AUCHE 110 - GENERAL CHEMISTRY I



Elizabeth McGinitie
University of Alberta Augustina

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AUCHE 110 - General Chemistry I

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This text was compiled on 10/28/2026

TABLE OF CONTENTS

Licensing

1: Review

1.1: The Scientific Method

1.2: SI Units

1.3: Measurements

1.4: Significant Figures

1.5: Converting Units

1.6: Atomic Theory

1.7: Molecules and Ions

1.8: Polyatomic Ions

1.9: An Introduction to the Periodic Table

1.10: Measurement and Scale - The Mole Concept

1.11: Molar Mass

1.12: Mole-Mass Conversions

1.13: Concentration and Molarity

1.14: Balancing Chemical Equations

1.15: Stoichiometric Calculations- Amounts of Reactants and Products

1.16: Calculations Involving a Limiting Reactant

2: Atomic Structure and Periodic Trends

2.1: Electromagnetic Radiation

2.2: Quantum Theory

2.3: Atomic Spectra

2.4: The Bohr Atom

2.5: Two Ideas Leading to a New Quantum Mechanics

2.6: Wave Mechanics and Quantum Numbers

2.7: Electron Spin- A Fourth Quantum Number

2.8: Orbital Shapes and Energies

2.9: Polyelectronic Atoms

2.10: The History of the Periodic Table

2.11: Electron Configurations

2.12: Magnetic Properties

2.13: Sizes of Atoms and Ions

2.14: Ionization Energy

2.15: Electron Affinity

2.16: Electronegativity

2.17: Periodic Properties of the Elements

3: Lewis Structures and Molecular Shapes

3.1: Prelude to Chemical Bonding and Molecular Geometry

3.2: Ionic Bonding

3.3: Covalent Bonding

3.4: Lewis Theory- An Overview

3.5: Writing Lewis Structures

3.6: Resonance

3.7: Exceptions to the Octet Rule

3.8: Shapes of Molecules

4: Bonding Theories

4.1: Hybrid Atomic Orbitals

4.2: Multiple Covalent Bonds

5: Functional Groups and IR Spectroscopy

5.1: Organic Structural Representations- Bond-Line Notation

5.2: Functional Groups and Classes of Organic Compounds

5.3: IR Spectroscopy Background

5.4: Interpreting Infrared Spectra

5.5: Identifying the Presence of Particular Groups

5.6: The Fingerprint Region

6: States of Matter and Intermolecular Forces

6.1: Overview of States of Matter

6.2: Intermolecular forces

6.3: Vapor Pressure

6.4: Solubility

6.5: Unique Properties of Liquids

6.6: Crystalline and Amorphous Solids

6.7: The Solid State of Matter

6.8: Gaseous Elements and Compounds

6.9: Gas Pressure

6.10: The Ideal Gas Law

6.11: Gas Mixtures

6.12: Kinetic Theory of Gases

6.13: Real Gases

6.14: Overview of Chromatography

6.15: General Separation Theory

Index

Glossary

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1: REVIEW

1.1: The Scientific Method

1.2: SI Units

1.3: Measurements

1.4: Significant Figures

1.5: Converting Units

1.6: Atomic Theory

1.7: Molecules and Ions

1.8: Polyatomic Ions

1.9: An Introduction to the Periodic Table

1.10: Measurement and Scale - The Mole Concept

1.11: Molar Mass

1.12: Mole-Mass Conversions

1.13: Concentration and Molarity

1.14: Balancing Chemical Equations

1.15: Stoichiometric Calculations- Amounts of Reactants and Products

1.16: Calculations Involving a Limiting Reactant

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1.1: 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 1.1.1).

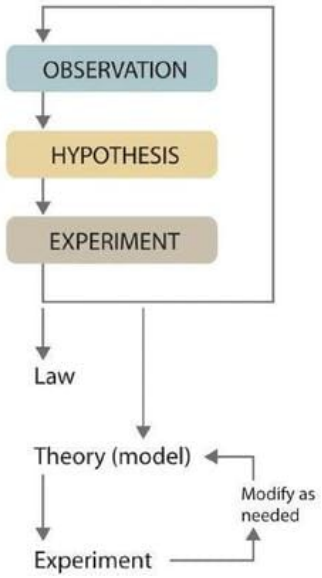


Figure 1.1.1: The Scientific Method. As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

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 1.1.2 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 1.1.2 summarizes the application of the scientific method in this case.

