/g carbon. How long ago did the man die?

Given: isotope and final activity

Asked for: elapsed time

Strategy:

A Use Equation 20.2.5 to calculate N_0/N. Then substitute the value for the half-life of ^{14}C into Equation 20.2.3 to find the rate constant for the reaction.

B Using the values obtained for N_0/N and the rate constant, solve Equation 20.2.8 to obtain the elapsed time.

Solution

We know the initial activity from the isotope's identity (15 dpm/g), the final activity (8.0 dpm/g), and the half-life, so we can use the integrated rate law for a first-order nuclear reaction (Equation 20.2.8) to calculate the elapsed time (the amount of time elapsed since the wood for the tools was cut and began to decay).

$$\ln \frac{N}{N_0} = -kt \tag{20.2.10}$$

$$\frac{\ln(N/N_0)}{k} = t \tag{20.2.11}$$

A From Equation 20.2.5, we know that $A = kN$. We can therefore use the initial and final activities (A_0 = 15 dpm and A = 8.0 dpm) to calculate N_0/N:

$$\frac{A_0}{A} = \frac{kN_0}{kN} = \frac{N_0}{N} = \frac{15}{8.0}$$

Now we need only calculate the rate constant for the reaction from its half-life (5730 yr) using Equation 20.2.3:

$$t_{1/2} = \frac{0.693}{k}$$

This equation can be rearranged as follows:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ yr}} = 1.22 \times 10^{-4} \text{ yr}^{-1}$$

B Substituting into the equation for *t*,

$$t = \frac{\ln(N_0/N)}{k} = \frac{\ln(15/8.0)}{1.22 \times 10^{-4}\ \text{yr}^{-1}} = 5.2 \times 10^3\ \text{yr}$$

From our calculations, the man died 5200 yr ago.

? Exercise 20.2.2

It is believed that humans first arrived in the Western Hemisphere during the last Ice Age, presumably by traveling over an exposed land bridge between Siberia and Alaska. Archaeologists have estimated that this occurred about 11,000 yr ago, but some argue that recent discoveries in several sites in North and South America suggest a much earlier arrival. Analysis of a sample of charcoal from a fire in one such site gave a ^{14}C decay rate of 0.4 dpm/g of carbon. What is the approximate age of the sample?

Answer

30,000 yr

Summary

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

The half-life of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction: $t_{1/2} = 0.693/k$. Radioactive decay reactions are first-order reactions. The rate of decay, or activity, of a sample of a radioactive substance is the decrease in the number of radioactive nuclei per unit time.

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20.3: Nuclear Transformations

Learning Objectives

- Describe the synthesis of transuranium nuclides

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Science learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \longrightarrow ^{17}_{8}\mathrm{O} + ^{1}_{1}\mathrm{H}$$

The $^{17}_{8}\mathrm{O}$ and $^{1}_{1}\mathrm{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called **particle accelerators** are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors.

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure $20.3.1$). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.

Figure $20.3.1$: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2103 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$\begin{aligned} {}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} &\longrightarrow {}^{239}_{92}\text{U} \\ {}^{239}_{92}\text{U} &\longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{e} \qquad \text{half-life} = 23.5\ \text{min} \\ {}^{239}_{93}\text{Np} &\longrightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e} \qquad \text{half-life} = 2.36\ \text{days} \end{aligned}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

$${}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{92}\text{U} \xrightarrow{\beta^-} {}^{239}_{93}\text{Np} \xrightarrow{\beta^-} {}^{239}_{94}\text{Pu} \tag{20.3.1}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called transuranium elements. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table 20.3.1.

Table 20.3.1: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	${}^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \longrightarrow {}^{240}_{95}\text{Am} + {}^{0}_{-1}\text{e}$
curium	Cm	96	${}^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
californium	Cf	98	${}^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{243}_{97}\text{Bk} + 2\,{}^{1}_{0}\text{n}$
einsteinium	Es	99	${}^{238}_{92}\text{U} + 15\,{}^{1}_{0}\text{n} \longrightarrow {}^{253}_{99}\text{Es} + 7\,{}^{0}_{-1}\text{e}$
mendelevium	Md	101	${}^{253}_{99}\text{Es} + {}^{4}_{2}\text{He} \longrightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}\text{n}$
nobelium	No	102	${}^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{No} + 4\,{}^{1}_{0}\text{n}$
rutherfordium	Rf	104	${}^{249}_{98}\text{Cf} + {}^{12}_{6}\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + 4\,{}^{1}_{0}\text{n}$
seaborgium	Sg	106	${}^{206}_{82}\text{Pb} + {}^{54}_{24}\text{Cr} \longrightarrow {}^{257}_{106}\text{Sg} + 3\,{}^{1}_{0}\text{n}$ ${}^{249}_{98}\text{Cf} + {}^{18}_{8}\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + 4\,{}^{1}_{0}\text{n}$
meitnerium	Mt	107	${}^{209}_{83}\text{Bi} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{266}_{109}\text{Mt} + {}^{1}_{0}\text{n}$

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20.4: Detections and Applications of Radioactivity

Learning Objectives

- Understand how the Geiger counter can be used to quantify the rate of ionization radiation.

When alpha, beta or gamma particles collide with a target, some of the energy in the particle is transferred to the target, typically resulting in the promotion of an electron to an “excited state”. In many “targets”, especially gasses, this results in *ionization*. Alpha, beta and gamma radiation are broadly referred to as **ionizing radiation**. A **Geiger counter** (or Geiger-Müller counter) takes advantage of this in order to detect these particles. In a Geiger tube, the electron produced by ionization of a captive gas travels to the anode and the change in voltage is detected by the attached circuitry. Most counters of this type are designed to emit an audible “click” in response to the change in voltage, and to also show it on a digital or analog meter. A simple schematic of a Geiger counter is shown in Figure 20.4.1.

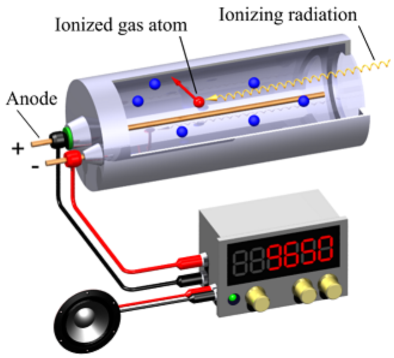

Figure 20.4.1: Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia(opens in new window)).

Although scientists were not aware at the time of the Geiger counter's invention, all of us are subjected to a certain amount of radiation every day. This radiation is called **background radiation** and comes from a variety of natural and artificial radiation sources. Approximately 82% of background radiation comes from natural sources. These natural sources include:

1. Sources in the earth—including naturally occurring radioactive elements—which are incorporated in building materials, and also in the human body.
2. Sources from space in the form of cosmic rays.
3. Sources in the atmosphere, such as radioactive radon gas released from the earth; and radioactive atoms like carbon-14, produced in the atmosphere by bombardment from high-energy cosmic rays.

Measuring Radiation Exposure

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20.5: Thermodynamic Stability of Nuclei

Learning Objectives

- To understand the 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

Each element can be represented by the notation $^{A}_{Z}\text{X}$, 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 **nucleons**, and an atom with a particular number of protons and neutrons is called a **nuclide**. 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:

stable isotopes of oxygen represented in different ways

$^{A}_{Z}\text{X}$	$^{16}_{8}\text{O}$	$^{17}_{8}\text{O}$	$^{18}_{8}\text{O}$
^{A}X	^{16}O	^{17}O	^{18}O
element-A:	oxygen-16	oxygen-17	oxygen-18

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 **radioactive**, emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called **radioisotopes**.

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 force**, an extremely powerful but very short-range attractive force between nucleons (Figure 20.5.1). All stable nuclei except the hydrogen-1 nucleus (^{1}H) 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.

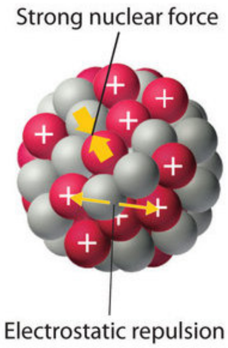

Figure $20.5.1$: Competing Interactions within the Atomic Nucleus. Electrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful 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 $20.5.2$. The stable isotopes form a “peninsula of stability” in a “sea of instability.” Only two stable isotopes, ^1H and ^3He, 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_2He, $^{10}_5B$, and $^{40}_{20}Ca$). 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.

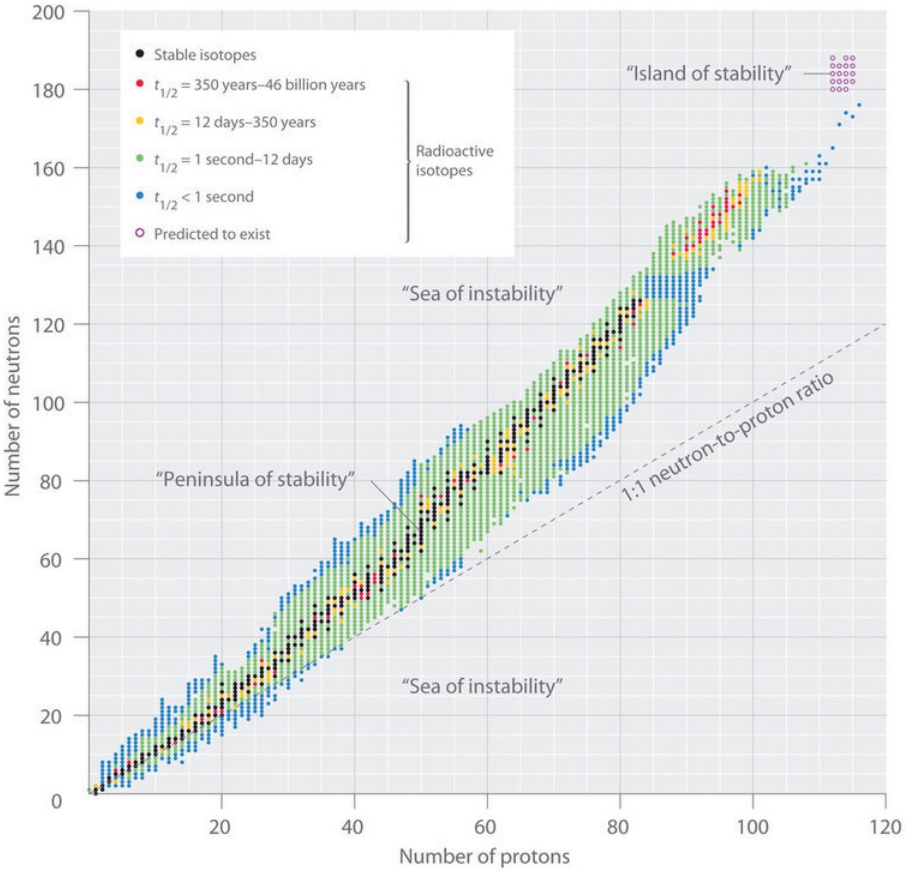

Figure 20.5.2: The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio. In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer 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.

Graph of number or neutrons against the number or protons. The graph is divided into sections of "sea of instability", "peninsula of stability", "sea of instability" and "island of stability"

As shown in Figure 20.5.3, 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 $^{4}_{2}\text{He}$, with 2 protons and 2 neutrons, and $^{208}_{82}\text{Pb}$, with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

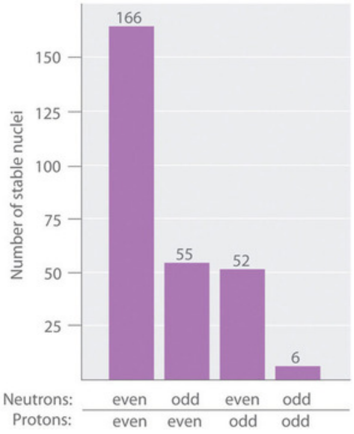

Figure 20.5.3: The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability.

> *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 $20.5.2$, 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.

Origin of the Magic Numbers

Multiple models have been formulated to explain the origin of the magic numbers and two popular ones are the Nuclear Shell Model and the Liquid Drop Model. Unfortuneatly, both require advanced quantum mechanics to fully understand and are beyond the scope of this text.

✓ Example 20.5.1

Classify each nuclide as stable or radioactive.

a. $^{30}_{15}\text{P}$
b. $^{98}_{43}\text{Tc}$
c. tin-118
d. $^{239}_{94}\text{Pu}$

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:

a. 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 $20.5.2$, 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, $^{30}_{15}\text{P}$ is predicted to be radioactive, and it is.

b. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which places $^{98}_{43}\text{Tc}$ 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 $^{98}_{43}\text{Tc}$ might be stable. However, $^{98}_{43}\text{Tc}$ has an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, $^{98}_{43}\text{Tc}$ is predicted to be radioactive, and it is.

c. 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 $^{118}_{50}\text{Sn}$should be particularly stable.

d. This nuclide has an atomic number of 94. Because all nuclei with Z > 83 are unstable, $^{239}_{94}\text{Pu}$ must be radioactive.

? Exercise 20.5.1

Classify each nuclide as stable or radioactive.

a. $^{232}_{90}\text{Th}$
b. $^{40}_{20}\text{Ca}$
c. $^{15}_{8}\text{O}$
d. $^{139}_{57}\text{La}$

Answer a

radioactive

Answer b

stable

Answer c

radioactive

Answer d

stable

Superheavy Elements

In addition to the “peninsula of stability” there is a small “island of stability” that is predicted to exist in the upper right corner. This island corresponds to the **superheavy elements**, 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.

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20.6: Nuclear Fission and Fusion

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20.7: Effects of Radiation on Matter

Learning Objectives

- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle is an ionized helium nucleus (He^{2+}) that can act as a powerful oxidant. In this section, we describe how radiation interacts with matter and the some of the chemical and biological effects of radiation.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. **Nonionizing radiation** is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, **ionizing radiation** is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$\text{atom} + \text{ionizing radiation} \rightarrow \text{ion}^+ + \text{e}^- \tag{20.7.1}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure $20.7.1$). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle:

$$1\ \text{MeV/particle} = 96\ \text{billion J/mol}.$$

Figure 20.7.1: Radiation Damage. When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue. (CC BY-SA-NC; anonymous)

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

The relative abilities of the various forms of ionizing radiation to penetrate biological tissues are illustrated in Figure 20.7.2. Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

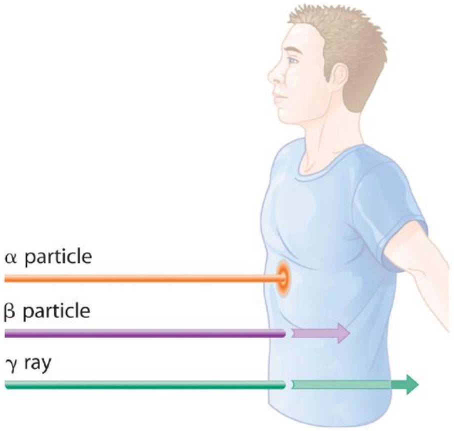

Figure 20.7.2: Depth of Penetration of Ionizing Radiation. The depth of penetration of alpha, beta, and gamma radiation varies with the particle. Because α particles interact strongly with matter, they do not penetrate deeply into the human body. In contrast, β particles do not interact as strongly with matter and penetrate more deeply. Gamma rays, which have no charge, are stopped by only very dense materials and can pass right through the human body without being absorbed. (CC BY-SA-NC; anonymous)

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 20.7.1.

Table 20.7.1: Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
x-rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2}–10^{1}	< 20 cm	> 3 m
*Distance at which half of the radiation has been absorbed.			

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air. The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1 \text{ rad} = 0.010 \text{ J/kg} \qquad 1 \text{ Gy} = 1 \text{ J/kg} \tag{20.7.2}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the **rem (roentgen equivalent in man)** was devised to describe the actual amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the RBE (relative biological effectiveness) factor, which is 1 for β particles, γ rays, and x-rays and about 20 for α particles. Because actual radiation doses tend to be very small, most measurements are reported in millirems (1 mrem = 10^{-3} rem).

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

Natural Sources of Radiation

We are continuously exposed to measurable background radiation from a variety of natural sources, which, on average, is equal to about 150–600 mrem/yr (Figure 20.7.3). One component of background radiation is *cosmic rays*, high-energy particles and γ rays emitted by the sun and other stars, which bombard Earth continuously. Because cosmic rays are partially absorbed by the atmosphere before they reach Earth's surface, the exposure of people living at sea level (about 30 mrem/yr) is significantly less than the exposure of people living at higher altitudes (about 50 mrem/yr in Denver, Colorado). Every 4 hours spent in an airplane at greater than 30,000 ft adds about 1 mrem to a person's annual radiation exposure.

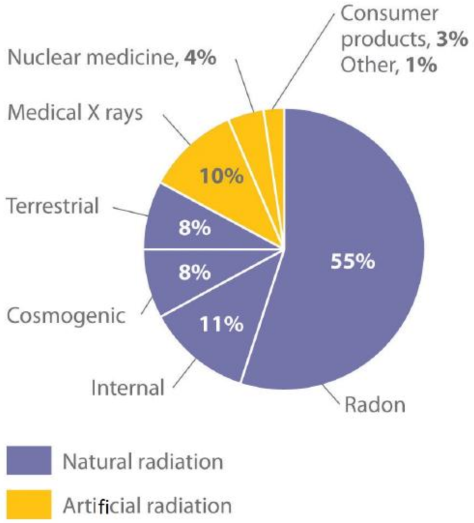

Figure 20.7.3: The Radiation Exposure of a Typical Adult in the United States. The average radiation dose from natural sources for an adult in the United States is about 150–600 mrem/yr. Radon accounts for more than half of an adult's total radiation exposure, whereas background radiation (terrestrial and cosmogenic) and exposure from medical sources account for about 15% each. Data source: Office of Civilian Radioactive Waste Management (CC BY-SA-NC; anonymous)

A second component of background radiation is *cosmogenic radiation*, produced by the interaction of cosmic rays with gases in the upper atmosphere. When high-energy cosmic rays collide with oxygen and nitrogen atoms, neutrons and protons are released. These, in turn, react with other atoms to produce radioactive isotopes, such as ^{14}C:

$$^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{n} \rightarrow ^{14}_{6}\mathrm{C} + ^{1}_{1}\mathrm{p} \tag{20.7.3}$$

The carbon atoms react with oxygen atoms to form CO_2, which is eventually washed to Earth's surface in rain and taken up by plants. About 1 atom in 1 × 10^{12} of the carbon atoms in our bodies is radioactive ^{14}C, which decays by beta emission. About 5000

^{14}C nuclei disintegrate in your body during the 15 s or so that it takes you to read this paragraph. Tritium (^{3}H) is also produced in the upper atmosphere and falls to Earth in precipitation. The total radiation dose attributable to ^{14}C is estimated to be 1 mrem/yr, while that due to ^{3}H is about 1000 times less.

The third major component of background radiation is *terrestrial radiation*, which is due to the remnants of radioactive elements that were present on primordial Earth and their decay products. For example, many rocks and minerals in the soil contain small amounts of radioactive isotopes, such as $^{232}\mathrm{Th}$ and $^{238}\mathrm{U}$ as well as radioactive daughter isotopes, such as$^{226}\mathrm{Ra}$. The amount of background radiation from these sources is about the same as that from cosmic rays (approximately 30 mrem/yr). These isotopes are also found in small amounts in building materials derived from rocks and minerals, which significantly increases the radiation exposure for people who live in brick or concrete-block houses (60–160 mrem/yr) instead of houses made of wood (10–20 mrem/yr). Our tissues also absorb radiation (about 40 mrem/yr) from naturally occurring radioactive elements that are present in our bodies. For example, the average adult contains about 140 g of potassium as the K^+ ion. Naturally occurring potassium contains 0.0117% $^{40}\mathrm{K}$, which decays by emitting both a β particle and a (\gamma\) ray. In the last 20 seconds, about the time it took you to read this paragraph, approximately 40,000 $^{40}\mathrm{K}$ nuclei disintegrated in your body.

By far the most important source of background radiation is radon, the heaviest of the noble gases (group 18). Radon-222 is produced during the decay of^{238}U, and other isotopes of radon are produced by the decay of other heavy elements. Even though radon is chemically inert, all its isotopes are radioactive. For example, ^{222}Rn undergoes two successive alpha-decay events to give ^{214}Pb:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^4_2\alpha + {}^{218}_{84}\mathrm{Po} + {}^4_2\alpha + {}^{214}_{82}\mathrm{Pb} \tag{20.7.4}$$

Because radon is a dense gas, it tends to accumulate in enclosed spaces such as basements, especially in locations where the soil contains greater-than-average amounts of naturally occurring uranium minerals. Under most conditions, radioactive decay of radon poses no problems because of the very short range of the emitted α particle. If an atom of radon happens to be in your lungs when it decays, however, the chemically reactive daughter isotope polonium-218 can become irreversibly bound to molecules in the lung tissue. Subsequent decay of $^{218}\mathrm{Po}$ releases an α particle directly into one of the cells lining the lung, and the resulting damage can eventually cause lung cancer. The $^{218}\mathrm{Po}$ isotope is also readily absorbed by particles in cigarette smoke, which adhere to the surface of the lungs and can hold the radioactive isotope in place. Recent estimates suggest that radon exposure is a contributing factor in about 15% of the deaths due to lung cancer. Because of the potential health problem radon poses, many states require houses to be tested for radon before they can be sold. By current estimates, radon accounts for more than half of the radiation exposure of a typical adult in the United States.

Artificial Sources of Radiation

In addition to naturally occurring background radiation, humans are exposed to small amounts of radiation from a variety of artificial sources. The most important of these are the x-rays used for diagnostic purposes in medicine and dentistry, which are photons with much lower energy than γ rays. A single chest x-ray provides a radiation dose of about 10 mrem, and a dental x-ray about 2–3 mrem. Other minor sources include television screens and computer monitors with cathode-ray tubes, which also produce x-rays. Luminescent paints for watch dials originally used radium, a highly toxic alpha emitter if ingested by those painting the dials. Radium was replaced by tritium (^{3}H) and promethium (^{147}Pr), which emit low-energy β particles that are absorbed by the watch crystal or the glass covering the instrument. Radiation exposure from television screens, monitors, and luminescent dials totals about 2 mrem/yr. Residual fallout from previous atmospheric nuclear-weapons testing is estimated to account for about twice this amount, and the nuclear power industry accounts for less than 1 mrem/yr (about the same as a single 4 h jet flight).

✓ Example 20.7.1

Calculate the annual radiation dose in rads a typical 70 kg chemistry student receives from the naturally occurring ^{40}K in his or her body, which contains about 140 g of potassium (as the K$^+$ ion). The natural abundance of ^{40}K is 0.0117%. Each 1.00 mol of ^{40}K undergoes 1.05 × 10^7 decays/s, and each decay event is accompanied by the emission of a 1.32 MeV β particle.