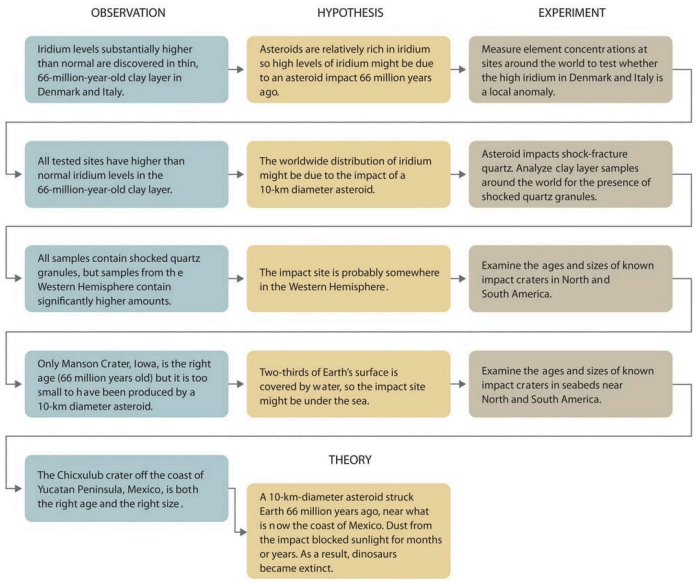


Figure 1.1.2: A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth

Example 1.1.1

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 1.1.1

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 available at the end of this section.

Because scientists can enter the cycle shown in Figure 1.1.1 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.

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

Answers

Exercise 1.1.1

experiment
law
theory
hypothesis
qualitative observation
quantitative observation

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1.2: SI Units

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 1.2.1, 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:

$$K = °C + 273 \tag{1.2.1}$$

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.

Table 1.2.1: 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 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 1.2.1). 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.

Common prefixes and their multiplicative factors are listed in Table 1.2.2. (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 1.2.2: 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.



Figure 1.2.1: 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.

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.

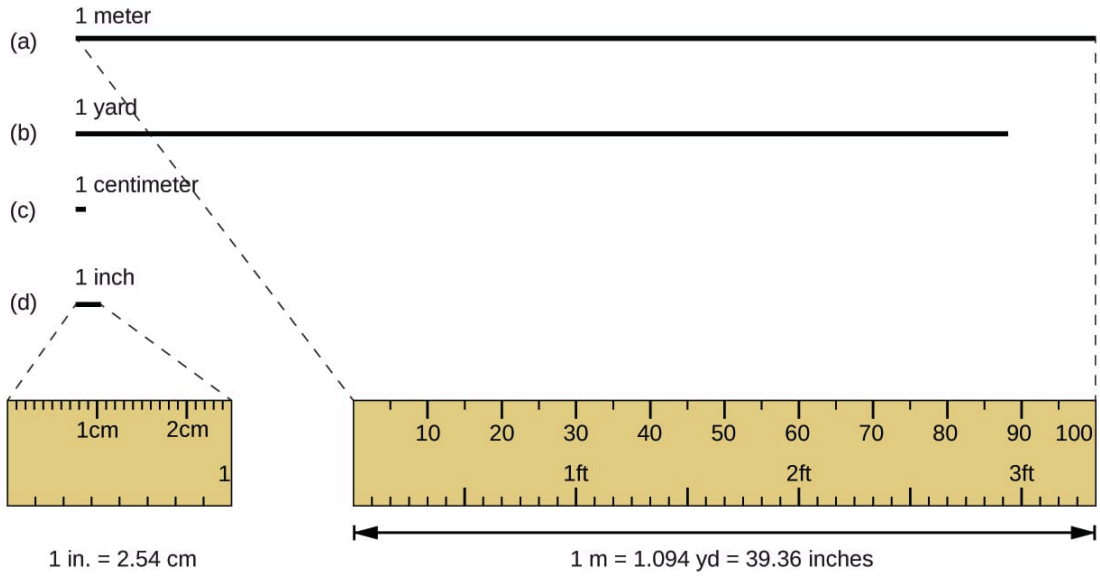


Figure 1.2.2: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd. (CC BY 4.0; OpenStax)

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

As shown in Figure 1.2.3, 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.

$$1\ mL = 1\ cm^3 \tag{1.2.2}$$

Example 1.2.1

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 available at the end of this section.

Exercise 1.2.1

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 available at the end of this section.

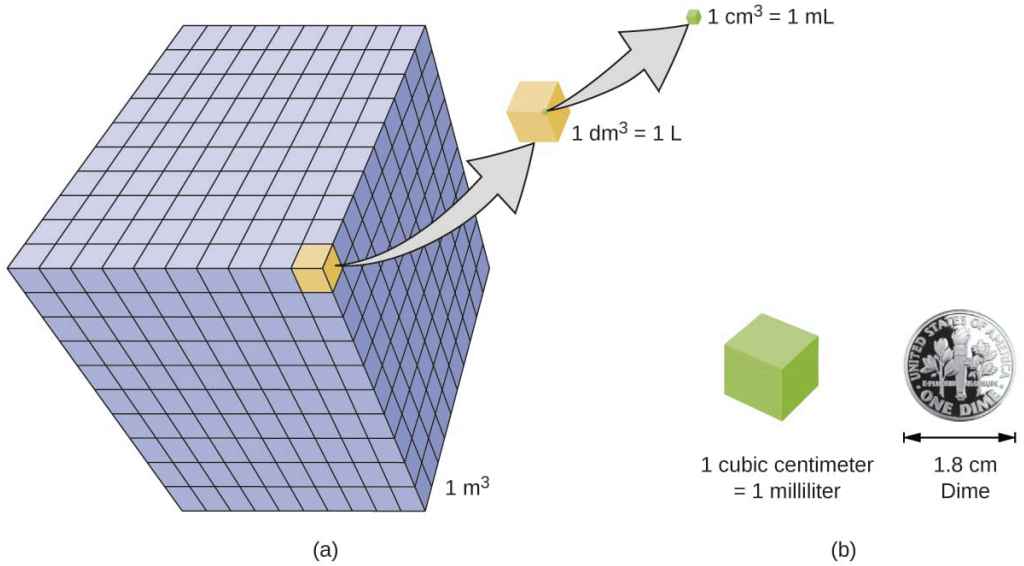


Figure 1.2.3: Units of Volume. (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). A liter (L) is defined as a cube 1 dm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter. (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube. (CC BY 4.0; OpenStax)

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.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.2.3}$$

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 1.2.2: 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 1.2.2: 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 1.2.2: Density of Oxygen

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

Answer available at the end of this section.

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; $\mathrm{mL} \times \frac{\mathrm{g}}{\mathrm{mL}} = \mathrm{g}$ (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.

Answers

Example 1.2.1

The abbreviation for a kiloliter is kL. Because kilo means "1,000 ×," 1 kL equals 1,000 L.
The abbreviation for microsecond is µs. Micro implies 1/1,000,000th of a unit, so 1 µs equals 0.000001 s.
The abbreviation for decimeter is dm. Deci means 1/10th, so 1 dm equals 0.1 m.
The abbreviation for nanogram is ng and equals 0.000000001 g.

Exercise 1.2.1

km (1,000 m)
mg (0.001 g)
ns (0.000000001 s)
cL (0.01L)

Exercise 1.2.2**: Density of Oxygen**

1.45 g/L

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1.3: Measurements

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.