Given: mass of student, mass of isotope, natural abundance, rate of decay, and energy of particle

Asked for: annual radiation dose in rads

Strategy:

A. Calculate the number of moles of ^{40}K present using its mass, molar mass, and natural abundance.
B. Determine the number of decays per year for this amount of ^{40}K.
C. Multiply the number of decays per year by the energy associated with each decay event. To obtain the annual radiation dose, use the mass of the student to convert this value to rads.

Solution

A The number of moles of ^{40}K present in the body is the total number of potassium atoms times the natural abundance of potassium atoms present as ^{40}K divided by the atomic mass of ^{40}K:

$$\text{moles } ^{40}\text{K} = 140 \text{ g K} \times \frac{0.0117 \text{ mol } ^{40}\text{K}}{100 \text{ mol K}} \times \frac{1 \text{ mol K}}{40.0 \text{ g K}} = 4.10 \times 10^{-4} \text{ mol } ^{40}\text{K}$$

B We are given the number of atoms of ^{40}K that decay per second in 1.00 mol of ^{40}K, so the number of decays per year is as follows:

$$\frac{\text{decays}}{\text{year}} = 4.10 \times 10^{-4} \text{ mol}^{40}\text{ K} \times \frac{1.05 \times 10^{7} \text{ decays/s}}{1.00 \text{ mol } ^{40}\text{K}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{365 \text{ days}}{1 \text{ yr}}$$

C The total energy the body receives per year from the decay of ^{40}K is equal to the total number of decays per year multiplied by the energy associated with each decay event:

$$\begin{aligned} \text{total energy per year} &= \frac{1.36 \times 10^{11} \text{ decays}}{\text{yr}} \times \frac{1.32 \text{ MeV}}{\text{decays}} \times \frac{10^{6} \text{ eV}}{\text{MeV}} \times \frac{1.602 \times 10^{-19} \text{ J}}{\text{eV}} \\ &= 2.87 \times 10^{-2} \text{ J/yr} \end{aligned}$$

We use the definition of the rad (1 rad = 10^{-2} J/kg of tissue) to convert this figure to a radiation dose in rads. If we assume the dose is equally distributed throughout the body, then the radiation dose per year is as follows:

$$\begin{aligned} \text{radiation dose per year} &= \frac{2.87 \times 10^{-2} \text{ J/yr}}{70.0 \text{ kg}} \times \frac{1 \text{ rad}}{1 \times 10^{-2} \text{ J/kg}} \\ &= 4.10 \times 10^{-2} \text{ rad/yr} = 41 \text{ mrad/yr} \end{aligned}$$

This corresponds to almost half of the normal background radiation most people experience.

? Exercise 20.7.1

Because strontium is chemically similar to calcium, small amounts of the Sr^{2+} ion are taken up by the body and deposited in calcium-rich tissues such as bone, using the same mechanism that is responsible for the absorption of Ca^{2+}. Consequently, the radioactive strontium (^{90}Sr) found in fission waste and released by atmospheric nuclear-weapons testing is a major health concern. A normal 70 kg human body has about 280 mg of strontium, and each mole of ^{90}Sr undergoes 4.55×10^{14} decays/s by the emission of a 0.546 MeV β particle. What would be the annual radiation dose in rads for a 70 kg person if 0.10% of the strontium ingested were ^{90}Sr?

Answer

5.7×10^{3} rad/yr (which is 10 times the fatal dose)

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 20.7.2 Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table 20.7.2: The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Both patterns are plotted in Figure $20.7.4$, but which of the two is applicable to humans? According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that all exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

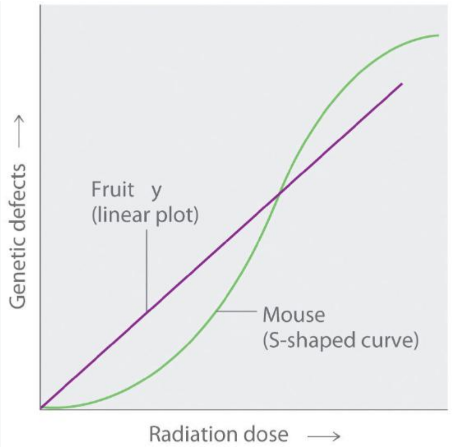

Figure 20.7.4: Two Possible Relationships between the Number of Genetic Defects and Radiation Exposure. Studies on fruit flies show a linear relationship between the number of genetic defects and the magnitude of the radiation dose and exposure time, which is consistent with a cumulative effect of radiation. In contrast, studies on mice show an S-shaped curve, which suggests that the number of defects is lower when radiation exposure occurs over a longer time. Which of these relationships is more applicable to humans is a matter of considerable debate. (CC BY-SA-NC; anonymous)

Graph of genetic defects against radiation dose. Fruit is graphed in purple and has a linear plot. Mouse is graphed in green and has a S shaped curve.

Summary

Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive. The effects of radiation on matter depend on the energy of the radiation. Nonionizing radiation is relatively low in energy, and the energy is transferred to matter in the form of heat. Ionizing radiation is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the roentgen (R), the amount of energy absorbed by dry air, and the rad (radiation absorbed dose), the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The rem (roentgen equivalent in man) measures the actual amount of tissue damage caused by a given amount of radiation. Natural sources of radiation include cosmic radiation, consisting of high-energy particles and γ rays emitted by the sun and other stars; cosmogenic radiation, which is produced by the interaction of cosmic rays with gases in the upper atmosphere; and terrestrial radiation, from radioactive elements present on primordial Earth and their decay products. The risks of ionizing radiation depend on the intensity of the radiation, the mode of exposure, and the duration of the exposure.

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- **21.8: Biological Effects of Radiation** by Anonymous is licensed CC BY-NC-SA 3.0.

CHAPTER OVERVIEW

21: Organic and Biological Chemistry

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Organic chemistry is the study of the chemistry of carbon compounds. Why focus on carbon? Carbon has properties that give its chemistry unparalleled complexity. It forms four covalent bonds, which give it great flexibility in bonding. It makes fairly strong bonds with itself (a characteristic called *catenation*), allowing for the formation of large molecules; it also forms fairly strong bonds with other elements, allowing for the possibility of a wide variety of substances. No other element demonstrates the versatility of carbon when it comes to making compounds. So an entire field of chemistry is devoted to the study of the compounds and reactivity of one element.

It was thought that organic compounds could only be manufactured in living organisms, and chemistry was divided into the subfields of inorganic and organic on this basis. This subdivision persists today, but the definition of organic has changed in response to the discovery of numerous ways to make organic compounds from inorganic starting materials. Biochemistry is the study of chemical elements found in living systems, and how these elements combine to form molecules and collections of molecules which carry out the biological functions and behaviors that we associate with life.

Topic hierarchy

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SECTION OVERVIEW

21.1: Alkanes: Saturated Hydrocarbons

Alkanes are organic compounds that consist entirely of single-bonded carbon and hydrogen atoms and lack any other functional groups. Alkanes have the general formula C_nH_{2n+2} and can be subdivided into the following three groups: the **linear straight-chain alkanes**, **branched alkanes**, and **cycloalkanes**. Alkanes are also *saturated hydrocarbons*. Alkanes are the simplest and least reactive hydrocarbon species containing only carbons and hydrogens. They are commercially very important, being the principal constituent of gasoline and lubricating oils and are extensively employed in organic chemistry; though the role of pure alkanes (such as hexanes) is delegated mostly to solvents. The distinguishing feature of an alkane, making it distinct from other compounds that also exclusively contain carbon and hydrogen, is its lack of unsaturation. That is to say, it contains no double or triple bonds, which are highly reactive in organic chemistry. Though not totally devoid of reactivity, their lack of reactivity under most laboratory conditions makes them a relatively uninteresting, though very important component of organic chemistry. As you will learn about later, the energy confined within the carbon-carbon bond and the carbon-hydrogen bond is quite high and their rapid oxidation produces a large amount of heat, typically in the form of fire.

Contributors

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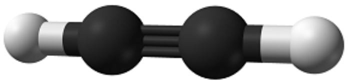
SECTION OVERVIEW

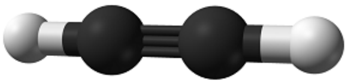
21.2: Alkenes and Alkynes

Alkenes are a class of hydrocarbons (e.g, containing only carbon and hydrogen) unsaturated compounds with at least one carbon-to-carbon double bond. Another term used to describe alkenes is olefins. Alkenes are more reactive than alkanes due to the presence of the double bond.

Alkynes are organic molecules made of one ore more carbon-carbon triple bonds. They are unsaturated hydrocarbons and are written in the empirical formula of C_nH_{2n-2}.



Nomenclature of Alkynes



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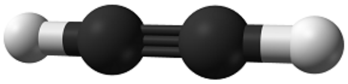

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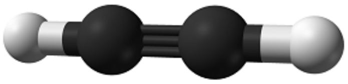

Synthesis of Alkynes

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SECTION OVERVIEW

21.3: Aromatic Hydrocarbons

Arenes are aromatic hydrocarbons. The term "aromatic" originally referred to their pleasant smells (e.g., from cinnamon bark, wintergreen leaves, vanilla beans and anise seeds), but now implies a particular sort of delocalized bonding. Aromatic hydrocarbons (or sometimes called arenes or aryl hydrocarbon) are hydrocarbons with sigma bonds and delocalized π electrons between carbon atoms forming rings.

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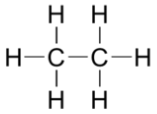
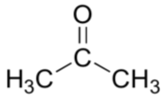
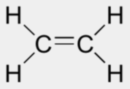
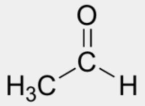
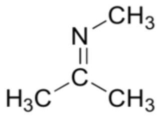
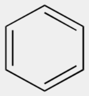
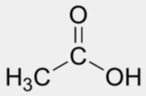
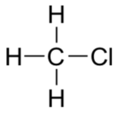
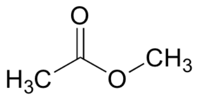
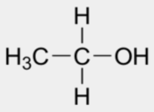
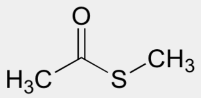
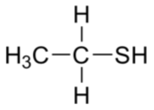
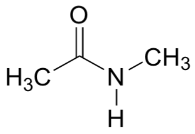
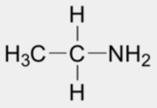
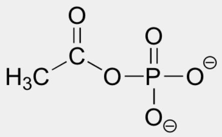
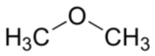
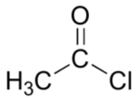
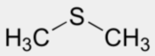
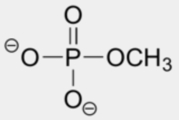
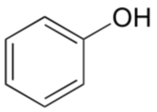
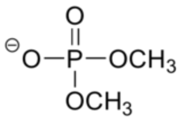
21.4: Hydrocarbon Derivatives

alkane	 $\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}$	**ketone**	
alkene		**aldehyde**	
alkyne	$\mathrm{H-C\equiv C-H}$	**imine** **(Schiff base)**	
aromatic		**carboxylic acid**	
alkyl halide	 $\mathrm{H-\underset{H}{\overset{H}{C}}-Cl}$	**ester**	
alcohol	 $\mathrm{H_3C-\underset{H}{\overset{H}{C}}-OH}$	**thioester**	
thiol	 $\mathrm{H_3C-\underset{H}{\overset{H}{C}}-SH}$	**amide**	
amine	 $\mathrm{H_3C-\underset{H}{\overset{H}{C}}-NH_2}$	**acyl phosphate**	
ether		**acid chloride**	
thioether		**phosphate monoester**	 $\mathrm{{}^{\ominus}O-\underset{O^{\ominus}}{\overset{O}{\overset{\Vert}{P}}}-OCH_3}$
phenol		**phosphate diester**	 $\mathrm{{}^{\ominus}O-\underset{OCH_3}{\overset{O}{\overset{\Vert}{P}}}-OCH_3}$

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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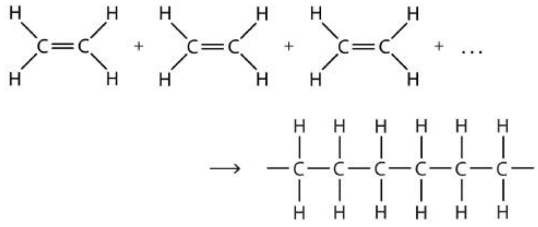
21.5: Polymers

Learning Objectives

- To draw structures for monomers that can undergo addition polymerization and for four-monomer-unit sections of an addition polymer.

The most important commercial reactions of alkenes are *polymerizations*, reactions in which small molecules, referred to in general as monomers (from the Greek *monos*, meaning "one," and *meros*, meaning "parts"), are assembled into giant molecules referred to as polymers (from the Greek *poly*, meaning "many," and *meros*, meaning "parts"). A polymer is as different from its monomer as a long strand of spaghetti is from a tiny speck of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene—a gas.

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers. Ethylene molecules are joined together in long chains. The polymerization can be represented by the reaction of a few monomer units:



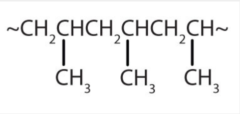
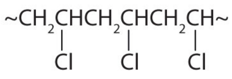
The bond lines extending at the ends in the formula of the product indicate that the structure extends for many units in each direction. Notice that all the atoms—two carbon atoms and four hydrogen atoms—of each monomer molecule are incorporated into the polymer structure. Because displays such as the one above are cumbersome, the polymerization is often abbreviated as follows:

$$n\mathrm{CH_2{=}CH_2} \rightarrow \left[\mathrm{CH_2CH_2}\right]_n$$

> Many natural materials—such as proteins, cellulose and starch, and complex silicate minerals—are polymers. Artificial fibers, films, plastics, semisolid resins, and rubbers are also polymers. More than half the compounds produced by the chemical industry are synthetic polymers.

Some common addition polymers are listed in Table $21.5.1$. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table 21.5.1: *Some Addition Polymers*

Monomer	Polymer	Polymer Name	Some Uses
$CH_2{=}CH_2$	$\sim CH_2CH_2CH_2CH_2CH_2CH_2\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
$CH_2{=}CHCH_3$	 $\sim CH_2\underset{CH_3}{CH}CH_2\underset{CH_3}{CH}CH_2\underset{CH_3}{CH}\sim$	polypropylene	carpeting, bottles, luggage, exercise clothing
$CH_2{=}CHCl$	 $\sim CH_2\underset{Cl}{CH}CH_2\underset{Cl}{CH}CH_2\underset{Cl}{CH}\sim$	polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$CF_2{=}CF_2$	$\sim CF_2CF_2CF_2CF_2CF_2CF_2\sim$	polytetrafluoroethylene	nonstick coatings, electrical insulation

Medical Uses of Polymers

An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers.

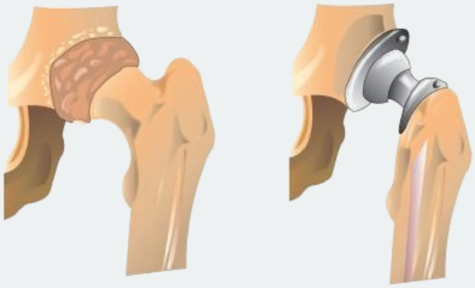


Figure 21.5.1: Hip Joint Replacement. Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup.

Key Takeaway

- Molecules having carbon-to-carbon double bonds can undergo addition polymerization.

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SECTION OVERVIEW

21.6: Natural Polymers

Polymers are long chain, giant organic molecules are assembled from many smaller molecules called monomers. Polymers consist of many repeating monomer units in long chains, sometimes with *branching* or *cross-linking* between the chains.

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CHAPTER OVERVIEW

6: Chemical Equilibrium

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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6.1: The Equilibrium State

Equilibrium

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6.2: Equilibrium Constants

Equilibrium

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6.3: Equilibrium Expressions Involving Pressures

When calculating equilibrium constants of solutions, the concentrations of each component in the solution are used to calculate K, which is the equilibrium constant. When working with concentrations, the equilibrium constant is designated as K_c. However, when working with a mixture of gases, concentrations are not used, but instead the gases' partial pressures. By first calculating the equilibrium constant in terms of pressure, designated K_p, K_c can then be calculated by using a simple formula.

How do you begin writing the equilibrium constant for a mixture of gases?

To explain this clearly, let us look at a simple example, the reaction:

$$2NH_3(g) <\text{---}> N_2(g) + 3H_2(g).$$

1) First, each component of the mixture in the equilibrium constant is written in terms of their activities. The activity of each component is the partial pressure of each component divided by their partial pressure "reference-states." Writing the equilibrium constant in terms of partial pressures requires it to be referred to as K_p.

$$K = (\ (a_{N2})(a_{H2})^3\ /\ (a_{NH3})^2)\ \text{eq}$$

$$a_{N2} = P_{N2}/P^o$$

$$a_{H2} = P_{H2}/P^o$$

$$a_{NH3} = P_{NH3}/P^o$$

2) Next, take the activities, showed in terms of pressure, of the products raised to the power of their coefficients, and divided by the activities of the reactants. The activities of the reactants are also raised to the power of their coefficients. To simplify the expression, the partial pressure "reference-state" of each component can be divided out.

$$K_p = (\ (P_{N2}/P^o)(P_{H2}/P^o)^3\ /\ (P_{NH3}/P^o)^2\ )\ \text{eq}$$

$$P^o\ (\ (P_{N2})(P_{H2})^3/(P_{NH3})^2)\ \text{eq}$$

3) To relate the pressures of this expression to concentrations, the ideal gas law is used. The ideal gas law is **PV=nRT**, where P is the pressure, V is the volume, n is the number of moles of the substnace, R is the constant 0.08206 L atm/K mol, and T is the temperature in Kelvins. By inverting the ideal gas law equation and solving for the concentration, n/V, or moles per liter, the concentrations of the gases are expressed by their partial pressures divided by RT.

$$\{N2\} = n/v = P_{N2}/RT$$

$$\{H2\} = n/V = P_{H2}/RT$$

$$\{NH3\} = n/V = P_{NH3}/RT$$

4) Now, since we have solved for the concentrations of each gas component, we write them in terms of concentration activities. This is the concentrations of each component divided by the concentration reference state.

$$a_{N2} = \{N2\}/c^o = (P_{N2}/RT)/c^o$$

$$a_{H2} = \{H2\}/c^o = (P_{H2}/RT)/c^o$$

$$a_{NH3} = \{NH3\}/c^o = (P_{NH3}/RT)/c^o$$

The last and final step is entering these activities into the expression we earlier derived in step 2 and dividing out RT.

$$K_p = P^o(\ (\{N2\}RT)(\{H2\}RT)^3/(\{NH3\}RT)^2\ )\ \text{eq}$$

$$K_p = (P^o/RT)(\{N2\}\{H2\}^3/\{NH3\}^2)\ \text{eq}$$

This gives the equilibrium constant expression for a mixture of gases (K_p).

K_p and K_c can be related by setting the two equations equal to each other and divided out the reference states. This gives the simple formula:

$K_p = K_c(RT)^{\text{difference in coefficients of gas components only}}$

Please Note:

P^o is the partial pressure reference-state and it equals about 1 atm

c^o is the concentration reference-state and it equals about 1mol/L

eq is the term used to indicate that the components are at equilibrium

{x} is the concentration of the component x where x is a variable used to indicate a substance

Equilibrium constant expression do not include those components in a reaction that are pure solids or liquids (please refer to the corresponding internal link below)

Internal Links

- Writing equilibrium constant expressions involving solids and liquids
- Gas equilibrium constants, Kp and Kc?
- Meaning of the equilibrium constant, K

Practice Problems

1) Gas A and Gas B react to form Gas C. The reaction performed can be written as A(g)+B(g)

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C(g). At equilibrium, the partial pressures of A, B, and C are 1 atm, 0.50 atm, and 0.75 atm respectively. Find K_p for the reaction.

Solution:

First, write out the equilibrium constant expression for K_p. K_p= P^o(

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)eq

Remember that P^o= 1 bar which is essentially equal to 1 atm. Next, plug in the partial pressures for the corresponding gases.

K_p=

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)

=1.5

2) A(g), at 750 mmHg, reacts with B(g), at 760 mmHg, to form C(g). K_p for the reaction is 1.5 X 10^{-5} and the reaction at equilibrium can be written A(g)+B(g)

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2C(g). Find the partial pressure of C.

Solution

First set up the equilibrium constant expression for K_p. K_p= P^o(

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)eq

C is raised to the power of 2 since 2 is the coefficient of C. Since we know K_p we can subsitute that into the equation. Also, convert the partial pressure of A and B to atm. P_A= 750 mmHg X

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=0.98684 & P_B= 1 atm

$1.5 \text{ X } 10^5 =$

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$(1.5 \text{ X}10^{-5})(0.98684)= C^2$

$\text{sqrt}(1.48026\text{X}10^{-5})=C$

$C= 3.8474147\text{X}10^{-3}$ or $C= 3.9\text{X}10^{-3}$

3) For the following reaction at equilibrium $2SO_2(g)+ O_2$

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$2SO_3(g)$ K_p is 3.4 at 1000K. What is K_c for the reaction?

Solution:

We know that $K_p=K_c(RT)^{\text{(Difference in coefficients of gaseous products and reactants)}}$

We also know K_p= 3.4, R is a constant which is 0.08206L atm $mol^{-1}K^{-1}$, T=1000K

(RT) is raised to the power of (Difference in coefficients of gaseous products and reactants) so since **2**$SO_2(g)$+ **1**O_2

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2$SO_3(g)$ (Difference in coefficients of gaseous products and reactants)= (2)-(2+1)= -1

Rewrite the equation, $K_p=K_c(RT)^{\text{(Difference in coefficients of gaseous products and reactants)}}$, to solve for Kc and subsitute in the values. ^K_c=

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$K_c= 2.79\text{X}10^2$

4) For the following reaction at equilibrium, $N_2(g)+ 3H_2(g)$

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$2NH_3(g)$, K_p is $2.25\text{X}10^{-6}$. If the values of the partial pressures of N_2 and NH_3 are $3.5\text{X}10^{-3}$ and $2.0\text{X}10^{-5}$ respectively, what is the partial pressure of H_2?

Solution

Set up the equilibrium constant expression for K_p. K_p= K_p= P^o

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eq

Substitute the values in to the correct places.

$2.25X10^{-6}$=

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 UndefinedNameError: reference to undefined name 'math' (click for details)

=

 UndefinedNameError: reference to undefined name 'math' (click for details)

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=0.0507936508

Take the cubed root of the number to find the Partial pressure of H_2

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=0.37 atm

5) 1 mol of A and 1 mol of B are placed in a 2.0 L flask. The following reaction at equilibrium is established at 500K. A(g)+B(g)

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C(g) K_p= 15.0 For the equilibrium established, find the partial pressure of C.

Solution

First, we must find the partial pressures of A and B. We know that by using P=

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, we can say P_A=P_B=

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= 20.515

Now create an ICE table.