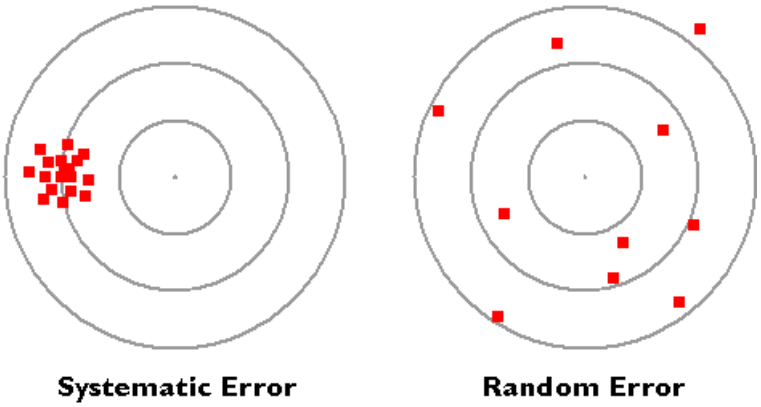
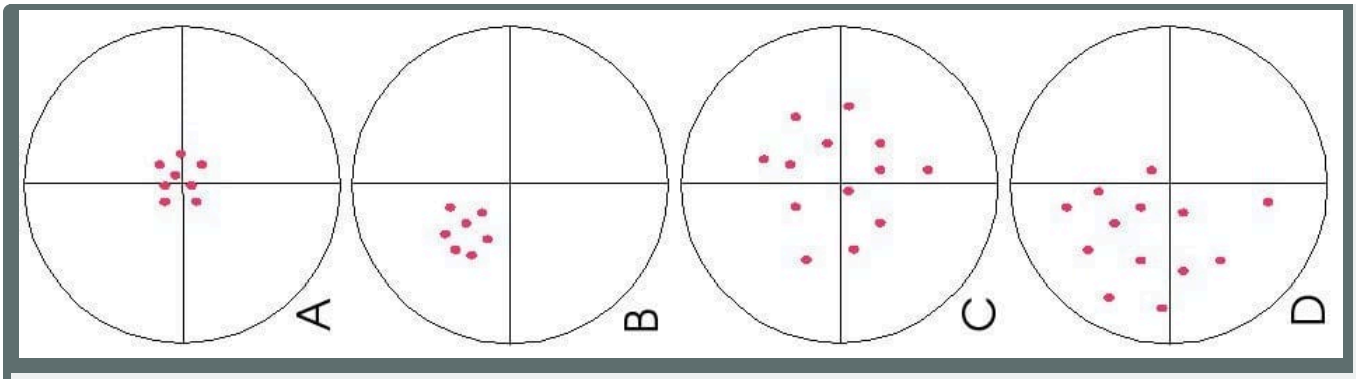


***Figure 2:** Systematic and random errors. Figure used with permission from David DiBiase (Penn State U).*

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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1.4: Significant Figures

Learning Objective

- Apply the concept of significant figures to limit a measurement to the proper number of digits.
- Recognize the number of significant figures in a given quantity.
- Limit mathematical results to the proper number of significant figures.

If you use a calculator to evaluate the expression 337/217, you will get the following:

$$337 \div 217 = 1.5529953917$$

and so on for many more digits. Although this answer is correct, it is somewhat presumptuous. You start with two values that each have three digits, and the answer has *twelve* digits? That does not make much sense from a strict numerical point of view.

Consider using a ruler to measure the width of an object, as shown in Figure 1.4.1. The object is definitely more than 1 cm long, so we know that the first digit in our measurement is 1. We see by counting the tick marks on the ruler that the object is at least three ticks after the 1. If each tick represents 0.1 cm, then we know the object is at least 1.3 cm wide. But our ruler does not have any more ticks between the 0.3 and the 0.4 marks, so we can't know exactly how much the next decimal place is. But with a practiced eye we can estimate it. Let us estimate it as about six-tenths of the way between the third and fourth tick marks, which estimates our hundredths place as 6, so we identify a measurement of 1.36 cm for the width of the object.