A(g) + B(g)

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C(g)

I 20.515 20.515 0

C -x -x +x

E (20.515-x) (20.515-x) (x)

Now set up the equilibrium constant expression for K_p= 15.0=

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$15(20.515-x)^2= x$ Use FOIL

$15(420.865225-41.03x+x^2)= x$ distribute & multiply by 15

$15x^2-615.45x+6312.978375=x$ subtract the x to make the equation equal to 0

$15x^2-616.45x+6312.978375=0$ Use the quadratic formula

UndefinedNameError: reference to undefined name 'math' (click for details)

and

UndefinedNameError: reference to undefined name 'math' (click for details)

a=15 b=-616.45 c= 6312.978375

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and

UndefinedNameError: reference to undefined name 'math' (click for details)

We find that there are two solutions. P_C= 19.38 or 21.7

19.38 is the correct solution since 21.7 is too large.

References

1. Petrucci, Ralph H., et al. General Chemistry: Principles and Modern Applications. Upper Saddle River, NJ: Prentice Hall, 2007.

Contributors and Attributions

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6.4: Activity is an Effective Concetration

Effective Concentrations in Gases

In chemical thermodynamics, activity (symbol a) is a measure of the “effective concentration” of a species in a mixture, in the sense that the species' chemical potential depends on the activity of a real solution in the same way that it would depend on concentration for an ideal solution. By convention, activity is treated as a dimensionless quantity, although its value depends on customary choices of standard state for the species. The activity of pure substances in condensed phases (solid or liquids) is normally taken as unity (the number 1). Activity depends on temperature, pressure and composition of the mixture, among other things. For gases, the activity is the effective partial pressure, and is usually referred to as *fugacity*.

The difference between activity and other measures of composition arises because molecules in non-ideal gases or solutions interact with each other, either to attract or to repel each other. The activity of an ion is particularly influenced by its surroundings. The use of activities allows chemists to explain various discrepancies between ideal solutions and real solutions. The mathematical description of an ideal solution must be modified to describe a real solution, just as the law for ideal gases (PV = nRT) must be modified to describe real gases.

✓ Example 6.4.1: Ideal vs. Real Gases

Compare the pressures predicted for one mole of ethane at 298.15 K under the following equations of states:

a. ethane is an ideal gas or
b. ethane is a van der Waal gas

What is the deviation of the two?

Solution

a) Ideal gas law equation of state: Calculate the pressure of 1.000 mole of ethane at 298.15 K in a 1.000 L flask using the ideal gas law.

$$\begin{aligned} P_{ideal} V &= nRT \\ P_{ideal} &= \frac{nRT}{V} \\ &= \frac{(1\ mole)(0.0821 L\ atm\ K^{-1}\ mol^{-1})(298.15\ K)}{1\ L} \\ &= 24.47\ atm \end{aligned} \tag{6.4.1}$$

b) Van der Waal's equation of state: Calculate the pressure of 1.00 mole of ethane at 298 K in a 1.00 L flask using the van der Waals equation. The van der Waals constants for ethane can found in Table A8.

- $a = 5.492\ atm\ \dfrac{L^2}{M^2}$ and
- $b = 0.06499\ L/m$

$$\begin{aligned} \left(P_{vdW} + \frac{an^2}{V^2}\right)(V - nb) &= nRT \\ P_{vdW} &= \frac{nRT}{V-nb} - \frac{an^2}{V^2} \\ &= 20.67\ atm \end{aligned} \tag{6.4.2}$$

Calculate the percent error between the P_{ideal} and the P_{vdW}

$$Error = \frac{P_{vdW} - P_{ideal}}{P_{vdW}} = 18.36\%$$

An error this large is often **too big to ignore** when carrying out a gas-phase reaction or designing a vessel in which to carry out such a reaction.

There are two ways to deal with real systems that deviate appreciably from ideal conditions:

1. Use a more accurate phenomenologically (i.e., real) Equation of State like the van der Waal' (Equation 6.4.2) that models the system more accurately. This must explicitly address intermolecular forces and other effects that exist in real system and the concentration used is 1 mol/L (i.e., the real concentration).
2. Use an ideal equation pf state like the ideal gas Equation of State in Equation 6.4.1), but use an "effective concentration" of 0.816 mol/L to generate the observed pressure (that is, the gas behaves as if it has a reduced concentration of 100%-18.36% = 81.6% of the real concentration).

Effective Concentrations in Solutions

In a similar fashion, the difference between the calculated solute concentrations in an ideal solution and in a real solution can lead to wide variations in experimental results. The following three examples compare the results obtained when formal concentrations are used (assuming ideality) and when activities are used (assuming non-ideality). Just like gases, "ideal solutions" have certain predictable physical properties (e.g. colligative properties) that real solutions often deviate from. As with the van der Waal equation in Example 1, this deviation originates from solute-solvent, solvent-solvent and solute-solute **interactions**. The magnitude of this non-ideality naturally greater with higher with solute concentrations and with greater intermolecular interaction (e.g., ions vs. non-charged species). Lewis introduced idea of 'effective concentration' or 'activity' to deal with this problem by allowing an "ideal solution" description for non-ideal solutions.

> Since the Van der Waals equation describes real gases instead of the ideal gases law, **activity** can be used in place of concentration to describe the behavior of real solutions vs. ideal solutions.

The activity of a substance (abbreviated as *a*) describes the effective concentration of that substance in the reaction mixture. Activity takes into account the non-ideality of the reaction mixture, including solvent-solvent, solvent-solute, and solute-solute interactions. Thus, activity provides a more accurate description of how all of the particles act in solution. For very dilute solutions, the activities of the substances in the solution closely approach the formal concentration (what the calculated concentration should be based on how much substance was measured out.) As solutions get more concentrated, the activities of all of the species tend to be smaller than the formal concentration. The decrease in activity as concentration increases is much more pronounced for ions than it is for neutral solutes.

Activities are actually **unitless** ratios that compare an effective pressure or an effective concentration to a standard state pressure or concentration (the correct term for the effective pressure is **fugacity**). There are several ways to define standard states for the different components of a solution, but a common system is

- the standard state for gas pressure, P°, is 1 bar (often approximated with 1 atm)
- the standard state for solute concentration, C°, is 1 molal (moles solute/kg solvent) for dilute solutions. Often molality is approximated with molarity (moles solute/Liter solution).
- the standard state for a liquid is the pure liquid
- the standard state for a solid is the pure solid

Thus, when we discuss the activity of a gas, we actually are discussing the ratio of the effective pressure to the standard state pressure:

$$a_{gas} = \frac{P}{P^{\circ}} \tag{6.4.3}$$

- a_{gas} is a ratio with **no units.**

Likewise, the activity of a solute in solution would be:

$$a_{solute} = \frac{C}{C^{\circ}} \tag{6.4.4}$$

- a_{solute} is a ratio with **no units.**

For all solids, the activity is a ratio of the concentration of a pure solid to the concentration of that same pure solid

$$a_{solid} = \frac{C_{\text{effective solid}}}{C^{\circ}_{\text{effective solid}}} = 1 \tag{6.4.5}$$

- a_{solid} **always** has a value of 1 with no units.

For all liquids, the activity is a ratio of the concentration of a pure liquid to the concentration of that same pure liquid:

$$a_{liquid} = \frac{C_{\text{effective liquid}}}{C^{\circ}_{\text{effective liquid}}} = 1 \tag{6.4.6}$$

- a_{liquid} **always** has a value of 1 with no units.

For most experimental situations, solutions are assumed to be dilute with respect to the solvent. This assumption implies the solvent can be approximated with pure liquid. According to Raoult's Law, the vapor pressure of the solvent in a solution is equal to the mole fraction of the solvent in the solution times the vapor pressure of the pure solvent:

$$\chi = \frac{P}{P^{\circ}} \tag{6.4.7}$$

The mole fraction of solvent in a dilute solution is approximately 1, so the vapor pressure of the solution is essentially identical to the vapor pressure of the pure solvent. This means that the activity of a solvent in dilute solution will always has a value of 1, with no units.

> Activity indicates how many particles "appear" to be present in the solution, which is different from how many actually are present. Hence, activity is a "fudge factor" to ideal solutions that correct the true concentration.
>
> - a_{gas} is a ratio with **no units.**
> - a_{solute} is a ratio with **no units.**
> - a_{solid} is **always** 1 with no units.
> - a_{liquid} is **always** 1 with no units.

Estimating Activities

The activity of a substance can be estimated from the nominal concentration of that substance (C) by using an activity coefficient, γ:

$$a = \gamma \cdot [C] \tag{6.4.8}$$

The value of γ depends upon the substance, the temperature, and the concentration of all solute particles in the solution. The lower the concentration of all solute particles in the solution, the closer the value of γ for each solute approaches 1:

$$\lim_{[C]\to 0} \gamma \to 1 \tag{6.4.9}$$

Therefore, as γ approaches 1, the value of a for the solute approaches C.

$$\lim_{\gamma \to 1} a \to [C] \tag{6.4.10}$$

The activity coefficient for a nonvolatile, neutral solute is often estimated by non-linear curve fitting, taking into account the molality of the solute and the activity of the solvent (usually its vapor pressure). In most situations, it is more practical to look up the values of the activity coefficient for a given solute than it is to carry out the curve fitting.

Table 6.4.1: Activity Coefficients

m/(mol kg^{-1})	HCl	LiCl	NaCl	$LiNO_3$	$NaNO_3$
0.01	0.904	0.903	0.902	0.903	0.900
0.02	0.875	0.873	0.870	0.872	0.866
0.05	0.830	0.825	0.820	0.825	0.811

$m/(mol\ kg^{-1})$	HCl	LiCl	NaCl	$LiNO_3$	$NaNO_3$
0.10	0.796	0.790	0.778	0.788	0.762
0.2	0.767	0.757	0.735	0.752	0.703
0.4	0.755	0.740	0.693	0.728	0.638
0.6	0.763	0.743	0.673	0.727	0.599
0.8	0.783	0.755	0.662	0.733	0.570
1.0	0.809	0.774	0.657	0.743	0.548
1.2	0.840	0.796	0.654	0.757	0.530
1.4	0.876	0.823	0.655	0.774	0.514
1.6	0.916	0.853	0.657	0.792	0.501
1.8	0.960	0.885	0.662	0.812	0.489
2.0	1.009	0.921	0.668	0.835	0.478
2.5	1.147	1.026	0.688	0.896	0.455
3.0	1.316	1.156	0.714	0.966	0.437
3.5	1.518	1.317	0.746	1.044	0.422
4.0	1.762	1.510	0.783	1.125	0.408
4.5	2.04	1.741	0.826	1.215	0.396
5.0	2.38	2.02	0.874	1.310	0.386

Estimating the activity coefficient of electrolytes (solutes that dissolve or react with the solvent to form ions) depends upon the number of ions formed by the dissociation of the solute in solution or the reaction of the solute with the solution, because each ion formed is dealt with individually. In a theoretical, infinitely dilute ideal solution, an electrolyte would dissociate or react completely to form an integer number of independent ions. For example, 1 mole of NaCl would dissociate to form 2 moles of ions (1 mole of Na^+ ions and 1 mole of Cl^- ions). In reality, it is found that electrolytes almost always act as if they contain **fewer** moles of ions than expected based on the formal concentration. This non-ideality is attributed to the degree of dissociation/reaction of the solute, to the solute-solvent interactions such as complex ion formation, and to the solute-solute interactions such as ion pairing. An activity coefficient incorporates the particle interactions into a single term that modifies the formal concentration to give an estimate of the effective concentration, or activity, of each ion.

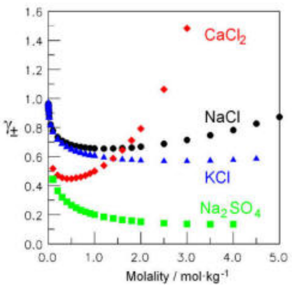

Figure 6.4.1: The dependence of the mean ionic activity coefficient for different salts at 25°C in water as function of concentration.

At infinite dilution, $gamma$ is solely determined by the Debye-Hückel limiting law (Equation 6.4.11) and depends only on the number and charges of the cations and anions. This means that the same limiting mean ionic activity coefficient is found for sodium chloride and potassium chloride and that also the values for the 2-1 and 1-2 salts sodium sulfate and calcium chloride are identical. At higher electrolyte concentrations though, these values change very strongly and are usually modeled using empirical parameters regressed to the experimental data.

> *Electrolytes almost always act as if they contain **fewer** moles of ions than expected based on the formal concentration.*

Single ion activity coefficients are calculated using various forms of the Debye-Hückel equation:

$$\log \gamma = \frac{-0.51 z^2 \sqrt{\mu}}{1 + \frac{\alpha \sqrt{\mu}}{305}} \tag{6.4.11}$$

This equation takes into account the solution environment as well as the individual characteristics of the specific ion of interest. It is not difficult to calculate single ion activity coefficients, but tables of these activity coefficients for many common ions in solutions of various concentrations are available (e.g., Table $6.4.1$).

Applications of Activities

The law of mass action states that a reaction at a constant temperature will proceed spontaneously and predominantly in one direction until a constant ratio of concentrations of products and reactants is obtained. For the generic reaction

$$aA + bB \rightleftharpoons cC + dD \tag{6.4.12}$$

the ratio of concentrations (called the mass action expression or equilibrium constant expression) is

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = Q \tag{6.4.13}$$

where [ ] represents concentration in

$$\frac{\text{moles of solute}}{\text{Liter of solution}} \tag{6.4.14}$$

This ratio can take on any value greater than zero, depending on the reaction conditions. Thus, it is often called the **instantaneous reaction quotient**, Q. The term “instantaneous” signifies that the reaction will (and is) proceeding spontaneously to reach a constant ratio of products and reactants. When the reaction attains that constant ratio of products and reactants, it has reached a state of dynamic equilibrium, and the ratio of concentrations can be represented by the symbol K, the equilibrium constant:

$$\frac{[C]^c_{eq} [D]^d_{eq}}{[A]^a_{eq} [B]^b_{eq}} = K \tag{6.4.15}$$

Laws of mass action and equilibrium constants are discussed in most general chemistry textbooks, but they are often discussed as if they were describing ideal systems. For instance, if all of the substances are gases, partial pressures are used in the mass-action expression. If the substances are in solution, molarities are used in the mass-action expression. To be thermodynamically correct, however, the **activities** of the substances must be compared in the mass-action expression.

Activities are needed for precise work because, unlike concentrations, activities contain information about the effects of the solvent and other surrounding particles on the behavior of the particles of interest. Using any unit of comparison other than activities will give an incorrect value for K, but it is assumed that the approximate value is close enough to the true value for most situations. Many tables list K values to 2-3 significant digits, but this degree of precision is valid only under the exact experimental conditions used to obtain those values.

The Derivation of Mass Action Expressions

Given all of the above information on activities, it is now possible to show how a true mass-action equation involving activities can be approximated by a mass-action equation involving molarities. It should be noted that just as the activities were unitless ratios, the molalities and molarities that appear in the following approximations should also be thought of as unitless ratios of concentrations divided by the standard state concentration.

Example 6.4.2: A Solution of Ammonia in Water

Starting with the mass action equation in terms of activities, show all the approximations needed to obtain the mass action equation in terms of molar concentrations for the reaction:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)} \tag{6.4.16}$$

Solution

$$Q = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3} a_{H_2O}} = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3}(1)} \tag{6.4.17}$$

- assume $a_{H_2O} \approx 1$ because water is the solvent in a dilute solution

$$Q = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3}} = \frac{\gamma_{NH_4^+} \gamma_{OH^-}}{\gamma_{NH_3}} \frac{m_{NH_4^+} m_{OH^-}}{m_{NH_3}} \tag{6.4.18}$$

- assume activity = (activity coefficient)(molality)

$$Q = \frac{\gamma_{NH_4^+} \gamma_{OH^-}}{\gamma_{NH_3}} \frac{m_{NH_4^+} m_{OH^-}}{m_{NH_3}} \approx \frac{\gamma_{NH_4^+} \gamma_{OH^-}}{\gamma_{NH_3}} \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{6.4.19}$$

- assume molarity [ ] ≈ molality in dilute solutions

$$Q \approx \frac{\gamma_{NH_4^+} \gamma_{OH^-}}{\gamma_{NH_3}} \frac{[NH_4^+][OH^-]}{[NH_3]} \approx \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{6.4.20}$$

- assume $\frac{\gamma_{NH_4^+} \gamma_{OH^-}}{\gamma_{NH_3}} \approx 1$ because the solution is dilute

Therefore the final mass action equation typically used for this reaction is

$$Q \approx \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{6.4.21}$$

Example 6.4.3: A Reaction of Two Solids that Produces a Solution

Starting with the mass action equation in terms of activities, show all the approximations needed to obtain the mass action equation in terms of molar concentrations for the reaction:

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4NO_3(s) \rightleftharpoons Ba^{2+}(aq) + 2NO_3^-(aq) + 2NH_3(aq) + 10H_2O(l) \tag{6.4.22}$$

Solution

$$Q = \frac{a_{Ba^{2+}} a^2_{NO_3^-} a^2_{NH_3} a^{10}_{H_2O}}{a_{Ba(OH)_2 \cdot 8H_2O} a_{NH_4NO_3}} = \frac{a_{Ba^{2+}} a^2_{NO_3^-} a^2_{NH_3} \cdot (1)}{(1) \cdot (1)} = a_{Ba^{2+}} a^2_{NO_3^-} a^2_{NH_3} \tag{6.4.23}$$

- a =1 for solids and for solvent

$$Q = a_{Ba^{2+}} a^2_{NO_3^-} a^2_{NH_3} = \gamma_{Ba^{2+}} \gamma^2_{NO_3^-} \gamma^2_{NH_3} m_{Ba^{2+}} m^2_{NO_3^-} m^2_{NH_3} \tag{6.4.24}$$

- activity = (activity coefficient)(molality)

$$Q = \gamma_{Ba^{2+}} \gamma^2_{NO_3^-} \gamma^2_{NH_3} m_{Ba^{2+}} m_{NO_3^-}{}^2 m^2_{NH_3} \approx \gamma_{Ba^{2+}} \gamma^2_{NO_3^-} \gamma^2_{NH_3} [Ba^{2+}][NO_3^-]^2[NH_3]^2 \tag{6.4.25}$$

- molarity [ ] ≈ molality in dilute solutions

$$Q \approx \gamma_{Ba^{2+}} \gamma^2_{NO_3^-} \gamma^2_{NH_3} [Ba^{2+}][NO_3^-]^2[NH_3]^2 \approx [Ba^{2+}][NO_3^-]^2[NH_3]^2 \tag{6.4.26}$$

- $\gamma_{Ba^{2+}} \gamma^2_{NO_3^-} \gamma^2_{NH_3} \approx 1$ because the solution is dilute

$Q \approx [Ba^{2+}][NO_3^-]^2[NH_3]^2$

✓ Salt

Determine the molar solubility $\frac{moles}{Liter}$ of the slightly soluble solid, $BaSO_4$, inPure Water and An Aqueous 0.1 M NaCl Solution?

Solution

Pure Water

Barium sulfate is a solid that is slightly soluble in water, with a K_{sp} value of 1.1 x 10^{-10}:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

This solution is dilute enough that the Ba^{2+}, SO_4^{2-}, OH^-, and H^+ ions will not affect each other greatly, thus the activity of the ions closely approaches their formal concentration. In this nearly ideal aqueous solution, the mass action expression would be

$$1.1 \times 10^{-10} = a_{Ba} \cdot a_{SO_4} \approx [Ba^{2+}][SO_4^{2-}] \tag{6.4.27}$$

Remember that $BaSO_4$ is a solid, with an activity equal to 1. At equilibrium, the $[Ba^{2+}] = [SO_4^{2-}]$ = 1.05 x 10^{-5} M.

An Aqueous 0.1 M NaCl Solution

A saturated aqueous solution of $BaSO_4$ that also is 0.1 M in NaCl is no longer near to ideality. The Na^+ and Cl^- ions surround the Ba^{2+} and SO_4^{2-} ions and prevent these ions from being able to reform solid $BaSO_4$ readily as they did in pure water. The activities of the Ba^{2+} and the SO_4^{2-} ions will be lower than their formal concentrations. However, the product of the activities must still be equal to the true (thermodynamic) equilibrium constant.

$$1.1x10^{-10} = a_{Ba} \cdot a_{SO_4} = \gamma_{Ba}[Ba^{2+}] \cdot \gamma_{SO_4}[SO_4^{2-}] \tag{6.4.28}$$

With the total amount of Na^+, Cl^-, Ba^{2+}, SO_4^{2-}, OH^-, and H^+ ions in the solution, γ_{Ba} = 0.38 and γ_{SO_4} = 0.355.

$$1.1x10^{-10} = a_{Ba} \cdot a_{SO_4} = (0.38)[Ba^{2+}](0.355)[SO_4^{2-}] \tag{6.4.29}$$

$$8.2x10^{-10} = [Ba^{2+}][SO_4^{2-}] \tag{6.4.30}$$

$$[Ba^{2+}] = [SO_4^{2-}] = 2.9x10^{-5} \tag{6.4.31}$$

The net result is that more solid $BaSO_4$ will dissolve in the 0.1M NaCl solution than in water, and the experimental equilibrium constant will seem to be larger than the thermodynamic equilibrium constant.

Colligative Properties

The van 't Hoff factor, *i*, is a term that often appears in colligative property calculations to account for the fact that electrolytes will form two or more moles of ions per every mole of electrolyte. In most cases, the solutions are treated as if they are ideal, in which case i will equal an integer representing the total number of independent ions per one formula unit of the solute (Table 2).

Table 6.4.2: Integer van 't Hoff factors for Colligative Properties

Compound	i
Sucrose	1
NaCl	2
$MgBr_2$	3
CaCl2	3
Na3PO4	4
Al2(SO4)3	5

The van 't Hoff factor is actually rarely an integer, and was, in fact, developed to take into account the non-ideality of solutes. Tables listing the i values for specific compounds in specific solutions are available, but it is also possible to use activities to estimate to effective concentrations of ions in solution for use in colligative property calculations.

✓ Example 6.4.5

What is the freezing point of a 0.1 m $BaCl_2$ aqueous solution?

Solution

The calculation for an ideal solution would be $\Delta T = mki$, where $m = 0.1 molal$, $k = 1.86\frac{°C}{molal}$, and $i = 3$. The resulting ΔT is

$$\Delta T = (0.1 molal)(1.86\frac{°C}{molal})(3) = 0.558°C \tag{6.4.32}$$

if non-ideality is assumed, the calculation becomes

$$\Delta T = \gamma_{Ba} \cdot (\gamma_{Cl})^2 \bullet (m_{Ba})(m_{Cl})^2 \tag{6.4.33}$$

Substituting in the estimated γ values of $\gamma_{Ba} = 0.38$ and$\gamma_{Cl} = 0.755$, the ion activities are

- $a_{Ba} = (0.38)(0.1) = 0.038$
- $a_{Cl} = (0.755)(0.2) = 0.151$

and the ΔT is

$$\Delta T = (0.038 + 0.151)(1.86°C) = 0.351°C \tag{6.4.34}$$

The ΔT obtained using activities is lower than the ΔT obtained when using an integer value for *i* because the activity values take into account the fact that the ions in the solution are not able to act as free and independent particles because of their interactions with each other and with the solvent,

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6.5: Heterogeneous Equilibria

The equilibrium constant, K, expresses the relationship between products and reactants of a reaction at equilibrium with respect to a specific unit.This article explains how to write equilibrium constant expressions, and introduces the calculations involved with both the concentration and the partial pressure equilibrium constant.

Homogeneous Reactions

A homogeneous reaction is one where the states of matter of the products and reactions are all the same (the word "homo" means "same"). In most cases, the solvent determines the state of matter for the overall reaction. For example, the synthesis of methanol from a carbon monoxide-hydrogen mixture is a *gaseous* **homogeneous** mixture, which contains two or more substances:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \tag{6.5.1}$$

At equilibrium, the rate of the forward and reverse reaction are equal, which is demonstrated by the arrows. The equilibrium constant, however, gives the ratio of the units (pressure or concentration) of the products to the reactants when the reaction is at equilibrium.

The synthesis of ammonia is another example of a *gaseous* **homogeneous** mixture:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \tag{6.5.2}$$

Heterogeneous Reactions

A heterogeneous reaction is one in which one or more states within the reaction differ (the Greek word "heteros" means "different"). For example, the formation of an aqueous solution of lead(II) iodide creates a **heterogeneous** mixture dealing with particles in both the *solid* and *aqueous* states:

$$PbI_{2(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2I^-_{(aq)} \tag{6.5.3}$$

The decomposition of sodium hydrogen carbonate (baking soda) at high elevations is another example of a **heterogeneous** mixture, this reaction deals with molecules in both the *solid* and *gaseous* states:

$$2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)} \tag{6.5.4}$$

$$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)} \tag{6.5.5}$$

This difference between homogeneous and heterogeneous reactions is emphasized so that students remember that solids, pure liquids, and solvents are treated differently than gases and solutes when approximating the activities of the substances in equilibrium constant expressions.

Writing Equilibrium Constant Expressions

The numerical value of an equilibrium constant is obtained by letting a single reaction proceed to equilibrium and then measuring the concentrations of each substance involved in that reaction. The ratio of the product concentrations to reactant concentrations is calculated. Because the concentrations are measured at equilibrium, the equilibrium constant remains the same for a given reaction independent of initial concentrations. This knowledge allowed scientists to derive a model expression that can serve as a "template" for any reaction. This basic "template" form of an equilibrium constant expression is examined here.

Equilibrium Constant of Activities

The thermodynamically correct equilibrium constant expression relates the activities of **all** of the species present in the reaction. Although the concept of activity is too advanced for a typical General Chemistry course, it is essential that the explanation of the derivation of the equilibrium constant expression starts with activities so that no misconceptions occur. For the hypothetical reaction:

$$bB + cC \rightleftharpoons dD + eE \tag{6.5.6}$$

the equilibrium constant expression is written as

$$K = \frac{a_D^d \cdot a_E^e}{a_B^b \cdot a_C^c} \tag{6.5.7}$$

*The lower case letters in the balanced equation represent the number of moles of each substance, the upper case letters represent the substance itself.

- If $K > 1$ then equilibrium favors products
- If $K < 1$ then equilibrium favors the reactants

Equilibrium Constant of Concentration

To avoid the use of activities, and to simplify experimental measurements, the equilibrium constant of concentration approximates the activities of solutes and gases in dilute solutions with their respective molarities. However, the activities of solids, pure liquids, and solvents are **not** approximated with their molarities. Instead these activities are defined to have a value equal to 1 (one).The equilibrium constant expression is written as K_c, as in the expression for the reaction:

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)} \tag{6.5.8}$$

$$K_c = \frac{a_{H_3O^+} \cdot a_{F^-}}{a_{HF} \cdot a_{H_2O}} \approx \frac{[H_3O^+][F^-]}{[HF](1)} = \frac{[H_3O^+][F^-]}{[HF]} \tag{6.5.9}$$

Here, the letters inside the brackets represent the concentration (in molarity) of each substance. Notice the mathematical product of the chemical products raised to the powers of their respective coefficients is the numerator of the ratio and the mathematical product of the reactants raised to the powers of their respective coefficients is the denominator. This is the case for every equilibrium constant. A ratio of molarities of products over reactants is usually used when most of the species involved are dissolved in water. A ratio of concentrations can also be used for reactions involving gases if the volume of the container is known.

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Equilibrium Constant of Pressure

Gaseous reaction equilibria are often expressed in terms of partial pressures. The equilibrium constant of pressure gives the ratio of pressure of products over reactants for a reaction that is at equilibrium (again, the pressures of all species are raised to the powers of their respective coefficients). The equilibrium constant is written as K_p, as shown for the reaction:

$$aA_{(g)} + bB_{(g)} \rightleftharpoons gG_{(g)} + hH_{(g)} \tag{6.5.10}$$

$$K_p = \frac{p^g_G \, p^h_H}{p^a_A \, p^b_B} \tag{6.5.11}$$

- Where p can have units of pressure (e.g., atm or bar).

Conversion of K_c to K_p

To convert K_c to K_p, the following equation is used:

$$K_p = K_c(RT)^{\Delta n_{gas}} \tag{6.5.12}$$

where:

- R=0.0820575 L atm mol^{-1} K^{-1} or 8.31447 J mol^{-1} K^{-1}
- T= Temperature in Kelvin
- Δn_{gas}= Moles of gas (product) - Moles of Gas (Reactant)

Reaction Quotient

Another quantity of interest is the reaction quotient, Q, which is the numerical value of the ratio of products to reactants at any point in the reaction. The reaction quotient is calculated the same way as is K, but is not necessarily equal to K. It is used to determine which way the reaction will proceed at any given point in time.

$$Q = \frac{[G]^g[H]^h}{[A]^a[B]^b} \tag{6.5.13}$$

- If $Q > K$, then the reactions shifts to the left to reach equilibrium
- If $Q < K$, then the reactions shifts to the right to reach equilibrium
- If $Q = K$ then the reaction is at equilibrium

The same process is employed whether calculating Q_c or Q_p.

Heterogeneous Mixture

The most important consideration for a heterogeneous mixture is that **solids and pure liquids and solvents have an activity that has a fixed value of 1**. From a mathematical perspective, with the activities of solids and liquids and solvents equal one, these substances do not affect the overall K or Q value. This convention is extremely important to remember, especially in dealing with heterogeneous solutions.

✓ Example 6.5.1

In a hypothetical reaction:

$$aA_{(s)} + bB_{(l)} \rightleftharpoons gG_{(aq)} + hH_{(aq)} \tag{6.5.14}$$

The equilibrium constant expression is written as follows:

$$K_c = \frac{[G]^g[H]^h}{1 \times 1} = [G]^g[H]^h \tag{6.5.15}$$

In this case, since solids and liquids have a fixed value of 1, the numerical value of the expression is independent of the amounts of A and B. If the product of the reaction is a solvent, the numerator equals one, which is illustrated in the following reaction:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \tag{6.5.16}$$

The equilibrium constant expression would be:

$$K_c = \frac{1}{[H^+][OH^-]} \tag{6.5.17}$$

which is the reciprocal of the autoionization constant of water (K_w)

$$K_c = \frac{1}{K_w} = 1 \times 10^{14} \tag{6.5.18}$$

Manipulation of Constants

The equilibrium constant expression must be manipulated if a reaction is reversed or split into elementary steps. When the reaction is reversed, the equilibrium constant expression is inverted. The new expression would be written as:

$$K' = \frac{1}{\frac{[G]^g[H]^h}{[A]^a[B]^b}} = \frac{[A]^a[B]^b}{[G]^g[H]^h} \tag{6.5.19}$$

When there are multiple steps in the reaction, each with its own K (in a scenario similar to Hess's law problems), then the successive K values for each step are *multiplied* together to calculate the overall K.

Activities

Because the concentration of reactants and products are not dimensionless (i.e. they have units) in a reaction, the actual quantities used in an equilibrium constant expression are *activities*. *Activity* is expressed by the dimensionless ratio $\frac{[X]}{c^\circ}$ where $[X]$ signifies the molarity of the molecule and c is the chosen reference state:

$$a_b = \frac{[B]}{c^\circ} \tag{6.5.20}$$

For gases that do not follow the ideal gas laws, using activities will accurately determine the equilibrium constant that changes when concentration or pressure varies. Thus, the units are canceled and K becomes unitless.

Practice Problems

1. Write the equilibrium constant expression for each reaction.
   a. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
   b. $N_2O_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons 2NO_{(g)}$
   c. $Cu_{(s)} + 2Ag^{+}_{(aq)} \rightleftharpoons Cu^{+2}_{(aq)} + 2Ag_{(s)}$
   d. $CaCO_{3(g)} \rightleftharpoons CaCO_{(s)} + CO_{2(g)}$
   e. $2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$
2. What is the K_c of the following reaction?

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \tag{6.5.21}$$

   with concentration $SO_{2(g)} = 0.2MO_{2(g)} = 0.5MSO_{3(g)} = 0.7\ M$ Also, What is the K_p of this reaction? At room temperature?
3. For the same reaction, the differing concentrations:

$$SO_{2(g)} = 0.1\ MO_{2(g)} = 0.3\ M\ SO_{3(g)} = 0.5\ M \tag{6.5.22}$$

   Would this go towards to product or reactant?
4. Write the Partial Pressure Equilibrium:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{6.5.23}$$

5. Write the chemicl reaction for the following equilibrium constant:

$$K_p = \frac{P^2_{HI}}{P_{H_2} \times P_{I_2}} \tag{6.5.24}$$

References

1. Petrucci, Ralph H. General Chemistry: Principles and Modern Applications 9th Ed. New Jersey: Pearson Education Inc. 2007.

Outside Links

- For more information on equilibrium constant expressions please visit the Wikipedia site: http://en.Wikipedia.org/wiki/Equilibrium_constant
- The image below can be found here: image.tutorvista.com/content/chemical-equilibrium/reaction-rate-time-graph.gif

Answers to Practice Problems

1. $K_c = \frac{[SO_3]^2}{[O_2][SO_2]^2}$
2. $Kc = \frac{[NO]^2}{[O_2]^{0.5}[N_2O]}$
3. $Kc = \frac{[Cu^{+2}]}{[Ag^{+}]^2}$
4. $Kc = \frac{[CO_2]}{[CaCO_3]}$
5. $K_c = [H_2O][CO_2]$

What is K_c for the Reaction

1) Kc: 24.5

Kp: 1.002 Atm

2) Q_c= 83.33 > K_c therefore the reaction shifts to the left

1. $K_p = \frac{P_{CO_2}}{P_{O_2}}$
2. $H_2(g) + I_2(g) \rightarrow 2HI(g)$

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SECTION OVERVIEW

6.6: Applications of the Equilibrium Constant

The concept of an ideal solution is fundamental to chemical thermodynamics and its applications, such as the use of colligative properties. An **ideal solution** or ideal mixture is a solution in which the enthalpy of solution ($\Delta H_{solution} = 0$) is zero; with the closer to zero the enthalpy of solution, the more "ideal" the behavior of the solution becomes. Since the enthalpy of mixing (solution) is zero, the change in Gibbs energy on mixing is determined solely by the entropy of mixing ($\Delta S_{solution}$).

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6.7: Solving Equilibrium Problems

An ICE (**I**nitial, **C**hange, **E**quilibrium) table is simple matrix formalism that used to simplify the calculations in reversible equilibrium reactions (e.g., weak acids and weak bases or complex ion formation).

Introduction

ICE tables are composed of the concentrations of molecules in solution in different stages of a reaction, and are usually used to calculate the K, or equilibrium constant expression, of a reaction (in some instances, K may be given, and one or more of the concentrations in the table will be the unknown to be solved for). ICE tables automatically set up and organize the variables and constants needed when calculating the unknown.

ICE is a simple acronym for the titles of the first column of the table.

- **I** stands for **initial** concentration. This row contains the initial concentrations of products and reactants.
- **C** stands for the **change** in concentration. This is the concentration change required for the reaction to reach equilibrium. It is the difference between the equilibrium and initial rows. The concentrations in this row are, unlike the other rows, expressed with either an appropriate positive (+) or negative (-) sign and a variable; this is because this row represents an increase or decrease (or no change) in concentration.
- **E** is for the concentration when the reaction is at **equilibrium**. This is the summation of the initial and change rows. Once this row is completed, its contents can be plugged into the equilibrium constant equation to solve for K_c.

The procedure for filling out an ICE table is best illustrated through example.

✓ Example 1

Use an ICE table to determine K_c for the following balanced general reaction:

$$2\,\mathrm{X(g)} \rightleftharpoons 3\,\mathrm{Y(g)} + 4\,\mathrm{Z(g)}$$

where the capital letters represent the products and reactants.

- This equation will be placed horizontally above the table, with each product and reactant having a separate column.

A sample consisting of 0.500 mol of x is placed into a system with a volume of 0.750 liters.

- This statement implies that there are no initial amounts of Y and Z. For the I row of the Y and Z columns, 0.000 mol will be entered.
- Notice that the initial composition is given in moles. The amounts can either be converted to concentrations before putting them into the ICE table or after the equilibrium amounts have been calculated. This example uses moles for the ICE table, and calculates concentrations later.

At equilibrium, the amount of sample x is known to be 0.350 mol.

- For the equilibrium row of X, 0.350 mol will be entered.

Desired Unknown

$$K_c = ?$$

Solution

The equilibrium constant expression is expressed as products over reactants, each raised to the power of their respective stoichiometric coefficients:

$$K_c = \frac{[Y]^3[Z]^4}{[X]^2}$$

The equilibrium concentrations of Y and Z are unknown, but they can be calculated using the ICE table.

STEP 1: Fill in the given amounts

Reaction:	2X	3Y	4Z

Reaction:	2X	3Y	4Z
Initial amounts	0.500 mol	0.000 mol	0.000 mol
Change in amount	?	?	?
Equilibrium amount	0.350 mol	?	?

This is the first step in setting up the ICE table. As mentioned above, the ICE mnemonic is vertical and the equation heads the table horizontally, giving the rows and columns of the table, respectively. The numerical amounts were given. Any amount not directly given is unknown.

STEP 2: Fill in the amount of change for each compound

Reaction	2X	3Y	4Z
Initial amounts	0.500 mol	0.000 mol	0.000 mol
Change in amount	-0.150 mol	+0.225 mol	+0.300 mol
Equilibrium amounts	0.350 mol	?	?

Notice that the equilibrium in this equation is shifted to the right, meaning that some amount of reactant will be taken away and some amount of product will be added (for the Change row).

The change in amount (x) can be calculated using algebra:

$$Equilibrium\ Amount = Initial\ Amount + Change\ in\ Amount$$

Solving for the Change in the amount of $2x$ gives:

$$0.350\ mol - 0.500\ mol = -0.150\ mol$$

The change in reactants and the balanced equation of the reaction is known, so the change in products can be calculated. The stoichiometric coefficients indicate that for every 2 mol of x reacted, 3 mol of Y and 4 mol of Z are produced. The relationship is as follows:

$$\begin{align} Change\ in\ Product &= -\left(\frac{\text{Stoichiometric Coefficient of Product}}{\text{Stoichiometric Coefficient of Reactant}}\right)(\text{Change in Reactant}) \tag{6.7.1} \\ Change\ in\ Y &= -\left(\frac{3}{2}\right)(-0.150\ mol) \tag{6.7.2} \\ &= +0.225\ mol \tag{6.7.3} \end{align}$$

Try obtaining the change in Z with this method (the answer is already in the ICE table).

STEP 3: Solve for the equilibrium amounts

Reaction	2X	3Y	4Z
Initial amounts	0.500 mol	0.000 mol	0.000 mol
Change in amounts	-0.150 mol	+0.225 mol	+0.300 mol
Equilibrium amounts	0.350 mol	0.225 mol	0.300 mol

If the initial amounts of Y and/or Z were nonzero, then they would be added together with the change in amounts to determine equilibrium amounts. However, because there was no initial amount for the two products, the equilibrium amount is simply equal to the change:

$$\begin{align} Equilibrium\ Amount &= Initial\ Amount + Change\ in\ Amount \tag{6.7.4} \\ Equilibrium\ Amount\ of\ Y &= 0.000\ mol\ + 0.225\ mol \tag{6.7.5} \\ &= +0.225\ mol \tag{6.7.6} \end{align}$$

Use the same method to find the equilibrium amount of Z. Convert the equilibrium amounts to concentrations. Recall that the volume of the system is 0.750 liters.

$$[Equilibrium\ Concentration\ of\ Substance] = \frac{Amount\ of\ Substance}{Volume\ of\ System}$$

$$[X] = \frac{0.350\ mol}{0.750\ L} = 0.467\ M$$

$$[Y] = \frac{0.225\ mol}{0.750\ L} = 0.300\ M$$

$$[Z] = \frac{0.300\ mol}{0.750\ L} = 0.400\ M$$

Use the concentration values to solve the K_c equation:

$$K_c = \frac{[Y]^3[Z]^4}{[X]^2} \tag{6.7.7}$$

$$= \frac{[0.300]^3[0.400]^4}{[0.467]^2} \tag{6.7.8}$$

$$K_c = 3.17 \times 10^{-3} \tag{6.7.9}$$

✓ Example 2: Using an ICE Table with Concentrations

n this example an ICE table is used to find the equilibrium concentration of the reactants and products. (This example will be less in depth than the previous example, but the same concepts are applied.) These calculations are often carried out for weak acid titrations.

Find the concentration of A^- for the generic acid dissociation reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

with $[HA(aq)]_{initial} = 0.150M$ and $K_a = 1.6 \times 10^{-2}$

Solution

This equation describes a weak acid reaction in solution with water. The acid (HA) dissociates into its conjugate base (A^-) and protons (H_3O^+). Notice that water is a liquid, so its concentration is not relevant to these calculations.

STEP 1: Fill in the given concentrations

Reaction:	HA	A^-	H_3O^+
I	0.150 M	0.000 M	0.000 M
C	?	?	?
E	?	?	?

- The contents of the leftmost column column are shortened for convenience.

STEP 2: Calculate the change concentrations by using a variable 'x'

Reaction:	HA	A^-	H_3O^+
I	0.150 M	0.000 M	0.000 M
C	-x M	+x M	+x M
E	?	?	?

- The change in concentration is unknown, so the variable x is used to denote the change. x is the same for both products and reactants because equal stoichiometric amounts of A^- and H_3O^+ are generated when HA dissociates in water.

STEP 3: Calculate the concentrations at equilibrium

Reaction:	HA	A^-	H_3O^+
I	0.150 M	0.000 M	0.000 M
C	-x M	+x M	+x M
E	0.150 - x M	x M	x M

- To find the equilibrium amounts the I row and the C row are added. Use these values and K_a (the equilibrium constant for acids) to find the concentration *x*.

STEP 4: Use the ICE table to calculate concentrations with K_a

The expression for K_a is written by dividing the concentrations of the products by the concentrations of the reactants. Plugging in the values at equilibrium into the equation for K_a gives the following:

$$K_a = \frac{x^2}{0.150 - x} = 1.6 \times 10^{-2}$$

To find the concentration x, rearrange this equation to its quadratic form, and then use the quadratic formula to find x*:*

$$\begin{aligned}(1.6 \times 10^{-2})(0.150 - x) &= x^2 \\ x^2 + (1.6 \times 10^{-2})x - (0.150)(1.6 \times 10^{-2}) &= 0\end{aligned}$$

This is the typical form for a quadratic equation:

$$Ax^2 + Bx + C = 0$$

where, in this case:

- $A = 1$
- $B = 1.6 \times 10^{-2}$
- $C = (-0.150)(1.6 \times 10^{-2}) = -2.4 \times 10^{-3}$

The quadratic formula gives two solutions (but only one physical solution) for x:

$$x = \frac{-B + \sqrt{B^2 - 4AC}}{2A}$$

and

$$x = \frac{-B - \sqrt{B^2 - 4AC}}{2A}$$

Intuition must be used in determining which solution is correct. If one gives a negative concentration, it can be eliminated, because negative concentrations are unphysical.

The x value can be used to calculate the equilibrium concentrations of each product and reactant by plugging it into the elements in the E row of the ice table.

[Solution: x = 0.0416, -0.0576. x = 0.0416 makes chemical sense and is therefore the correct answer.]

> For some problems like example 2, if x is significantly less than the value for K_a, then the x of the reactants (in the denominator) can be omitted and the concentration for x should not be greatly affected. This will make calculations faster by eliminating the necessity of the quadratic formula.

Checklist for ICE tables

- Make sure the reversible equation is **balanced** at the start of the problem; otherwise, the wrong amounts will be used in the table.
- The given data should be in **amounts, concentrations, partial pressures**, or somehow able to be converted to such. If it is not, then an ICE table will not help solve the problem.

- If the ICE table has the **equilibrium in amounts, make sure to convert equilibrium values to concentrations** before plugging in to solve for K_c.
- If the given data is in **amounts or concentrations**, use the ICE table to find K_c. If the given data is in **partial pressures**, use the ICE table to find K_p. If you desire to convert from one to the other, remember that

$$K_p = K_c(RT)^{\Delta n_{gas}}$$

  It is simpler to use the ICE table with the appropriate givens and convert at the end of the problem.
- Enter in **known data first**, and then calculate the unknown data.
- If there is **a negative value in the "initial" or "equilibrium" rows, reexamine the calculation.** A negative concentration, amount, or partial pressure is physically impossible. Obviously, the "change" row can contain a negative value.
- **Pay attention to the state of each reactant and product.** If a compound is a solid or a liquid, its concentrations are not relevant to the calculations. Only concentrations of gaseous and aqueous compounds are used.
- In the "change" row the values will usually be a variable, denoted by *x*. It must first be understood which direction the equation is going to reach equilibrium (from left to right or from right to left). The value for "change" in the "from" direction of the reaction will be the opposite of *x* and the "to" direction will be the positive of x (adding concentration to one side and take away an equal amount from the other side).
- Know the **direction of the reaction**. This knowledge will affect the "change" row of the ICE table (for our example, we knew the reaction would proceed forward, as there was no initial products). Direction of reaction can be calculated using Q, the reaction quotient, which is then compared to a known K value.
- It is easiest to **use the same units** every time an ICE table is used (molarity is usually preferred). This will minimize confusion when calculating the equilibrium constants. ICE tables are usually used for weak acid or weak base reactions because all of the nature of these solutions. The amount of acid or base that will dissociate is unknown (for strong acids and strong bases it can be assumed that all of the acid or base will dissociate, meaning that the concentration of the strong acid or base is the same as its dissociated particles).

> **Partial pressures** may also be substituted for **concentrations** in the ICE table, if desired (i.e., if the concentrations are not known, K_p instead of K_c is desired, etc.). "Amount" is also acceptable (the ICE table may be done in amounts until the equilibrium amounts are found, after which they will be converted to concentrations). For simplicity, assume that the word "concentration" can be replaced with "partial pressure" or "amounts" when formulating ICE tables.