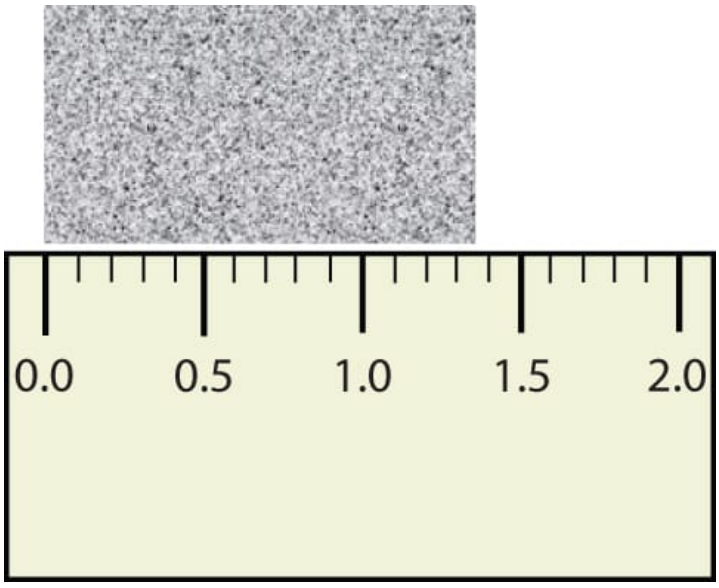


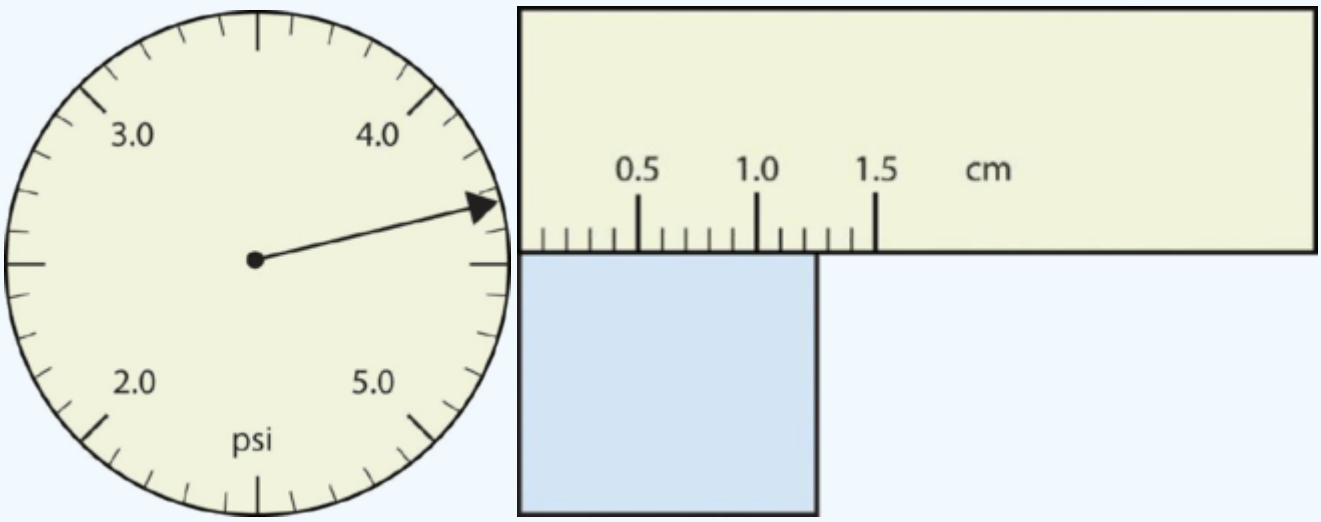
Figure 1.4.1: Expressing Width. What is the proper way to express the width of this object?

Does it make any sense to try to report a thousandths place for the measurement? No, it doesn't; we are not exactly sure of the hundredths place (after all, it was an estimate only), so it would be fruitless to estimate a thousandths place. Our best measurement, then, stops at the hundredths place, and we report 1.36 cm as proper measurement.

This concept of reporting the proper number of digits in a measurement or a calculation is called significant figures. Significant figures (sometimes called significant digits) represent the limits of what values of a measurement or a calculation we are sure of. The convention for a measurement is that the quantity reported should be all known values and the first estimated value. The conventions for calculations are discussed as follows.

Example 1.4.1

Use each diagram to report a measurement to the proper number of significant figures.