? Exercise 6.7.1

0.200 M acetic acid is added to water. What is the concentration of H_3O^+ in solution if $K_c = 1.8 \times 10^{-6}$?

Answer

5.99×10^{-4}

? Exercise 6.7.2

If the initial concentration of NH_3 is 0.350 M and the concentration at equilibrium is 0.325 M, what is K_c for this reaction?

Answer

1.92×10^{-3}

? Exercise 6.7.3

How is K_c derived from K_p?

Answer

$K_p = K_c(RT)^{\Delta n}$ then solve for K_c

Exercise 6.7.4

Complete this ICE table:

Reaction:	[HA]	[A^-]	[H_3O^+]
I	0.650 mol	?	?
C	?	?	?
E	0.250 mol	?	?

Answer

Reaction:	**HA**	**A-**	**H_3O^+**
I	0.650 mol	0.000 mol	0.000 mol
C	-0.400 mol	+0.400 mol	+0.400 mol
E	0.250 mol	0.400 mol	0.400 mol

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SECTION OVERVIEW

6.8: Le Châtelier's Principle

Le Chatelier's principle states that if a **dynamic equilibrium** is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium. If a chemical reaction is at equilibrium and experiences a change in pressure, temperature, or concentration of products or reactants, the equilibrium shifts in the opposite direction to offset the change. This page covers changes to the position of equilibrium due to such changes and discusses briefly why catalysts have no effect on the equilibrium position.

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6.9: Equilibria of Real Gases

Le Chatelier's principle states that if a **dynamic equilibrium** is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium. If a chemical reaction is at equilibrium and experiences a change in pressure, temperature, or concentration of products or reactants, the equilibrium shifts in the opposite direction to offset the change. This page covers changes to the position of equilibrium due to such changes and discusses briefly why catalysts have no effect on the equilibrium position.

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CHAPTER OVERVIEW

7: Acids and Bases

Chemical Principles (Zumdahl and Decoste)

Textmap Alternative

Topic hierarchy

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SECTION OVERVIEW

7.1: The Nature of Acids and Bases

Topic hierarchy

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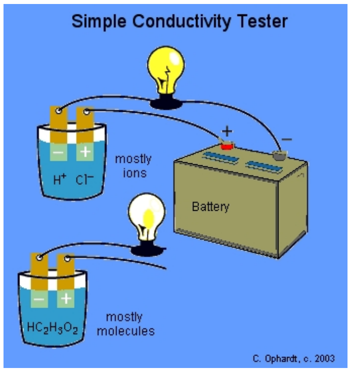
7.2: Acid Strength

All acids and bases do not ionize or dissociate to the same extent. This leads to the statement that acids and bases are not all of equal strength in producing H^+ and OH^- ions in solution. The terms "strong" and "weak" give an indication of the strength of an acid or base. The terms strong and weak describe the ability of acid and base solutions to conduct electricity. If the acid or base conducts electricity strongly, it is a strong acid or base. If the acid or base conducts electricity weakly, it is a weak acid or base.

Demonstration of Acid and Base Conductivity

The instructor will test the conductivity of various solutions with a light bulb apparatus. The light bulb circuit is incomplete. If the circuit is completed by a solution containing a large number of ions, the light bulb will glow brightly indicating a strong ability to conduct electricity as shown for HCl. If the circuit is completed by a solution containing large numbers of molecules and either no ions or few ions, the solution does not conduct or conducts very weakly as shown for acetic acid.



An acid or base which strongly conducts electricity contains a large number of ions and is called a **strong acid or base** and an acid or base which conducts electricity only weakly contains only a few ions and is called a **weak acid or base**.

Conductivity Behavior of Acids and Bases

Compounds	Appearance of light bulb	Classification Weak or Strong	Inference of Ions or Molecules
H_2O	no light	weak	molecules
HCl	bright	strong	ions
$HC_2H_3O_2$	dim	weak	molecules
H_2SO_4	bright	Answer	Answer
H_2CO_3	dim	Answer	Answer
NaOH	bright	Answer	Answer
KOH	bright	Answer	Answer
NH_4OH	dim	Answer	Answer

Bond Strength

The bond strengths of acids and bases are implied by the relative amounts of molecules and ions present in solution. The bonds are represented as:

acid	base
H-A	M-OH

where A is a negative ion, and M is a positive ion

- Strong acids have mostly ions in solution, therefore the bonds holding H and A together must be weak. Strong acids easily break apart into ions.
- Weak acids exist mostly as molecules with only a few ions in solution, therefore the bonds holding H and A together must be strong. Weak acids do not readily break apart as ions but remain bonded together as molecules.

Bond Strength Principle

Acids or bases with strong bonds exist predominately as molecules in solutions and are called "weak" acids or bases. Acids or bases with weak bonds easily dissociate into ions and are called "strong" acids or bases.

Table 1: Summary List of Characteristics for Strong and Weak Acids and Bases. All characteristics of acids and bases are related to whether the predominate forms are molecules and ions.

Characteristic	Strong Acid or Base	Weak Acid or Base
Molecules	few	large number
Ions	large number	small number
Conductivity	strong	weak
Bond Strength	weak	strong

Acids and bases behave differently in solution based on their strength. Acid or base "strength" is a measure of how readily the molecule ionizes in water.

Introduction Again

Some acids and bases ionize rapidly and almost completely in solution; these are called strong acids and strong bases. For example, hydrochloric acid (HCl) is a strong acid. When placed in water, virtually every HCl molecule splits into a H^+ ion and a Cl^- ion in the reaction.[1]

$$\mathrm{HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)}$$

For a strong acid like HCl, if you place 1 mole of HCl in a liter of water, you will get roughly 1 mole of H_30^+ ions and 1 mole of Cl^- ions. In a weak acid like hydrofluoric acid (HF), not all of the HF molecules split up, and although there will be some H^+ and F^- ions released, there will still be HF molecules in solution[1]. A similar concept applies to bases, except the reaction is different. A strong base like sodium hydroxide (NaOH) will also dissociate completely into water; if you put in 1 mole of NaOH into water, you will get 1 mole of hydroxide ions.[1]

$$\mathrm{NaOH(aq) + H_2O(l) \rightleftharpoons Na^+(aq) + OH^-(aq) + H_2O(l)}$$

The terms "strong" and "weak" in this context do not relate to how corrosive or caustic the substance is, but only its capability to ionize in water. The ability of a substance to eat through other materials or damage skin is more of a function of the properties of that acid, as well as its concentration. Although, strong acids are more directly dangerous at lower concentrations a strong acid is not necessarily more dangerous than a weak one. For example, hydrofluoric acid is a weak acid[1], but it is extremely dangerous and should be handled with great care. Hydrofluoric acid is particularly dangerous because it is capable of eating through glass, as seen in the video in the links section[V1]. The percent dissociation of an acid or base is mathematically indicated by the acid ionization constant (K_a) or the base ionization constant (K_b)[1]. These terms refer to the ratio of reactants to products in equilibrium when the acid or base reacts with water. For acids the expression will be

$$K_a = [H_3O^+][A^-]/[HA]$$

where HA is the concentration of the acid at equilibrium, and A^- is the concentration of its conjugate base at equilibrium and for bases the expression will be

$$K_b = \frac{[\mathrm{OH^-}][\mathrm{HB^+}]}{\mathrm{B}} \tag{7.2.1}$$

where B is the concentration of the base at equilibrium and HB^+ is the concentration of its conjugate acid at equilibrium

The stronger an acid is, the lower the pH it will produce in solution. pH is calculated by taking the negative logarithm of the concentration of hydronium ions. For strong acids, you can calculate the pH by simply taking the negative logarithm of its molarity as it completely dissociates into its conjugate base and hydronium. The same goes for strong bases, except the negative logarithm gives you the pOH as opposed to the pH. For weak acids and bases, the higher the K_a or K_b, the more acidic or basic the solution. To find the pH for a weak acid or base, you must use the K equation and a RICE table to determine the pH.

All acids have a conjugate base that forms when they react with water, and similarly, all bases have a conjugate acid that reacts when they form with water.[1] You can judge the relative strength of a conjugate by the K_a or K_b value of the substance because $K_a \times K_b$ is equal to the ionization constant of water, K_w which is equal to 1×10^{-14} at room temperature. The higher the Ka, the stronger the acid is, and the weaker its conjugate base is. Similarly, the higher the K_b, the stronger the substance is as a base, and the more weakly acidic its conjugate acid is.[1]

Calculation of K_a

For an acid that reacts with water in the reaction

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{7.2.2}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{7.2.3}$$

where each bracketed term represents the concentration of that substance in solution.

Relation of K_w, K_b, K_a

$$K_w = K_a \times K_b$$

Partial List of Strong Acids: Hydrochlroic acid (HCl), Nitric Acid (HNO_3), Perchloric Acid ($HClO_4$), Sulfuric Acid (H_2SO_4)

Partial List of Strong Bases: Sodium Hydroxide (NaOH), Barium Hydroxide ($Ba(OH)_2$), Calcium Hydroxide ($Ca(OH)_2$), Lithium Hydroxide (LiOH) (Hydroxides of Group I and II elements are generally strong bases)

Partial List of Weak Acids: Acetic Acid (CH_3COOH), Carbonic Acid (H_2CO_3), Phosphoric Acid (H_3PO_4)

Partial List of Weak Bases: Ammonia (NH_3), Calcium Carbonate ($CaCO_3$), Sodium Acetate ($NaCH_3COO$)

✓ Example 7.2.1

Find the pH of 0.5 grams of HCl disolved into 100 ml of water:

Solution

First find moles of acid:

grams / molar mass = moles

0.5 grams / (36.5 g/mole) = 0.014 moles HCl

Then find molarity:

moles / volume = molarity

0.014 moles / 0.100 L = 0.14 M

HCl is a strong acid and completely dissociates in water, therefore the pH will be equal to the negative logarithm of the concentration of HCl

pH = -log(H_3O^+)

pH = -log(0.14) = 0.85

✓ Example 7.2.2

The K_a value for acetic acid is $1.76*10^{-5}$, and the K_a value for benzoic acid is $6.46*10^{-5}$, if two solutions are made, one from each acid, with equal concentrations, which one will have the lower pH?

Solution

The K_a value is a measure of the ratio between reactants and products at equilibrium. For an acid, the reaction will be HA + H_2O --> A^- + H_3O^+ . PH is based on the concentration of the hydronium ion (H_3O^+) which is a product of the reaction of acid and water. A higher K_a value means a higher ratio of reactants to products, and so the acid with the higher K_a value will be producing more hydronium, and therefore have a lower pH. Therefore the solution of benzoic acid will have a lower pH.

✓ Example 7.2.3

The K_a value of ammonium (NH_4^+) is $5.6*10^{-10}$, the K_b value of ammonia (NH_3) $1.8*10^{-5}$, is ammonium more strongly acidic than ammonia is basic?

Solution

The relative strength of an acid or base depends on how high its K_a or K_b value is, in this case, the K_a value is far lower than the K_b value so the ammonia is more strongly basic than ammonium is acidic.

References

1. Oxtboy, Gillis, Campion, David W., H.P., Alan. "Acid-Base Equilibria." Principles of Modern Chemistry. Belmont: Thomson Higher Education, 2008.

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7.3: The pH Scale

Learning Objectives

- To define the pH scale as a measure of acidity of a solution
- Tell the origin and the logic of using the pH scale.
- Apply the same strategy for representing other types of quantities such as pK_a, pK_b, pK_w.

Auto-Ionization of Water

Because of its *amphoteric* nature (i.e., acts as both an acid or a base), water does not always remain as H_2O molecules. In fact, two water molecules react to form hydronium and hydroxide ions:

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{7.3.1}$$

This is also called the self-ionization of water. The concentration of H_3O^+ and OH^- are equal in pure water because of the 1:1 stoichiometric ratio of Equation 7.3.1. The molarity of H_3O^+ and OH^- in water are also both $1.0 \times 10^{-7}\ M$ at 25° C. Therefore, a constant of water (K_w) is created to show the equilibrium condition for the self-ionization of water. The product of the molarity of hydronium and hydroxide ion is always 1.0×10^{-14} (at room temperature).

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{7.3.2}$$

Equation 7.3.2 also applies to all aqueous solutions. However, K_w does change at different temperatures, which affects the pH range discussed below.

> *H^+ and H_3O^+ is often used interchangeably to represent the hydrated proton, commonly call the hydronium ion.*

Equation 7.3.1 can also be written as

$$H_2O \rightleftharpoons H^+ + OH^- \tag{7.3.3}$$

As expected for any equilibrium, the reaction can be shifted to the reactants or products:

- If an acid (H^+) is added to the water, the equilibrium shifts to the left and the OH^- ion concentration decreases
- If base (OH^-) is added to water, the equilibrium shifts to left and the H^+ concentration decreases.

pH and pOH

Because the constant of water, K_w is 1.0×10^{-14} (at 25° C), the pK_w is 14, the constant of water determines the range of the pH scale. To understand what the pK_w is, it is important to understand first what the "p" means in pOH and pH. The addition of the "p" reflects the negative of the logarithm, $-\log$. Therefore, the pH is the negative logarithm of the molarity of H, the pOH is the negative logarithm of the molarity of OH^-, and the pK_w is the negative logarithm of the constant of water:

$$pH = -\log[H^+] \tag{7.3.4}$$

$$pOH = -\log[OH^-] \tag{7.3.5}$$

$$pK_w = -\log[K_w] \tag{7.3.6}$$

At room temperature,

$$K_w = 1.0 \times 10^{-14} \tag{7.3.7}$$

So

$$pK_w = -\log[1.0 \times 10^{-14}] \tag{7.3.8}$$

$$= 14 \tag{7.3.9}$$

Using the properties of logarithms, Equation 7.3.8 can be rewritten as

$$10^{-pK_w} = 10^{-14}. \tag{7.3.10}$$

The equation also shows that each increasing unit on the scale decreases by the factor of ten on the concentration of H^+. Combining Equations 7.3.4 - 7.3.6 and 7.3.8 results in this important relationship:

$$pK_w = pH + pOH = 14 \tag{7.3.11}$$

Equation 7.3.11 is correct only at room temperature since changing the temperature will change K_w.

> *The pH scale is logarithmic, meaning that an increase or decrease of an integer value changes the concentration by a tenfold. For example, a pH of 3 is ten times more acidic than a pH of 4. Likewise, a pH of 3 is one hundred times more acidic than a pH of 5. Similarly a pH of 11 is ten times more basic than a pH of 10.*

Properties of the pH Scale

From the simple definition of pH in Equation 7.3.4, the following properties can be identified:

- This scale is convenient to use, because it converts some odd expressions such as 1.23×10^{-4} into a single number of 3.91.
- This scale covers a very large range of $[\mathrm{H}^+]$, from 0.1 to 10^{-14}. When $[\mathrm{H}^+]$ is high, we usually do not use the pH value, but simply the $[\mathrm{H}^+]$. For example, when $[\mathrm{H}^+] = 1.0$, pH = 0. We seldom say the pH is 0, and that is why you consider pH = 0 such an odd expression. A pH = -0.30 is equivalent to a $[\mathrm{H}^+]$ of 2.0 M. Negative pH values are only for academic exercises. Using the concentrations directly conveys a better sense than the pH scales.
- The pH scale expands the division between zero and 1 in a linear scale or a compact scale into a large scale for comparison purposes. In mathematics, you learned that there are infinite values between 0 and 1, or between 0 and 0.1, or between 0 and 0.01 or between 0 and any small value. Using a log scale certainly converts infinite small quantities into infinite large quantities.
- The non-linearity of the pH scale in terms of $[\mathrm{H}^+]$ is easily illustrated by looking at the corresponding values for pH between 0.1 and 0.9 as follows:

pH	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$[\mathrm{H}^+]$	1	0.79	0.63	0.50	0.40	0.32	0.25	0.20	0.16	0.13

- Because the negative log of $[\mathrm{H}^+]$ is used in the pH scale, the pH scale *usually* has positive values. Furthermore, the larger the pH, the smaller the $[\mathrm{H}^+]$.

The Effective Range of the pH Scale

It is common that the pH scale is argued to range from 0-14 or perhaps 1-14, but neither is correct. The pH range does not have an upper nor lower bound, since as defined above, the pH is an indication of concentration of H^+. For example, at a pH of zero the hydronium ion concentration is one molar, while at pH 14 the hydroxide ion concentration is one molar. Typically the concentrations of H^+ in water in most solutions fall between a range of 1 M (pH=0) and 10^{-14} M (pH=14). Hence a range of 0 to 14 provides sensible (but not absolute) "bookends" for the scale. One can go somewhat below zero and somewhat above 14 in water, because the concentrations of hydronium ions or hydroxide ions can exceed one molar. Figure 7.3.1 depicts the pH scale with common solutions and where they are on the scale.

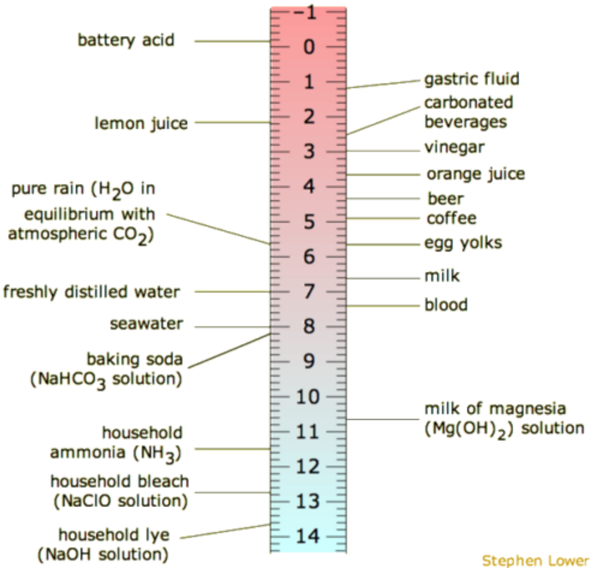

Figure 7.3.1: Solutions and the placement of them on pH scale. (CC-BY-SA 3.0; Stephen Lower).

Quick Interpretation

- If pH >7, the solution is basic. The pOH should be looked in the perspective of OH^- instead of H^+. Whenever the value of pOH is less than 7, then it is considered basic. And therefore there are more OH^- than H^+ in the solution.
- At pH 7, the substance or solution is at neutral and means that the concentration of H^+ and OH^- ion is the same.
- If pH < 7, the solution is acidic. There are more H^+ than OH^- in an acidic solution.
- The pH scale **does not** have an upper nor lower bound.

Example 7.3.1

If the concentration of $NaOH$ in a solution is $2.5 \times 10^{-4}\ M$, what is the concentration of H_3O^+?

Solution

We can assume room temperature, so

$$1.0 \times 10^{-14} = [H_3O^+][OH^-]$$

to find the concentration of H_3O^+, solve for the $[H_3O^+]$.

$$\frac{1.0 \times 10^{-14}}{[OH^-]} = [H_3O^+] \tag{7.3.12}$$

$$\frac{1.0 \times 10^{-14}}{2.5 \times 10^{-4}} = [H_3O^+] = 4.0 \times 10^{-11}\ M \tag{7.3.13}$$

Example 7.3.2

a. Find the pH of a solution of 0.002 M of HCl.
b. Find the pH of a solution of 0.00005 M NaOH.

Solution

a. The equation for pH is -log [H+]

$$[H^+] = 2.0 \times 10^{-3}\ M$$

$$pH = -\log[2.0 \times 10^{-3}] = 2.70$$

b. The equation for pOH is -log $[OH^-]$

$$[OH^-] = 5.0 \times 10^{-5}\ M$$

$$pOH = -\log[5.0 \times 10^{-5}] = 4.30$$

$$pK_w = pH + pOH$$

and

$$pH = pK_w - pOH$$

then

$$pH = 14 - 4.30 = 9.70$$

✓ Example 7.3.3: Soil

If moist soil has a pH of 7.84, what is the H^+ concentration of the soil solution?

Solution

$$pH = -\log[H^+]$$

$$7.84 = -\log[H^+]$$

$$[H^+] = 1.45 \times 10^{-8} M$$

Hint

Place -7.84 in your calculator and take the antilog (often inverse log or 10^x) = 1.45 x 10^{-8}M

Proper Definition of pH

The pH scale was originally introduced by the Danish biochemist S.P.L. Sørenson in 1909 using the symbol p_H. The letter *p* is derived from the German word *potenz* meaning power or exponent of, in this case, 10. In 1909, S.P.L. Sørenson published a paper in Biochem Z in which he discussed the effect of H^+ ions on the activity of enzymes. In the paper, he invented the term pH (purported to mean *pondus hydrogenii* in Latin) to describe this effect and defined it as the $-\log[H^+]$. In 1924, Sørenson realized that the pH of a solution is a function of the "activity" of the H^+ ion and not the concentration. Thus, he published a second paper on the subject. A better definition would be

$$pH = -\log\, a\{\mathrm{H}^+\} \tag{7.3.14}$$

where $a\{H^+\}$ denotes the activity (an effective concentration) of the H^+ ions. The activity of an ion is a function of many variables of which concentration is one.

- *Concentration* is abbreviated by using square brackets, e.g., $[H_3O^+]$ is the concentration of hydronium ion in solution.
- *Activity* is abbreviated by using "a" with curly brackets, e.g., $a\{H_3O^+\}$ is the activity of hydronium ions in solution

> Because of the difficulty in accurately measuring the activity of the H^+ ion for most solutions the International Union of Pure and Applied Chemistry (IUPAC) and the National Bureau of Standards (NBS) has defined pH as the reading on a pH meter that has been standardized against standard buffers. The following equation is used to calculate the pH of all solutions:
>
> $$pH = \frac{F(E - E_{standard})}{RT\ \ln 10} + pH_{standard} \tag{7.3.15}$$
>
> $$= \frac{5039.879(E - E_{standard})}{T} + pH_{standard} \tag{7.3.16}$$
>
> with
>
> - R is the ideal gas constant,
> - F is the Faraday's constant, and
> - T is absolute temperature (in K)

> The activity of the H^+ ion is determined as accurately as possible for the standard solutions used. The identity of these solutions vary from one authority to another, but all give the same values of pH to ± 0.005 pH unit. The historical definition of pH is correct for those solutions that are so dilute and so pure the H^+ ions are not influenced by anything but the solvent molecules (usually water).

When measuring pH, $[H^+]$ is in units of moles of H^+ per liter of solution. This is a reasonably accurate definition at low concentrations (the dilute limit) of H^+. At very high concentrations (10 M hydrochloric acid or sodium hydroxide, for example,) a significant fraction of the ions will be associated into neutral pairs such as $H^+Cl^–$, thus reducing the concentration of “available” ions to a smaller value which we will call the *effective concentration*. It is the *effective concentration* of H^+ and $OH^–$ that determines the pH and pOH. The pH scale as shown above is called sometimes "concentration pH scale" as opposed to the "thermodynamic pH scale". The main difference between both scales is that in thermodynamic pH scale one is interested not in H^+concentration, but in H^+activity. What a person measures in the solution is just activity, not the concentration. Thus it is thermodynamic pH scale that describes real solutions, not the concentration one.

For solutions in which ion concentrations don't exceed 0.1 M, the formulas pH = –log $[H^+]$ and pOH = –log$[OH^–]$ are generally reliable, but don't expect a 10.0 M solution of a strong acid to have a pH of exactly –1.00! However, this definition is only an approximation (albeit very good under most situations) of the proper definition of pH, which depends on the **activity** of the hydrogen ion:

$$pH = -\log a\{H^+\} \approx -\log[H^+] \tag{7.3.17}$$

The activity is a measure of the "effective concentration" of a substance, is often related to the true concentration via an activity coefficient, γ:

$$aH^+ = \gamma[H^+] \tag{7.3.18}$$

Calculating the activity coefficient requires detailed theories of how charged species interact in solution at high concentrations (e.g., the Debye-Hückel Theory). In most solutions the pH differs from the -log$[H^+]$ in the first decimal point. The following table gives experimentally determined pH values for a series of HCl solutions of increasing concentration at 25 °C.

Table 7.3.1: HCl Solutions with corresponding pH values. Data taken from Christopher G. McCarty and Ed Vitz, Journal of Chemical Education, 83(5), 752 (2006) and G.N. Lewis, M. Randall, K. Pitzer, D.F. Brewer, Thermodynamics (McGraw-Hill: New York, 1961; pp. 233-34).

Molar Concentration of HCl	pH defined as Concentration	Experimentally Determined pH	Relative Deviation
0.00050	3.30	3.31	0.3%
0.0100	2	2.04	1.9%
0.100	1	1.10	9%
0.40	0.39	0.52	25%
7.6	-0.88	-1.85	52%

> *While the pH scale formally measures the activity of hydrogen ions in a substance or solution, it is typically approximated as the concentration of hydrogen ions; this approximation is applicable only under low concentrations.*

Living Systems

Molecules that make up or are produced by living organisms usually function within a narrow pH range (near neutral) and a narrow temperature range (body temperature). Many biological solutions, such as blood, have a pH near neutral. pH influences the structure and the function of many enzymes (protein catalysts) in living systems. Many of these enzymes have narrow ranges of pH activity. Cellular pH is so important that death may occur within hours if a person becomes acidotic (having increased acidity in the blood). As one can see pH is critical to life, biochemistry, and important chemical reactions. Common examples of how pH plays a very important role in our daily lives are given below:

- Water in swimming pool is maintained by checking its pH. Acidic or basic chemicals can be added if the water becomes too acidic or too basic.
- Whenever we get a heartburn, more acid build up in the stomach and causes pain. We needs to take antacid tablets (a base) to neutralize excess acid in the stomach.
- The pH of blood is slightly basic. A fluctuation in the pH of the blood can cause in serious harm to vital organs in the body.
- Certain diseases are diagnosed only by checking the pH of blood and urine.
- Certain crops thrive better at certain pH range.
- Enzymes activate at a certain pH in our body.

Table 7.3.2: pH in Living Systems

Compartment	**pH**
Gastric Acid	1
Lysosomes	4.5
Granules of Chromaffin Cells	5.5
Human Skin	5.5
Urine	6
Neutral H_2O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal Fluid	7.3
Blood	7.43-7.45
Mitochondrial Matrix	7.5
Pancreas Secretions	8.1

Problems

1. In a solution of $2.4 \times 10^{-3} M$ of HI, find the concentration of OH^-.
2. Determine the pH of a solution that is 0.0035 M HCl.
3. Determine the $[H_3O^+]$ of a solution with a pH = 5.65
4. If the pOH of NH_3, ammonia, in water is 4.74. What is the pH?
5. Pepsin, a digestive enzyme in our stomach, has a pH of 1.5. Find the concentration of OH^- in the stomach.

Solutions

1. We use the dissociation of water equation to find $[OH^-]$.
   $K_w = [H_3O^+][OH^-] = 1.0 \text{ X } 10^{-14}$
   Solve for $[OH^-]$
   $[OH^-] = (1.0 \text{ X } 10^{-14}) / [H_3O^+]$
   Plug in the molarity of HI and solve for OH^-.
   $[OH^-] = (1.0 \text{ X } 10^{-14}) / [2.4 \text{ X } 10^{-3}] = 4.17 \text{ X } 10^{-12}$ M.
2. pH = $-\log[H_3O^+]$
   Plug the molarity of the HCl in and solve for pH.
   pH = -log[0.0035] = 2.46
3. pH = $-\log[H_3O^+]$
   Plug in the pH and solve for [H3O+]
   $5.65 = -\log[H_3O^+]$
   Move the negative sign to the pH. $-5.65 = \log[H_3O^+]$
   $10^{-5.65} = 10^{\log[H_3O+]} = 2.24 \text{ X } 10^{-6}$ M
4. pH + pOH = 14
   Solve for pH.

14 - pOH = pH
14 - 4.74 = pH = 9.26

5. There are several ways to do this problem.
   Answer 1.
   pH + pOH = 14
   Solve for pOH.
   pOH = 14 - pH
   pOH = 14 - 1.5 = 12.5
   When the pOH is solved, solve for the concentration by using log.
   pOH = -log[OH^-]
   12.5 = -log[OH^-]
   -12.5 = log[OH^-]
   $10^{-12.5} = 10^{\log[OH-]} = 3.16 \text{ X } 10^{-13}$ M.

   Answer 2.
   pH = -log[H^+]
   Plug in the pH and solve for the molarity of H+ of pepsin.
   1.5 = -log[H^+]
   -1.5 = log[H^+]
   $10^{-1.5} = 10^{\log[H+] =}$ [H^+]= 0.032
   Use the concentration of H^+ to solve for the concentration of OH^-.
   [H^+][OH^-] = 1.0 X 10^{-14}
   Plug in the [H^+] and solve for [OH^-].
   [OH^-] = (1.0 X 10^{-14})/[H_3O^+]
   [OH^-] = (1.0 X 10^{-14})/(0.032) = 3.125 X 10^{-14} M

References

1. Petrucci, et al. "Self-Ionization of Water and the pH Scale." *General Chemistry: Principles & Modern Applications*. 7th ed. Upper Saddle River: Pearson Prentice Hall, 2007. 669-71.
2. Segel, Irwin H. "Acid and Base." *Biochemical Calculations*. 2nd ed. Wiley: BK Book, 1976. 12.
3. Christopher G. McCarty and Ed Vitz, Journal of Chemical Education, 83(5), 752 (2006)

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7.4: Calculating the pH of Strong Acid Solutions

How To Predict The Relative Strength Of Acids

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7.5: Calculating the pH of Weak Acid Solutions

Thus far, we have been discussing problems and answers in equilibria--perhaps the most popular type of problem being how to find the pH of a weak acid solution given a certain concentration of a molecule. However, those problems in particular usually only involve what is called a monoprotic acid. “Mono” in the word “monoprotic” indicates that there is only one ionizeable hydrogen atom in an acid when immersed in water, whereas the concept of Polyprotic Acids and Bases allows for two or more ionizeable hydrogen atoms.

Introduction

Consider the following chemical equation as the molecule acetic acid equilibrates in the solution:

$$\mathrm{CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-}$$

Although acetic acid carries a four hydrogen atoms, only a single becomes ionized. Not to get into too much detail between monoprotic and polyprotic acids, but if you desire to find the pH given a concentration of a weak acid (in this case, acetic acid), you would create and complete an ICE Table adjusting for how much acetic acid disassociates. However, if you wish to find the pH of a solution after a **polyprotic acid** disassociates, there are extra steps that would need to be done. Let's first take a look at a unique example:

✓ Example 7.5.1: Finding the pH of sulfuric Acid

What is the pH of 0.75 M sulfuric acid?

Solution

In sulfuric acid (H_2SO_4), there are two ionizable hydrogen atoms. What makes this molecule interesting is that its ionization constant for the first hydrogen (K_{a1}) ionized is significantly larger than is the second ionization constant (K_{a2}). The K_{a1} constant for sulfuric acid is conveniently dubbed “very large” while the K_{a2} constant is 1.1 x 10^{-2}. As such, the sulfuric acid will completely disassociate into HSO_4^- and H_3O^+ ions (as a strong acid).

$$\mathrm{H_2SO_4(aq) + H_2O \longrightarrow HSO_4^-(aq) + H_3O^+}$$

Since the sulfuric acid completely disassociates in the solution, we can skip the ICE table process for sulfuric acid, and assert that the concentration $\mathrm{HSO_4^-}$ and $\mathrm{H_3O^+}$ are the same as that of H_2SO_4, that is 0.75 M. (This neglects the background concentration of $\mathrm{H_3O^+}$ in water of $1 \times 10^{-7} M$).

Equation:

$$\mathrm{HSO_4^-(aq) + H_2O \rightleftharpoons SO_4^{2-}(aq) + H_3O^+}$$

ICE Table:

	HSO_4^-	SO_4^{2-}	H_3O^+
Initial	0.75 M	0 M	0.75 M
Change	-x M	+x M	+x M
Equilibrium	(0.75 - x) M	+x M	(0.75 + x) M

$$K_{a2} = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = 1.1 \times 10^{-2} = 0.011 = \frac{x(0.75+x)}{0.75-x}$$

Assume x in the denominator is negligible. Therefore,

$$x = 0.011M = [SO_4^{2-}]$$

Since we know the value of x, we can use the equation from the ICE table to find the value of [HSO_4^-].

$$[HSO_4^-] = 0.75\ M - x = 0.75 - 0.011 = 0.74\ M$$

We can also find [H_3O^+] using the equation from the ICE table.

$$[H_3O+] = 0.75\ M + x = 0.75 + 0.011 = 0.76\ M$$

We can then find the pH from the calculated [H_3O^+] value.

$$pH = -log[H_3O^+] = -log 0.76 = 0.119$$

Let's say our task is to find the pH given a polyprotic base which gains protons in water. Thankfully, the process is essentially the same as finding the pH of a polyprotic acid except in this case we deal with the concentration of OH^- instead of H_3O^+.

✓ Example 7.5.2: Finding the pH of a polyprotic base

Let's take a look at how to find the pH of $C_{20}H_{24}O_2N_2$, a diprotic base with a concentration of 0.00162 M, and a K_{b1} of 10^{-6} and a K_{b2} of $10^{-9.8}$.

Equation:

$$C_{20}H_{24}O_2N\ (aq) + H_2O \rightleftharpoons C_{20}H_{24}O_2N_2H^+ + OH^-$$

	$C_{20}H_{24}O_2N_2$	$C_{20}H_{24}O_2N_2H^+$	OH^-
Initial	0.00162 M	0 M	0 M
Change	-x M	+x M	+x M
Equilibrium	0.00162 M	x M	x M

$$K_{b1} = \frac{[C_{20}H_{24}O_2N_2H^+][OH^-]}{[C_{20}H_{24}O_2N_2]} = 10^{-6} = 0.011 = \frac{(x)(x)}{0.00162 - x}$$

Again, assume x in the denominator is negligible. Therefore,

$$0.011 \approx \frac{x^2}{0.00162}$$

Then,

$$x \approx 4 \times 10^{-5}$$

We can then find the pH.

$$pOH = -log(4 \times 10^{-5}) = 4.4$$

$$pH = 14 - 4.4 = 9.6$$

As we determine the pH of the solution, we realize that the OH^- gained using the second ionization constant is so insignificant that it does not impact the final pH value. For good measure, the following is the process to determine the pH in case the second use of the ICE table would indeed make a difference.

Equation:

$$C_{20}H_{24}O_2N_2H^+ + H_2O \rightleftharpoons C_{20}H_{24}O_2N_2H_2^{2+} + OH^-$$

ICE Table:

	$C_{20}H_{24}O_2N_2H^+$	$C_{20}H_{24}O_2N_2H_2^{2+}$	OH^-
Initial	4 x 10^{-5} M	0 M	4 x 10^{-5} M
Change	-x M	+x M	+x M
Equilibrium	(4 x 10^{-5} - x) M	x M	(4 x 10^{-5} + x) M

$$K_{b2} = \frac{[C_{20}H_{24}O_2N_2H_2^{2+}][OH^-]}{[C_{20}H_{24}O_2N_2H^+]} = 10^{-9.8}$$

$$10^{-9.8} = \frac{(4 \times 10^{-5} + x)(x)}{(4 \times 10^{-5} - x)}$$

$$10^{-9.8} = \frac{0.00004\ x + x^2}{0.00004 - x}$$

$$10^{-9.8}(0.00004 - x) = 0.00004x + x^2$$

$$x^2 + (4 \times 10^{-5})x - 6.3 \times 10^{-15} = 0$$

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-4 \times 10^{-5} \pm \sqrt{(4 \times 10^{-5})^2 - 4(1)(6.3 \times 10^{-15})}}{2(1)} \\ &= 0 \end{aligned}$$

References

1. Petrucci, et al. General Chemistry: Principles & Modern Applications; Ninth Edition. Pearson/Prentice Hall; Upper Saddle River, New Jersey 07.

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SECTION OVERVIEW

7.6 Bases

Topic hierarchy

Template:HideTOC

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7.7: Polyprotic Acids

The name "polyprotic" literally means many protons. Therefore, in this section we will be observing some specific acids and bases which either lose or accept *more than one* proton. Then, we will be talking about the equations used in finding the degree of dissociation. Finally, with given examples, we will be able to approach problems dealing with polyprotic acids and bases.

Introduction

Polyprotic acids are specific acids that are capable of *losing* more than a single proton per molecule in acid-base reactions. (In other words, acids that have more than one ionizable H^+ atom per molecule). Protons are lost through several stages (one at each stage), with the first proton being the fastest and most easily lost. Contrast with *monoprotic acids* in section Monoprotic Versus Polyprotic Acids And Bases.

Common Polyprotic Acids	Formula	Strong/Weak Acid	Number of Ionizable Hydrogens	K_{a1}	K_{a2}	K_{a3}
Sulfuric acid	H_2SO_4	Strong	2 (diprotic)	Very Large	1.1E-2	
Sulfurous acid	H_2SO_3	Weak	2 (diprotic)	1.3E-2	6.2E-8	
Phosphoric acid	H_3PO_4	Weak	3 (triprotic)	7.1E-3	6.3E-8	4.2E-13
Carbonic acid	H_2CO_3	Weak	2 (diprotic)	4.4E-7	4.7E-11	
Hydrosulfuric acid or Hydrogen sulfide	H_2S	Weak	2 (diprotic)	1.0E-7	1E-19	
Oxalic acid	$H_2C_2O_4$	Weak	2 (diprotic)	5.4E-2	5.3E-5	
Malonic acid	$H_2C_3H_2O_4$	Medium Strong	2 (diprotic)	1.5E-3	2.0E-6	

From the table above, we see that sulfuric acid is the strongest.

Ionization Constant

It is important to know that K_1>K_2>K_3, where K stands for the acidity constant or **acid ionization constant** (first, second, and third, respectively). These constants are used to measure the degree of dissociation of hydrogens in the acid. For a more in depth discussion on this, go to Ionization Constants.

✓ Example 1: Hydrosulfuric acid

To find K_{a1} of Hydrosulfuric acid (H_2S), you must first write the reaction:

$$H_2S \rightleftharpoons H^+ + HS^-$$

Dividing the products by the reactants, we then have:

$$K_{a1} = \frac{[H^+][HS^-]}{[HS-]}$$

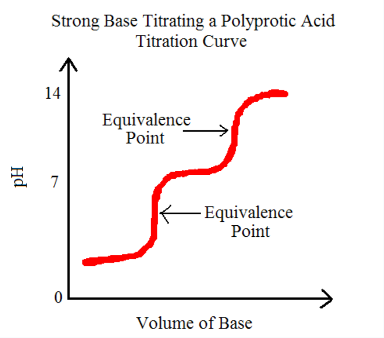
To find K_{a2}, we start with the reaction:

$$HS^- \rightleftharpoons H^+ + S_2^-$$

Then, like when finding K_{a1}, write the products over the reactants:

$$K_{a2} = \frac{[H^+][S_2^-]}{[HS^-]}$$

From these reactions we can observe that it takes two steps to fully remove the H$^+$ ion. This also means that this reaction will produce two **equivalence points** or **stoichiometric points**. The equivalence point, by definition, is the point during an acid-base titration in which there has been equal amounts of acid and base reacted. If we were to graph this, we would be able to see exactly just what two equivalence points looks like. Let's check it out:



Note the multiple equivalence points and notice that they are almost straight lines at that point, indicating equal added quantities of acid and base.

Titrations

In strong acid + strong base titrations, the pH changes slowly at first, rapidly through the equivalence point of pH=7, and then slows down again. If it is being titrated in a strong acid, the pH will go up as the base is added to it. Conversely, if it is in a strong base, the pH will fall down as acid is added.

- In strong acid + weak base titrations, the pH changes slowly at the equivalence point and the pH equals the pK$_a$ of the acid. The pH is below 7.
- For the weak acid + strong base, the pH is above 7 at the equivalence point.
- If there is strong acid or strong base left over after the equivalence point, this can be used to find the pH of the solution.

Next, let's take a look at sulfuric acid. This unique polyprotic acid is the only one to be completely deprotonated after the first step:

$$H_2SO_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HSO^-_{4(aq)}$$

Now let's try something a little harder. The ionization of phosphoric acid (three dissociation reactions this time) can be written like this:

Start with H_3PO_4:

$$K_{a1} : H_3PO_{4(aq)} \rightleftharpoons H^+_{(aq)} + H_2PO^-_{4(aq)}$$

$$K_{a2} : H_2PO^-_{4(aq)} \rightleftharpoons HPO_{4(aq)} + H^+_{(aq)}$$

$$K_{a3} : HPO^-_{4(aq)} \rightleftharpoons H^+_{(aq)} + PO^{3-}_{4(aq)}$$

So from *these* above reactions we can see that it takes three steps to fully remove the H$^+$ ion. This also means that this reaction will produce three equivalence points. **Polyprotic Bases** are bases that can *accept* at least one H$^+$ ion, or proton, in acid-base reactions.

Common Polyprotic Bases	Formula	Strong/Weak Base	Diprotic/Triprotic Base
Phosphate ion	PO_4^{3-}	Weak	Triprotic
Sulfate ion	SO_4^{2-}	Very Weak	Diprotic
Carbonate ion	CO_3^{2-}	Strong	Diprotic

Example 2: Some examples for calculating the constant, K_b

First, start with the reaction $A^{3-} + H_2O$? $HA^{2-} + OH^-$

$$K_{b1}= [OH^-][HA^{2-}]/[A^{3-}]=K_W/K_{a3}$$

Then, we plug in the products over the reactants:

$$HA^{2-} + H_2O \text{ ? } H_2A^- + OH^-$$

$$K_{b2} = [OH^-][H_2A^{2-}]/[HA^{2-}]=K_W/K_{a2}$$

Finally, we are left with the third dissociation, or K_{b3}:

$$H_2A^- + H_2O \text{ ? } H_3A + OH^-$$

$$K_{b3} = [OH^-][H_3A]/[H_2A^-]=K_W/K_{a1}$$

References

1. Petrucci, et al. General Chemistry: Principles & Modern Applications: AIE (Hardcover). Upper Saddle River: Pearson/Prentice Hall, 2007.

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7.8: Acid-Base Properties of Salts

Salts, when placed in water, will often react with the water to produce H_3O^+ or OH^-. This is known as a hydrolysis reaction. Based on how strong the ion acts as an acid or base, it will produce varying pH levels. When water and salts react, there are many possibilities due to the varying structures of salts. A salt can be made of either a weak acid and strong base, strong acid and weak base, a strong acid and strong base, or a weak acid and weak base. The reactants are composed of the salt and the water and the products side is composed of the conjugate base (from the acid of the reaction side) or the conjugate acid (from the base of the reaction side). In this section of chemistry, we discuss the pH values of salts based on several conditions.

When is a salt solution basic or acidic?

There are several guiding principles that summarize the outcome:

1. **Salts that are from strong bases and strong acids do not hydrolyze.** The pH will remain neutral at 7. Halides and alkaline metals dissociate and do not affect the H^+ as the cation does not alter the H^+ and the anion does not attract the H^+ from water. This is why NaCl is a neutral salt. **In General:** Salts containing halides (except F^-) and an alkaline metal (except Be^{2+}) will dissociate into spectator ions.
2. **Salts that are from strong bases and weak acids do hydrolyze, which gives it a pH greater than 7.** The anion in the salt is derived from a weak acid, most likely organic, and **will *accept* the proton from the water in the reaction. This will have the water act as an acid that will, in this case, leaving a hydroxide ion (OH^-)**. The cation will be from a strong base, meaning from either the alkaline or alkaline earth metals and, like before, it will dissociate into an ion and not affect the H^+.
3. **Salts of weak bases and strong acids do hydrolyze, which gives it a pH less than 7**. This is due to the fact that the anion will become a spectator ion and fail to attract the H^+, while the cation from the weak base will donate a *proton* to the water forming a hydronium ion.
4. **Salts from a weak base and weak acid also hydrolyze as the others, but a bit more complex and will require the K_a and K_b to be taken into account.** Whichever is the stronger acid will be the dominate factor in determining whether it is acidic or basic. The cation will be the acid, and the anion will be the base and will form either form a hydronium ion or a hydroxide ion depending on which ion reacts more readily with the water.

Salts of Polyprotic Acids

Do not be intimidated by the salts of polyprotic acids. Yes, they're bigger and "badder" then most other salts. But they can be handled the exact same way as other salts, just with a bit more math. First of all, we know a few things:

- It's still just a salt. All of the rules from above still apply. Luckily, since we're dealing with acids, the pH of a salt of polyprotic acid will always be greater than 7.
- The same way that polyprotic acids lose H^+ stepwise, salts of polyprotic acids gain H^+ in the same manner, but in reverse order of the polyprotic acid.

Take for example dissociation of $\mathrm{H_2CO_3}$, carbonic acid.

$$\mathrm{H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)}$$

with $K_{a1} = 2.5 \times 10^{-4}$

$$\mathrm{HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)}$$

with $K_{a2} = 5.61 \times 10^{-11}$.

> This means that when calculating the values for K_b of CO_3^{2-}, the K_b of the first hydrolysis reaction will be $K_{b1} = \dfrac{K_w}{K_{a2}}$ since it will go in the reverse order.