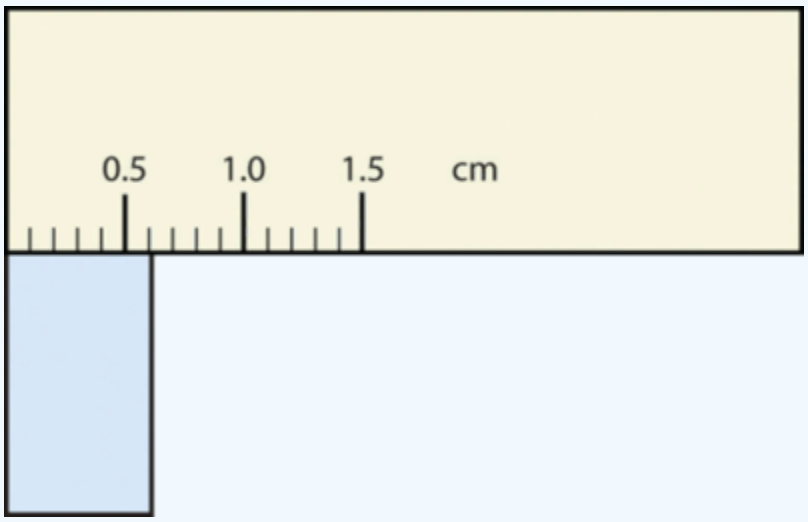


Solution

1. The arrow is between 4.0 and 5.0, so the measurement is at least 4.0. The arrow is between the third and fourth small tick marks, so it's at least 0.3. We will have to estimate the last place. It looks like about one-third of the way across the space, so let us estimate the hundredths place as 3. Combining the digits, we have a measurement of 4.33 psi (psi stands for "pounds per square inch" and is a unit of pressure, like air in a tire). We say that the measurement is reported to three significant figures.
2. The rectangle is at least 1.0 cm wide but certainly not 2.0 cm wide, so the first significant digit is 1. The rectangle's width is past the second tick mark but not the third; if each tick mark represents 0.1, then the rectangle is at least 0.2 in the next significant digit. We have to estimate the next place because there are no markings to guide us. It appears to be about halfway between 0.2 and 0.3, so we will estimate the next place to be a 5. Thus, the measured width of the rectangle is 1.25 cm. Again, the measurement is reported to three significant figures.

Exercise 1.4.1

What would be the reported width of this rectangle?



Answer available at the end of this section.

In many cases, you will be given a measurement. How can you tell by looking what digits are significant? For example, the reported population of the United States is 306,000,000. Does that mean that it is *exactly* three hundred six million, or is some estimation occurring?

The following conventions dictate which numbers in a reported measurement are significant and which are not significant:

1. Any nonzero digit is significant.
2. Any zeros between nonzero digits (i.e., embedded zeros) are significant.
3. Zeros at the end of a number without a decimal point (i.e., trailing zeros) are not significant; they serve only to put the significant digits in the correct positions. However, zeros at the end of any number with a decimal point are significant.
4. Zeros at the beginning of a decimal number (i.e., leading zeros) are not significant; again, they serve only to put the significant digits in the correct positions.

So, by these rules, the population figure of the United States has only three significant figures: the 3, the 6, and the zero between them. The remaining six zeros simply put the 306 in the millions position. (See Figure 1.4.2 for another example.)



Figure 1.4.2: Significant Figures. How many of the numbers in this display are actually significant? (Public Domain.)

Example 1.4.2

Give the number of significant figures in each measurement.

a. 36.7 m
b. 0.000600 s
c. 2,002 kg
d. 306,490,000 people

Solution

a. By rule 1, all nonzero digits are significant, so this measurement has three significant figures.
b. By rule 4, the first three zeros are not significant, but by rule 2 the zero between the sixes is; therefore, this number has four significant figures.
c. By rule 2, the two zeros between the twos are significant, so this measurement has four significant figures.
d. The four trailing zeros in the number are not significant, but the other five numbers are, so this number has five significant figures.

Exercise 1.4.2

Give the number of significant figures in each measurement.

a. 0.000601 m
b. 65.080 kg

Answer a available at the end of this section.

How are significant figures handled in calculations? It depends on what type of calculation is being performed. If the calculation is an addition or a subtraction, the rule is as follows: limit the reported answer to the rightmost column that all numbers have significant figures in common. For example, if you were to add 1.2 and 4.21, we note that the first number stops its significant figures in the tenths column, while the second number stops its significant figures in the hundredths column. We therefore limit our answer to the tenths column.

$$\begin{array}{r} 1.2 \\ +\ 4.41 \\ \hline 5.61 \end{array}$$

↑ limit final answer to the tenths column: 5.6

We drop the last digit—the 1—because it is not significant to the final answer.

The dropping of positions in sums and differences brings up the topic of rounding. Although there are several conventions, in this text we will adopt the following rule: the final answer should be rounded up if the first dropped digit is 5 or greater, and rounded down if the first dropped digit is less than 5.

$$\begin{array}{r} 77.2 \\ +\ 10.46 \\ \hline 87.66 \end{array}$$

↑ limit final answer to the tenths column and round up: 87.7

Example 1.4.3

Express the final answer to the proper number of significant figures.

a. 101.2 + 18.702 = ?
b. 202.88 – 1.013 = ?

Solution

a. If we use a calculator to add these two numbers, we would get 119.902. However, most calculators do not understand significant figures, and we need to limit the final answer to the tenths place. Thus, we drop the 02 and report a final answer of 119.9 (rounding down).
b. A calculator would answer 201.867. However, we have to limit our final answer to the hundredths place. Because the first number being dropped is 7, which is greater than 5, we round up and report a final answer of 201.87.