Summary of Acid Base Properties of Salts

Type of Solution	Cations	Anions	pH
Acidic	From weak bases NH_4^+, Al^{3+}, Fe^{3+}	From strong acids: Cl^-, Br^-, I^-, NO_3^-, ClO_4^-	**< 7**

Type of Solution	Cations	Anions	pH
Basic	From strong bases: Group 1 and Group 2, but not Be^{2+}	From weak acids: F$^-$, NO$_2^-$, CN$^-$, CH$_3$COO$^-$	> 7
Neutral	From strong bases: Group 1 and Group 2, but not Be^{2+}.	From strong acids: Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, ClO$_4^-$	= 7

Questions

1. Predict whether the pH of each of the following salts placed into water is acidic, basic, or neutral.
   a. $NaOCl_{(s)}$
   b. $KCN_{(s)}$
   c. $NH_4NO_{3(s)}$
2. Find the pH of a solution of .200 M NH_4NO_3 where ($K_a = 1.8 * 10^{-5}$).
3. Find the pH of a solution of .200 M Na_3PO_4 where ($K_{a1} = 7.25 * 10^{-5}$, $K_{a2} = 6.31 * 10^{-8}$, $K_{a3} = 3.98 * 10^{-3}$).

Answers

1

a. The ions present are Na^+ and OCl^- as shown by the following reaction:

$$NaOCl_{(s)} \rightarrow Na^+_{(aq)} + OCl^-_{(aq)}$$

While Na^+ will not hydrolyze, OCl^- will (remember that it is the conjugate base of HOCl). It acts as a base, accepting a proton from water.

$$OCl^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HOCl_{(aq)} + OH^-_{(aq)}$$

Na^+ is excluded from this reaction since it is a spectator ion.

Therefore, with the production of OH^-, it will cause a basic solution and raise the pH above 7.

$$pH > 7$$

b. The $KCN_{(s)}$ will dissociate into $K^+_{(aq)}$ and $CN^-_{(aq)}$ by the following reaction:

$$KCN_{(s)} \rightarrow K^+_{(aq)} + CN^-_{(aq)} \tag{7.8.1}$$

K^+ will not hydrolyze, but the CN^- anion will attract an H^+away from the water:

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)} \tag{7.8.2}$$

Because this reaction produces OH^-, the resulting solution will be basic and cause a pH>7.

$$pH > 7$$

c. The $NH_4NO_{3\,(s)}$ will dissociate into NH_4^+ and NO_3^- by the following reaction:

$$NH_4NO_{3(s)} \rightarrow NH^+_{4(aq)} + NO^-_{3(aq)} \tag{7.8.3}$$

Now, NO_3^- won't attract an H^+ because it is usually from a strong acid. This means the K_b will be very small. However, NH_4^+ will lose an electron and act as an acid (NH_4^+ is the conjugate acid of NH_3) by the following reaction:

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)} \tag{7.8.4}$$

This reaction produces a hydronium ion, making the solution acidic, lowering the pH below 7.

$$pH < 7$$

2. $NH^+_{4(aq)} + H_2O(l) \rightleftharpoons NH_{3(aq)} + H_3O_{(aq)}$

$$\frac{x^2}{0.2 - x} = \frac{1 * 10^{-14}}{1.8 \times 10^{-5}}$$

$$x = 1.05 * 10^-5M = [H_3O^+]$$

$$pH = 4.98$$

3. $PO^3-_{4(aq)} + H_2O_{(l)} \rightleftharpoons HPO^{2-}_{4(aq)} + OH^-_{(aq)}$

   The majority of the hydroxide ion will come from this first step. So only the first step will be completed here. To complete the other steps, follow the same manner of this calculation.

$$\frac{x^2}{0.2 - x} = \frac{1 * 10^-14}{3.98 \times 10{-}13} \tag{7.8.5}$$

$$x = 0.0594 = [OH^-] \tag{7.8.6}$$

$$pH = 12.77 \tag{7.8.7}$$

Practice Questions

1. Why does a salt containing a cation from a strong base and an anion from a weak acid form a basic solution?
2. Why does a salt containing a cation from a weak base and an anion from a strong acid form an acidic solution?
3. How do the K_a or K_b values help determine whether a weak acid or weak base will be the dominant driving force of a reaction?

The answers to these questions can be found in the attached files section at the bottom of the page.

References

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7.9: Acid Solutions that Water Contributes pH

Unlike strong acids/bases, weak acids and weak bases do not completely dissociate (separate into ions) at equilibrium in water, so calculating the pH of these solutions requires consideration of a unique ionization constant and equilibrium concentrations. Although this is more difficult than calculating the pH of a strong acid or base solution, most biochemically important acids and bases are considered weak, and so it is very useful to understand how to calculate the pH of these substances. The same basic method can be used to determine the pH of aqueous solutions of many different weak acids and bases.

Introduction

An aqueous solution of a weak acid or base contains both the protonated and unprotonated forms of the compound, so an ICE table can be made and used to plug in concentrations into an equilibrium constant expression. The ionization constant for the acid (K_a) or base (K_b) is a measure of how readily the acid donates protons or how readily a base accepts protons. Because you are calculating pH, you must solve for the unknown concentration of hydronium ions in solution at equilibrium.

The first step in calculating the pH of an aqueous solution of any weak acid or base is to notice whether the initial concentration is high or low relative to 10^{-7} M (the concentration of hydronium and hydroxide ions in water due to the autoionization of water). If the concentration of the acid or base is very close to or less than 10^{-7} M, then the solution is considered dilute and additional steps must be taken to calculate pH.

Weak Acids and Bases

You must first be familiar with equilibrium constant expressions and how to write them for a chemical reaction. Then, by making an ICE table, you can find unknown concentration values that can be plugged into this equilibrium expression.

✓ Example 7.9.1: Vinegar as a Weak Acid

What is the pH of 1.5 L of a vinegar that is 3% acetic acid by mass? (K_a = 1.8 x 10^{-5})

Solution

To start, you must find the initial concentration of acetic acid in the vinegar. Assume that the vinegar is really just a solution of acetic acid in water, and that density = 1 g/mL.

So if the vinegar is 3% acetic acid by mass and the molar mass of $HC_2H_3O_2$ = 60.05 g/mol, then

$$\frac{1.5L, vinegar}{} \times \frac{1000mL}{1L} \times \frac{1g}{1mL} \times \frac{3g, aceticacid}{100g, vinegar} \times \frac{1mol, aceticacid}{60.05g, aceticacid} = 0.75\ mol\ HC_2H_3O_2$$

Divide 0.75 mol by 1.5 L to get an initial concentration of 0.50 M.

Now make an ICE table, considering the ionization of acetic acid in water into acetate ion and hydronium ion. Because only solutes and gases are incorporated into the equilibrium expression, you can ignore the concentration of water (a pure liquid) in our calculations.

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \rightleftharpoons C_2H_3O^-_{2(aq)} + H_3O^+_{(aq)}$$

	$HC_2H_3O_2$	H_2O	$C_2H_3O_2^-$	H_3O^+
Initial	0.5	---	0	0
Change	-x	---	+x	+x
Equilibrium	0.5 - x	---	x	x

For every acetic acid molecule that dissociates, one acetate ion and one hydronium ion is produced. This can be represented by subtracting "x" from the original acetic acid concentration, and adding "x" to the original concentrations of the dissociated ions.

You can create a modified equilibrium constant expression

$$K_a = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]}$$

and then plug in the concentration values you found in the ICE table

$$1.8 \times 10^{-5} = \frac{x^2}{0.5 - x}$$

so

$$x^2 + (1.8 \times 10^{-5})x - (9 \times 10^{-6}) = 0$$

then use the quadratic formula to calculate

$$x = 0.0030\ M = [H_3O^+]$$

which can be plugged into the formula

$$pH = -\log[H_3O^+]$$

$$-\log(0.0030) = pH = 2.5$$

The same thing can be done for calculating the pH of a weak base.

✓ Example 7.9.2: Ammonia as a Weak Base

What is the pH of a 7.0×10^{-3} M NH_3 solution? (pK_b = 4.74)

Solution

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

	NH_3	H_2O	NH_4^+	OH^-
I	7.0×10^{-3}	---	0	0
C	-x	---	+x	+x
E	7.0×10^{-3} - x	---	x	x

Instead of K_b, you were given pK_b. So to get K_b

$$pK_b = -\log(K_b) = 4.74$$

$$K_b = 10^{-4.74} = 1.8 \times 10^{-5}$$

Plug these values into the equilibrium expression to get

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{x^2}{7 \times 10^{-3} - x}$$

and use the quadratic formula to find that

$$x = 3.46 \times 10^{-4}\ M = [OH^-]$$

so

$$pOH = -\log(3.46 \times 10^{-4}) = 3.46$$

and in water at 25 degrees

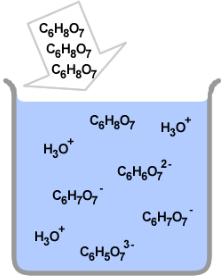
$$pH + pOH = 14$$

Hence:

$$14 - 3.46 = pH = 10.54$$

Weak Polyprotic Acids and Bases

Polyprotic acids have more than one proton to donate to water, and so they have more than one ionization constant (K_{a1}, K_{a2}, etc) that can be considered. Polyprotic bases take more than one proton from water, and also have more than one ionization constant (K_{b1}, K_{b2}, etc).



Dissociation of citric acid in water, showing all conjugate bases from each of the three dissociation steps.

Most often the first proton exchange is the only one that considerably affects pH. This is discussed more at the end of the first example.

✓ Example 7.9.3: Citric Acid as a Polyprotic Acid

What is the pH of a grapefruit that contains 0.007 M citric acid solution ($C_6H_8O_7$)?
(K_{a1} = 7.5 x 10^{-4}, K_{a2} = 1.7 x 10^{-5}, K_{a3} = 4.0 x 10^{-7})

Solution

Make an ICE table for the first dissociation

$$C_6H_8O_{7(aq)} + H_2O_{(l)} \rightleftharpoons C_6H_7O_7^- + H_3O^+_{(aq)}$$

	$C_6H_8O_7$	H_2O	$C_6H_7O_7^-$	H_3O^+
I	0.007	---	0	0
C	-x	---	+x	+x
E	0.007 - x	---	x	x

$$K_{a1} = \frac{[C_6H_7O_7^-][H_3O^+]}{[C_6H_8O_7]} = 7.5 \times 10^{-4} = \frac{x^2}{0.007 - x}$$

and use the quadratic formula to find that

$$x = 0.00195\ M = [H_3O^+]$$

Then a second ICE table can be made for the second dissociation

$$C_6H_7O^-_{7(aq)} + H_2O_{(l)} \rightleftharpoons C_6H_6O_7^{2-} + H_3O^+_{(aq)}$$

	$C_6H_7O_7^-$	H_2O	$C_6H_6O_7^{2-}$	H_3O^+
I	0.00195	---	0	0.00195
C	-x	---	+x	+x
E	0.00195 - x	---	x	0.00195 + x

Remember that, for the first dissociation, x = $[H_3O^+]$ = $[C_6H_7O_7^-]$, so you can plug in the first value of x in for the initial concentrations of $C_6H_7O_7^-$ and H_3O^+.

$$K_{a2} = \frac{[C_6H_6O_7^{2-}][H_3O^+]}{[C_6H_7O_7^-]} = 1.7 \times 10^{-5} = \frac{(x)(0.00195+x)}{0.00195-x}$$

and use the quadratic formula to find that

$$x = 1.67 \times 10^{-5}$$

$$[H_3O^+] = 0.00195 + 1.67 \times 10^{-5} = 0.00197\ M$$

$$-\log(0.00197) = pH = 2.71$$

Note that if you ignored the addition of hydronium from the second dissociation, then [H_3O^+] = 0.00195 M, and using this value to calculate pH still gives you the answer of 2.71.

So even though you made two ICE tables (you could even make a third table for K_{a3}), the protons donated in the second dissociation were negligible compared to the first dissociation. So you can see that it is really only the first dissociation that affects pH. Most often this is the case, and only one ICE table is necessary. It is up to you how certain you want to be and how many ICE tables you want to make when you calculate these problems.

✓ Example 7.9.4: Soda Ash as a Polyprotic Base

What is the pH of a saturated solution of sodium carbonate (Na_2CO_3)?
(solubility in water is 21.6 g/100mL at room temperature and for carbonic acid, H_2CO_3, K_{a1} = 4.5 x 10^{-7}, K_{a2} = 4.7 x 10^{-11}

Solution

First, you have to find the find the initial concentration of CO_3^{2-} which can be found from

$$\frac{21.6g, Na_2CO_3}{} \times \frac{1\ mol}{105.99\ g} = 0.204\ mol\ Na_2CO_3 = 0.204\ mol\ CO_3^{2-}$$

then divide 0.204 mol by 0.100 L to get 2.04 M CO_3^{2-}

Plug into an ICE table

$$CO^{2-}_{3(aq)} + H_2O_{(l)} \rightleftharpoons HCO^-_{3(aq)} + OH^-_{(aq)}$$

	CO_3^{2-}	H_2O	HCO_3^-	OH^-
I	2.04	---	0	0
C	-x	---	+x	+x
E	2.04 - x	---	x	x

But notice that the equilibrium constants are for carbonic acid. If you were considering the dissociation of carbonic acid, you would write the following expressions

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

for

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = 4.7 \times 10^{-11}$$

for

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

The second acid ionization constant corresponds to the first base ionization constant (because the base reactions go backwards). To convert the second acid ionization constant to the first base ionization constant, you use the equation

$$K_a \times K_b = K_w = 10^{-14}$$

so that

$$K_{a2} \times K_{b1} = 10^{-14}$$

$$K_{b1} = \frac{10^{-14}}{4.7 \times 10^{-11}} = 2.13 \times 10^{-4}$$

Use the same equation to convert the first acid ionization constant to the second base ionization constant

$$K_{a1} \times K_{b2} = 10^{-14}$$

$$K_{b2} = \frac{10^{-14}}{4.5 \times 10^{-7}} = 2.22 \times 10^{-8}$$

The expressions for the protonation of carbonate are now known to be

$$K_{b1} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.13 \times 10^{-4}$$

for

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$K_{b2} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = 2.22 \times 10^{-8}$$

for

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

Plug the ICE tables values into the first equilibrium expression

$$K_{b1} = \frac{x^2}{2.04 - x} = 2.13 \times 10^{-4}$$

and use the quadratic formula to solve

$$x = 0.0207\ M = [OH^-]$$

You can ignore the second base ionization constant because it removes a negligible amount of protons from water. If you want to test this by making an ICE table, you should get that the total hydroxide concentration is 0.0207000222 M \approx 0.0207 M

so pOH = -log(0.0207) = 1.68

pH + pOH = 14
14 - 1.68 = **pH = 12.32**

Dilute Weak Acids and Bases

'Dilute' refers to the concentration of the acid or base in water. If the concentration is close to or below 10^{-7} M, then you must consider the donation of hydronium ions from water as well as from your acid or base. This is done by making an ICE table to find the protonation of the acid or base, while also incorporating the ion product of water.

✓ Example 7.9.5: Dilute Weak Acid

An average bee sting contains 5 micrograms of formic acid (HCO_2H). What is the pH of a 500 mL solution of formic acid? (pK_a = 3.75)

Solution

First calculate the number of moles of formic acid was excreted.

$$\frac{5.00\mu g}{} \times \frac{1g}{10^6\mu g} \times \frac{1\ mol, HCO_2H}{46.03g, HCO_2H} = 1.09 \times 10^{-7} mol, HCO_2H$$

$$\frac{1.09 \times 10^{-7} mol}{0.500L} = 2.17 \times 10^{-7}\ M$$

$$HCO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons CO_2H^-_{(aq)} + H_3O^+_{(aq)}$$

	HCO_2H	H_2O	CO_2H^-	H_3O^+
I	2.17×10^{-7}	---	0	0
C	$-x$	---	+x	+x
E	$2.17 \times 10^{-7} - x$	---	x	x

A second ICE table can be made for the autoionization of water

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

	$2H_2O$	H_3O^+	OH^-
I	---	0	0
C	---	+y	+y
E	---	y	y

Notice that total $[H_3O^+]$ = x + y

$$pK_a = 3.75$$

$$K_a = 10^{-3.75} = 1.78 \times 10^{-4}$$

So you can simultaneously solve both equations

$$K_a = \frac{[CO_2H^-][H_3O^+]}{[HCO_2H]} = \frac{x(x+y)}{2.17 \times 10^{-7} - x} = 1.78 \times 10^{-4}$$

and

$$K_w = [H_3O^+][OH^-] = (x+y)(y) = 10^{-14}$$

These calculations can be tricky, and it is very easy to make mistakes. It is usually easier to use variables to solve these problems instead of handling awkward numbers.

For this problem use

- a = K_a = 1.78×10^{-4}
- c = initial $[HCO_2H]$ = 2.17×10^{-7}
- w = K_w = 10^{-14}

$$a = \frac{x(x+y)}{c-x}$$

and

$$(x+y)(y) = w$$

$$ac - ax = x^2 + xy$$

and

$$x = \frac{w}{y} - y$$

$$ac - a\left(\frac{w}{y} - y\right) = \left(\frac{w}{y} - y\right)^2 + \left(\frac{w}{y} - y\right)y$$

$$ac - \frac{aw}{y} + ay = \frac{w^2}{y^2} - \frac{2wy}{y} + y^2 + \frac{wy}{y} - y^2$$

$$ac - \frac{aw}{y} + ay = \frac{w^2}{y^2} - 2w + y^2 + w - y^2$$

$$ac - \frac{aw}{y} + ay = \frac{w^2}{y^2} - w$$

$$ac - \frac{aw}{y} + ay + w = \frac{w^2}{y^2}$$

$$acy^2 - awy + ay^3 + wy^2 = w^2$$

$$ay^3 + (ac + w)y^2 - awy - w^2 = 0$$

so when we plug back in the values

$$(1.78 \times 10^{-4})y^3 + ((1.78 \times 10^{-4})(2.17 \times 10^{-7}) + (10^{-14}))y^2 - (1.78 \times 10^{-4})(10^{-14})y - (10^{-14})^2 = 0$$

$$(1.78 \times 10^{-4})y^3 + (3.86 \times 10^{-11})y^2 - (1.78 \times 10^{-18})y - 10^{-28} = 0$$

and use a graphing calculator to find that

$$y = 3.91 \times 10^{-8}$$

and

$$x = \frac{w}{y} - y = \frac{10^{-14}}{3.91 \times 10^{-8}} - 3.91 \times 10^{-8} = 2.17 \times 10^{-7}$$

and total

$$[H_3O^+] = (x + y) = (2.17 \times 10^{-7} + 3.91 \times 10^{-8}) = 2.56 \times 10^{-7}\ M$$

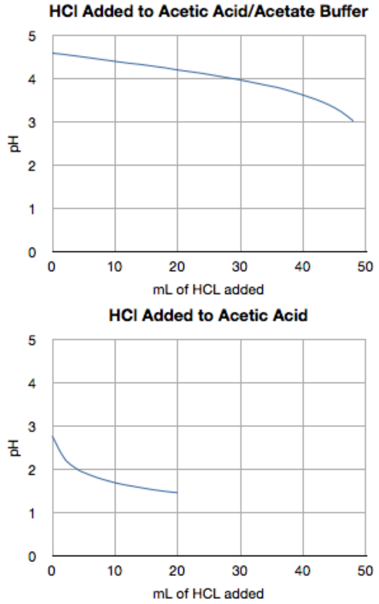
so

$$-\log[H_3O^+] = -\log(2.56 \times 10^{-7}) = pH = 6.59$$

Compare this value to pH = 6.66, which is what would have been calculated if the autoprotonization of water was not considered.

Buffer Solutions

Buffer solutions resist pH change when more acid or base is added. They are made from a weak acid and its conjugate base or a weak base and its conjugate acid. The Henderson-Hasselbalch approximation can be used to find the pH of a buffer solution, and is derived from the acid equilibrium expression.



Almost 50 mL of HCl was required to decrease the pH of an acetic acid/acetate buffer solution by about 1.5, but only 20 mL of HCl to decrease a pure acetic acid solution by the same amount.

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)}$$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

$$\log(K_a) = log\left(\frac{[A^-][H_3O^+]}{[HA]}\right)$$

$$\log(K_a) = \log[H_3O^+] + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$-pK_a = -pH + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

A similar equation can be used for bases

$$pOH = pK_b + \log\left(\frac{[HB^+]}{[B]}\right)$$

✓ Example 7.9.6: Blood

The pH of blood plasma is 7.40, and is maintained by a carbonic acid/hydrogen carbonate buffer system. What mass of sodium bicarbonate ($NaHCO_3$) should be added to a one liter solution of 0.250 M H_2CO_3 to maintain the solution at pH of 7.40? (pKa = 6.35)

Solution

$$pH = pK_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$7.40 = 6.35 + \log\left(\frac{[HCO_3^-]}{[0.250]}\right)$$

$$1.05 = \log[HCO_3^-] - \log(0.250)$$

$$0.448 = \log[HCO_3^-]$$

$$[HCO_3^-] = 0.356\ M$$

$$(0.356\ M) \times (1\ L\ solution) = 0.356\ mol\ HCO_3^-$$

$$[0.356 mol\, HCO_3^- \times \frac{1 mol\, NaHCO_3}{1 mol\, HCO_3^-} \times \frac{84.01 g}{1 mol, NaHCO_3} = 29.9 g \text{sodium bicarbonate}$$

It is also possible to use the Henderson-Hasselbalch equation to find pK$_a$, pH, or [HA] if the other variables are given or calculated. Also notice that because $\frac{[A^-]}{[HA]}$ will cancel out the unit of volume, moles of HA and A^- can be used instead of molarity.

References

1. *CRC Handbook of Chemistry and Physics*, 91st ed.; CRC Press: Boca Raton, FL., 2010.
2. *Merck Index*, 12th ed.; Merck & Co.: Whitehouse Station, NJ., 1996.

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7.10: Strong Acid Solutions that Water Contributes pH

Oxides are chemical compounds with one or more oxygen atoms combined with another element (e.g. Li_2O). Oxides are binary compounds of oxygen with another element, e.g., CO_2, SO_2, CaO, CO, ZnO, BaO_2, H_2O, etc. These are termed as oxides because here, oxygen is in combination with only one element. Based on their acid-base characteristics oxides are classified as acidic, basic, amphoteric or neutral:

1. An oxide that combines with water to give an acid is termed as an acidic oxide.
2. The oxide that gives a base in water is known as a basic oxide.
3. An amphoteric solution is a substance that can chemically react as either acid or base.
4. However, it is also possible for an oxide to be neither acidic nor basic, but is a neutral oxide.

There are different properties which help distinguish between the three types of oxides. The term **anhydride** ("without water") refers to compounds that assimilate H_2O to form either an acid or a base upon the addition of water.

Acidic Oxides

Acidic oxides are the oxides of non-metals (Groups 14-17) and these **acid anhydrides** form acids with water:

- Sulfurous Acid

$$\mathrm{SO_2 + H_2O \rightarrow H_2SO_3} \tag{7.10.1}$$

- Sulfuric Acid

$$\mathrm{SO_3 + H_2O \rightarrow H_2SO_4} \tag{7.10.2}$$

- Carbonic Acid

$$\mathrm{CO_2 + H_2O \rightarrow H_2CO_3} \tag{7.10.3}$$

Acidic oxides are known as acid anhydrides (e.g., sulfur dioxide is sulfurous anhydride and sulfur trioxide is sulfuric anhydride) and when combined with bases, they produce salts, e.g.,

$$\mathrm{SO_2 + 2\,NaOH \rightarrow Na_2SO_3 + H_2O} \tag{7.10.4}$$

Basic Oxides

Generally Group 1 and Group 2 elements form bases called base anhydrides or basic oxides e.g.,

$$\mathrm{K_2O\ (s) + H_2O\ (l) \rightarrow 2\,KOH\ (aq)} \tag{7.10.5}$$

Basic oxides are the oxides of metals. If soluble in water, they react with water to produce hydroxides (alkalies) e.g.,

$$\mathrm{CaO + H_2O \rightarrow Ca(OH)_2} \tag{7.10.6}$$

$$\mathrm{MgO + H_2O \rightarrow Mg(OH)_2} \tag{7.10.7}$$

$$\mathrm{Na_2O + H_2O \rightarrow 2\,NaOH} \tag{7.10.8}$$

These metallic oxides are known as basic anhydrides. They react with acids to produce salts, e.g.,

$$\mathrm{MgO + 2\,HCl \rightarrow MgCl_2 + H_2O} \tag{7.10.9}$$

$$\mathrm{Na_2O + H_2SO_4 \rightarrow Na_2SO_4 + H_2O} \tag{7.10.10}$$

Amphoteric Oxides

An amphoteric solution is a substance that can chemically react as either acid or base. For example, when HSO_4^- reacts with water it will make both hydroxide and hydronium ions:

$$HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+ \tag{7.10.11}$$

$$HSO_4^- + H_2O \rightarrow H_2SO_4 + OH^- \tag{7.10.12}$$

Amphoteric oxides exhibit both basic as well as acidic properties. When they react with an acid, they produce salt and water, showing basic properties. While reacting with alkalies they form salt and water showing acidic properties.

- For example ZnO exhibits basic behavior with HCl

$$ZnO + 2HCl \rightarrow \underset{zinc\ chloride}{ZnCl_2} + H_2O\,(basic\ nature) \tag{7.10.13}$$

- and acidic behavior with $NaOH$

$$ZnO + 2NaOH \rightarrow \underset{sodium\ zincate}{Na_2ZnO_2} + H_2O\,(acidic\ nature) \tag{7.10.14}$$

- Similarly, Al_2O_3 exhibits basic behavior with H_2SO_4

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O\,(basic\ nature) \tag{7.10.15}$$

- and acidic behavior with $NaOH$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O\,(acidic\ nature) \tag{7.10.16}$$

Neutral Oxides

Neutral oxides show neither basic nor acidic properties and hence do not form salts when reacted with acids or bases, e.g., carbon monoxide (CO); nitrous oxide (N_2O); nitric oxide (NO), etc., are neutral oxides.

Peroxides and Dioxides

Oxides: Group 1 metals react rapidly with oxygen to produce several different ionic oxides, usually in the form of M_2O. With the oyxgen exhibiting an oxidation number of -2.

$$4Li + O_2 \rightarrow 2Li_2O \tag{7.10.17}$$

Peroxides: Often Lithium and Sodium reacts with **excess** oxygen to produce the peroxide, M_2O_2. with the oxidation number of the oxygen equal to -1.

$$H_2 + O_2 \rightarrow H_2O_2 \tag{7.10.18}$$

Superoxides: Often Potassium, Rubidium, and Cesium react with excess oxygen to produce the superoxide, MO_2. with the oxidation number of the oxygen equal to -1/2.

$$Cs + O_2 \rightarrow CsO_2 \tag{7.10.19}$$

A peroxide is a metallic oxide which gives hydrogen peroxide by the action of dilute acids. They contain more oxygen than the corresponding basic oxide, e.g., sodium, calcium and barium peroxides.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2 \tag{7.10.20}$$

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2 \tag{7.10.21}$$

Dioxides like PbO_2 and MnO_2 also contain higher percentage of oxygen like peroxides and have similar molecular formulae. These oxides, however, do not give hydrogen peroxide by action with dilute acids. Dioxides on reaction with concentrated HCl yield Cl_2 and on reacting with concentrated H_2SO_4 yield O_2.

$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O \tag{7.10.22}$$

$$2PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O + O_2 \tag{7.10.23}$$

Compound Oxides

Compound oxides are metallic oxides that behave as if they are made up of two oxides, one that has a lower oxidation and one with a higher oxidation of the same metal, e.g.,

$$\text{Red lead: } Pb_3O_4 = PbO_2 + 2PbO \tag{7.10.24}$$

$$\text{Ferro-ferric oxide: } Fe_3O_4 = Fe_2O_3 + FeO \tag{7.10.25}$$

On treatment with an acid, compound oxides give a mixture of salts.

$$\underset{\text{Ferro-ferric oxide}}{Fe_3O_4} + 8HCl \rightarrow \underset{\text{ferric chloride}}{2FeCl_3} + \underset{\text{ferrous chloride}}{FeCl_2} + 4H_2O \tag{7.10.26}$$

Preparation of Oxides

Oxides can be generated via multiple reactions. Below are a few.

By direct heating of an element with oxygen: Many metals and non-metals burn rapidly when heated in oxygen or air, producing their oxides, e.g.,

$$2Mg + O_2 \xrightarrow{Heat} 2MgO$$

$$2Ca + O_2 \xrightarrow{Heat} 2CaO$$

$$S + O_2 \xrightarrow{Heat} SO_2$$

$$P_4 + 5O_2 \xrightarrow{Heat} 2P_2O_5$$

By reaction of oxygen with compounds at higher temperatures: At higher temperatures, oxygen also reacts with many compounds forming oxides, e.g.,

- sulfides are usually oxidized when heated with oxygen.

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$$

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

- When heated with oxygen, compounds containing carbon and hydrogen are oxidized.

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

- By thermal decomposition of certain compounds like hydroxides, carbonates, and nitrates

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$$

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$$

By oxidation of some metals with nitric acid

$$2Cu + 8HNO_3 \xrightarrow{Heat} 2CuO + 8NO_2 + 4H_2O + O_2$$

$$Sn + 4HNO_3 \xrightarrow{Heat} SnO_2 + 4NO_2 + 2H_2O$$

By oxidation of some non-metals with nitric acid

$$C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O$$

Trends in Acid-Base Behavior

The oxides of elements in a period become progressively more acidic as one goes from left to right in a period of the periodic table. For example, in third period, the behavior of oxides changes as follows:

$$\underbrace{Na_2O,\ MgO}_{Basic}\quad \underbrace{Al_2O_3,\ SiO_2}_{Amphoteric}\quad \underbrace{P_4O_{10},\ SO_3,\ Cl_2O_7}_{Acidic}$$

If we take a closer look at a specific period, we may better understand the acid-base properties of oxides. It may also help to examine the physical properties of oxides, but it is not necessary. Metal oxides on the left side of the periodic table produce basic solutions in water (e.g. Na_2O and MgO). Non-metal oxides on the right side of the periodic table produce acidic solutions (e.g.

Cl_2O, SO_2, P_4O_{10}). There is a trend within acid-base behavior: basic oxides are present on the left side of the period and acidic oxides are found on the right side.

Aluminum oxide shows acid and basic properties of an oxide, it is amphoteric. Thus Al_2O_3 entails the marking point at which a change over from a basic oxide to acidic oxide occurs. It is important to remember that the trend only applies for oxides in their highest oxidation states. The individual element must be in its highest possible oxidation state because the trend does not follow if all oxidation states are included. Notice how the amphoteric oxides (shown in blue) of each period signify the change from basic to acidic oxides,

Groups

1	2	3	14	15	16	17
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	Ga	Ge	As	Se	Br
Rb	Sr	In	Sn	Sb	Te	I
Cs	Ba	Tl	Pb	Bi	Po	At

The figure above show oxides of the *s*- and *p-block* elements.
purple: basic oxides blue: amphoteric oxides pink: acidic oxides

Problems

1. Can an oxide be neither acidic nor basic?
2. $Rb + O_2\ (excess) \rightarrow ?$
3. $Na + O_2 \rightarrow ?$
4. BaO_2 is which of the following: hydroxide, peroxide, or superoxide?
5. What is an amphoteric solution?
6. Why is it difficult to obtain oxygen directly from water?

Solutions

1. Yes, an example is carbon monoxide (CO). CO doesn't produce a salt when reacted with an acid or a base.
2. $Rb + O_2\ (excess) \rightarrow RbO_2$
   With the presence of excess oxygen, Rubidium forms a superoxide. Please review section regarding basic oxides above for more detail.
3. $2Na + O_2 \rightarrow Na_2O$
   Note: The problem does not specify that the oxygen was in excess, so it cannot be a peroxide. Please review section regarding basic oxides for more detail.
4. BaO_2 is a peroxide. Barium has an oxidation state of +2 so the oxygen atoms have oxidation state of -1. As a result, the compound is a peroxide, but more specifically referred to as barium peroxide.
5. An amphoteric solution is a substance that can chemically react as either acid or base. See section above on Properties of Amphoteric Oxides for more detail.
6. Water as such is a neutral stable molecule. It is difficult to break the covalent O-H bonds easily. Hence, electrical energy through the electrolysis process is applied to separate dioxygen from water. When a small amount of acid is added to water ionization is initiated which helps in electrochemical reactions as follows.

$$[H_2O\ (acidulated) \rightleftharpoons H^+\ (aq) + OH]^- \times 4$$

At cathode:

$$[H^+\ (aq) + e^- \rightarrow \frac{1}{2} H_2(g)] \times 4$$

At anode:

$$4OH^-\ (aq) \rightarrow O_2 + 2H_2O + 4e^-$$

Net reaction:

$$2H_2O \xrightarrow{electrolysis} 2H_2\,(g) + O_2\,(g)$$

Oxygen can thus be obtained from acidified water by its electrolysis.

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SECTION OVERVIEW

7.11: Approaches to Solve Acid-Base Problems

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8: Equilibria in Aqueous Solutions

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SECTION OVERVIEW

16.1 Spontaneous Processes and Entropy

The concept of an ideal solution is fundamental to chemical thermodynamics and its applications, such as the use of colligative properties. An **ideal solution** or ideal mixture is a solution in which the enthalpy of solution ($\Delta H_{solution} = 0$) is zero; with the closer to zero the enthalpy of solution, the more "ideal" the behavior of the solution becomes. Since the enthalpy of mixing (solution) is zero, the change in Gibbs energy on mixing is determined solely by the entropy of mixing ($\Delta S_{solution}$).

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16.2 Entropy and the Second Law of Thermodynamics

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16.4 Free Energy

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A **coordination compound** or **complex ion** is a molecule that contains a central metal ion to which are attached one or more **ligands**. In many complexes there is more than one way in which the ligands may be attached to or arranged around the metal center. **Isomers** are compounds that have the same molecular formula but possess different arrangements of atoms. Two isomers are **non-superimposable**, which means that one cannot mentally have the two compounds occur the same space with each atom in one isomer perfectly coinciding with the same atom in the other isomer.

The scheme and definitions provided below are commonly used to classify coordination chemistry isomers. A compound can exhibit multiple types of isomerism.

Isomerization in Coordination Compounds

Structural Isomers

The atoms are connected in different ways in structural isomers. Thus there is a difference in chemical bonding. Structural isomers possess different physical properties and chemical reactivities.

- **Coordination Isomers or Ionization Isomerism**
    - *Coordination isomers* yield different ions in solutions, because some ions are bound to the metal as ligands and some ions serve as counter-ions and are free to move about the solution.
- **Linkage Isomers**
    - When a ligand has multiple Lewis base sites, different sites (atoms) on the ligand can bond to the metal and linkage isomers exist. For example: oxalate and nitrate ligands.

Stereoisomers

Stereoisomers have the same connectivity of atoms (bonding), but the spatial arrangement of atoms differs.

- **Diastereomers or Geometric Isomers**
    - *Diastereomers* are non-mirror-image molecules that have the same chemical bonding but different spatial arrangements of atoms.
    - *cis/trans isomers*: The Latin words cis and trans mean "next to" and "across", respectively. This type of geometric isomerism involves a distintive pair of ligands that can either be next to each other (cis isomer) or on opposite sides of the molecule (trans isomer).
    - *fac/mer isomers*: In complexes with coordination numbers of five or greater containing three distinctive ligands, all three distintive ligands may lie on the same triangular face of the octahedral (fac or facial isomer) or on a plane bisecting the complex (mer or meridional isomer).
- **Enantiomers or Optical Isomers**
    - *Mirror-image molecules* that cannot be superimposed on each other are called enantiomers. That is, the mirror image of an isomer is not identical to itself. Such molecules are called **chiral** and are identified by their handedness: **?** (the right-handed isomer) and **?** (the left-handed isomer). Enantiomers possess identical physical properties. Their chemical properties are also identical, except in a chiral reaction environment.
    - *A chiral molecule* will rotate the plane of polarized light passing through the solution. The enantiomer that rotates the polarized light clockwise is denoted with **+** while the enantiomer that rotates the polarized light counterclockwise is denoted with **-**. Whether the ? or ? rotates the polarized light clockwise often depends upon the wavelength of light. A 50/50 mixture of ? and ? isomers is called a **racemic mixture** and does not rotate the plane of polarized light passing through the solution.

Compounds

● $[Cu(gly)_2]$
○ $[Co(en)_2Cl_2]^+$
○ $[CoCl_2Br_2]^{2-}$
○ $[Cr(py)(OH)(CN)Cl]$
○ $[Co(NH_3)_4Cl_2]^+$
○ $[Cr(H_2O)_4Cl_2]Cl.2H_2O$
○ $[Ru(pa)_3]^{2+}$
○ $[Pt(bpy)(SCN)_2]$
○ $[Ru(tpm)Cl_3]$

Ball and Stick | Show Answer

Exercise

Choose one of the coordination compounds from the list below. Carefully examine the chemical structure and answer the following questions.

- Does the complex have isomeric forms?
- If multiple isomers exist, draw their structures and identify the type(s) of isomerization.
- Write the chemical name of the complex.
- When isomers exist, do the isomers have identical physical properties and chemical reactivities?

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16.5 Entropy Changes in Chemical Reactions

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16.6 Free Energy and Chemical Reactions

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16.7 The Dependence of Free Energy on Pressure

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16.8 Free Energy and Equilibrium

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Index

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    - 2.8: An Introduction to the Periodic Table - *CC BY-NC-SA 4.0*
    - 2.9: Nomenclature of Simple Compounds - *CC BY-NC-SA 4.0*
  - 3: Stoichiometry - *CC BY-NC-SA 4.0*
    - 3.1: Atomic Mass - *CC BY-NC-SA 4.0*
    - 3.2: The Mole - *CC BY-NC-SA 4.0*
    - 3.3: Molar Mass - *CC BY-NC-SA 4.0*
    - 3.4: Problem Solving Exercises - *CC BY-NC-SA 4.0*
    - 3.5 Percent Composition of Compounds - *CC BY-NC-SA 4.0*
    - 3.6 Determining the Formula of a Compound - *CC BY-NC-SA 4.0*
    - 3.7 Chemical Equations - *CC BY-NC-SA 4.0*
    - 3.8 Balancing Chemical Equations - *CC BY-NC-SA 4.0*
    - 3.9 Stoichiometric Calculations: Amounts of Reactants and Products - *CC BY-NC-SA 4.0*
    - 3.10: Calculations Involving a Limiting Reactant - *CC BY-NC-SA 4.0*
    - 3.11: Complex Problem Solving Approaches - *CC BY-NC-SA 4.0*
  - 4: Chemical Reactions - *CC BY-NC-SA 4.0*
    - 4.1: Water, the Universal Solvent - *CC BY-NC-SA 4.0*
    - 4.2: Strong and Weak Electrolytes - *CC BY-NC-SA 4.0*
    - 4.3: The Composition of Solutions - *CC BY-NC-SA 4.0*
    - 4.4: Types of Chemical Reactions - *CC BY-NC-SA 4.0*
    - 4.5: Precipitation Reactions - *CC BY-NC-SA 4.0*
    - 4.6: Reactions in Solution - *CC BY-NC-SA 4.0*
    - 4.7: Selective Precipitation - *CC BY-NC-SA 4.0*
    - 4.8: Stoichiometry of Precipitation Reactions - *CC BY-NC-SA 4.0*
    - 4.9: Acid-Base Reactions - *CC BY-NC-SA 4.0*
    - 4.10: Oxidation-Reduction Reactions - *CC BY-NC-SA 4.0*
    - 4.11: Balancing Redox Equations - *CC BY-NC-SA 4.0*
    - 4.12: Redox Titrations - *CC BY-NC-SA 4.0*
  - 5: Gases - *CC BY-NC-SA 4.0*
    - 5.1: Early Efforts to Understand Gases - *CC BY-NC-SA 4.0*
    - 5.2: The Gas Laws of Boyle, Charles, and Avogadro - *CC BY-NC-SA 4.0*
    - 5.3: The Ideal Gas Law - *CC BY-NC-SA 4.0*

    - 15.3: Determining the Form of the Rate Law - *CC BY-NC-SA 4.0*
    - 15.4: The Integrated Rate Law - *CC BY-NC-SA 4.0*
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    - 15.7: The Steady-State Approximation - *CC BY-NC-SA 4.0*
    - 15.8: A Model for Chemical Kinetics - *CC BY-NC-SA 4.0*
    - 15.9: Catalysis - *CC BY-NC-SA 4.0*
  - 16: Liquids and Solids - *CC BY-NC-SA 4.0*
    - 16.1: Intermolecular Forces - *CC BY-NC-SA 4.0*
    - 16.2: The Liquid State - *CC BY-NC-SA 4.0*
    - 16.3: An Introduction to Structures and Types of Solids - *CC BY-NC-SA 4.0*
    - 16.4: Structure and Bonding in Metals - *CC BY-NC-SA 4.0*
    - 16.5: Carbon and Silicon: Network Atomic Solids - *CC BY-NC-SA 4.0*
    - 16.6: Molecular Solids - *CC BY-NC-SA 4.0*
    - 16.7: Ionic Solids - *CC BY-NC-SA 4.0*
    - 16.8: Structures of Ionic Solids - *CC BY-NC-SA 4.0*
    - 16.9: Lattice Defects - *CC BY-NC-SA 4.0*
    - 16.10: Vapor Pressure and Changes of State - *CC BY-NC-SA 4.0*
    - 16.11: Phase Diagrams - *CC BY-NC-SA 4.0*
    - 16.12: Nanotechnology - *CC BY-NC-SA 4.0*
    - 16.E: Exercises - *CC BY-NC-SA 4.0*
  - 17: Solutions - *CC BY-NC-SA 4.0*
    - 17.1: Solution Composition - *CC BY-NC-SA 4.0*
    - 17.2: The Energies of Solution Formation - *CC BY-NC-SA 4.0*
    - 17.3: Factors Affecting Solubility - *CC BY-NC-SA 4.0*
    - 17.4: The Vapor Pressures of Solutions - *CC BY-NC-SA 4.0*
    - 17.5: Boiling-Point Elevation and Freezing-Point Depression - *CC BY-NC-SA 4.0*
    - 17.7: Colligative Properties of Electrolyte Solutions - *CC BY-NC-SA 4.0*
    - 17.7: Osmotic Pressure - *CC BY-NC-SA 4.0*
    - 17.8: Colloids - *CC BY-NC-SA 4.0*
  - 18: The Representative Elements - *CC BY-NC-SA 4.0*
    - 18.1: A Survey of the Representative Elements - *CC BY-NC-SA 4.0*
    - 18.2: Group 1A Metals - *CC BY-NC-SA 4.0*
    - 18.3: The Chemistry of Hydrogen - *CC BY-NC-SA 4.0*
    - 18.4: Group 2A Elements - *CC BY-NC-SA 4.0*
    - 18.5: Group 3A Elements - *CC BY-NC-SA 4.0*
    - 18.6: Group 4A Elements - *CC BY-NC-SA 4.0*
    - 18.7: The Group 5A Elements - *CC BY-NC-SA 4.0*
    - 18.8: The Chemistry of Nitrogen - *CC BY-NC-SA 4.0*
    - 18.9: The Chemistry of Phosphorus - *CC BY-NC-SA 4.0*
    - 18.10: The Group 6A Elements - *CC BY-NC-SA 4.0*
    - 18.11: The Chemistry of Oxygen - *CC BY-NC-SA 4.0*
    - 18.12: The Chemistry of Sulfur - *CC BY-NC-SA 4.0*
    - 18.13: The Group 7A Elements - *CC BY-NC-SA 4.0*
    - 18.14: The Group 8A Elements - *CC BY-NC-SA 4.0*
  - 19: Transition Metals and Coordination Chemistry - *CC BY-NC-SA 4.0*
    - 19.1: The Transition Metals: A Survey - *CC BY-NC-SA 4.0*
    - 19.2: The First-Row Transition Metals - *CC BY-NC-SA 4.0*
    - 19.3: Coordination Compounds - *CC BY-NC-SA 4.0*
    - 19.4: Isomerism - *CC BY-NC-SA 4.0*
    - 19.5: Bonding in Complex Ions - *CC BY-NC-SA 4.0*
    - 19.6: The Crystal Field Model - *CC BY-NC-SA 4.0*
    - 19.7: Molecular Orbital Model - *CC BY-NC-SA 4.0*
    - 19.8: The Biologic Importance of Coordination Complexes - *CC BY-NC-SA 4.0*
  - 20: The Nucleus A Chemists View - *CC BY-NC-SA 4.0*
    - 20.1: Nuclear Stability and Radioactive Decay - *CC BY-NC-SA 4.0*
    - 20.2: Radioactive Kinetics - *CC BY-NC-SA 4.0*
    - 20.3: Nuclear Transformations - *CC BY-NC-SA 4.0*
    - 20.4: Detections and Applications of Radioactivity - *CC BY-NC-SA 4.0*
    - 20.5: Thermodynamic Stability of Nuclei - *CC BY-NC-SA 4.0*
    - 20.6: Nuclear Fission and Fusion - *CC BY-NC-SA 4.0*
    - 20.7: Effects of Radiation on Matter - *CC BY-NC-SA 4.0*
  - 21: Organic and Biological Chemistry - *CC BY-NC-SA 4.0*
    - 21.1: Alkanes: Saturated Hydrocarbons - *CC BY-NC-SA 4.0*
    - 21.2: Alkenes and Alkynes - *CC BY-NC-SA 4.0*
    - 21.3: Aromatic Hydrocarbons - *CC BY-NC-SA 4.0*
    - 21.4: Hydrocarbon Derivatives - *CC BY-NC-SA 4.0*
    - 21.5: Polymers - *CC BY-NC-SA 4.0*
    - 21.6: Natural Polymers - *CC BY-NC-SA 4.0*
  - Back Matter - *Undeclared*
    - Index - *Undeclared*
    - Glossary - *Undeclared*
    - Detailed Licensing - *Undeclared*