Exercise 1.4.3

Express the answer for

$$3.445 + 90.83 - 72.4$$

to the proper number of significant figures.

Answer available at the end of this section.

If the operations being performed are multiplication or division, the rule is as follows: limit the answer to the number of significant figures that the data value with the *least* number of significant figures has. So if we are dividing 23 by 448, which have two and three significant figures respectively, we should limit the final reported answer to two significant figures (the lesser of two and three significant figures):

$$23 \div 448 = 0.051339286 \approx 0.051$$

The same rounding rules apply in multiplication and division as they do in addition and subtraction.

Example 1.4.4: Significant Figures

Express the final answer to the proper number of significant figures.

a. 76.4 × 180.4 = ?
b. 934.9 ÷ 0.00455 = ?

Solution

a. The first number has three significant figures, while the second number has four significant figures. Therefore, we limit our final answer to three significant figures: 76.4 × 180.4 = 13,782.56 = 13,800.
b. The first number has four significant figures, while the second number has three significant figures. Therefore, we limit our final answer to three significant figures: 934.9 ÷ 0.00455 = 205,472.5275... = 205,000.

Exercise 1.4.4

Express the final answer to the proper number of significant figures.

a. 22.4 × 8.314 = ?
b. 1.381 ÷ 6.02 = ?

Answer a available at the end of this section.

As you have probably realized by now, the biggest issue in determining the number of significant figures in a value is the zero. Is the zero significant or not? One way to unambiguously determine whether a zero is significant or not is to write a number in scientific notation. Scientific notation will include zeros in the coefficient of the number *only if they are significant*. Thus, the number 8.666×10^6 has four significant figures. However, the number 8.6660×10^6 has five significant figures. That last zero is significant; if it were not, it would not be written in the coefficient. So, when in doubt about expressing the number of significant figures in a quantity, use scientific notation and include the number of zeros that are truly significant.

Summary

- Significant figures in a quantity indicate the number of known values plus one place that is estimated.
- There are rules for which numbers in a quantity are significant and which are not significant.
- In calculations involving addition and subtraction, limit significant figures based on the rightmost place that all values have

in common.
- In calculations involving multiplication and division, limit significant figures to the least number of significant figures in all the data values.

Answers

Exercise 1.4.1

0.63 cm

Exercise 1.4.2

three significant figures

five significant figures

Exercise 1.4.3

21.9

Exercise 1.4.4

186

0.229

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1.5: Converting Units

Learning Objective

- Convert from one unit to another unit of the same type.

In Section 2.2, we showed some examples of how to replace initial units with other units of the same type to get a numerical value that is easier to comprehend. In this section, we will formalize the process.

Consider a simple example: how many feet are there in 4 yards? Most people will almost automatically answer that there are 12 feet in 4 yards. How did you make this determination? Well, if there are 3 feet in 1 yard and there are 4 yards, then there are 4 × 3 = 12 feet in 4 yards.

This is correct, of course, but it is informal. Let us formalize it in a way that can be applied more generally. We know that 1 yard (yd) equals 3 feet (ft):

$$1\,yd = 3\,ft$$

In math, this expression is called an *equality*. The rules of algebra say that you can change (i.e., multiply or divide or add or subtract) the equality (as long as you do not divide by zero) and the new expression will still be an equality. For example, if we divide both sides by 2, we get:

$$\frac{1}{2}\,yd = \frac{3}{2}\,ft$$

We see that one-half of a yard equals 3/2, or one and a half, feet—something we also know to be true—so the above equation is still an equality. Going back to the original equality, suppose we divide both sides of the equation by 1 yard (number **and** unit):

$$\frac{1\,yd}{1\,yd} = \frac{3\,ft}{1\,yd}$$

The expression is still an equality, by the rules of algebra. The left fraction equals 1. It has the same quantity in the numerator and the denominator, so it must equal 1. The quantities in the numerator and denominator cancel, both the number *and* the unit:

$$\frac{1\,yd}{1\,yd} = \frac{3\,ft}{1\,yd}$$

When everything cancels in a fraction, the fraction reduces to 1:

$$1 = \frac{3\,ft}{1\,yd}$$

Conversion Factors

We have an expression that equals 1.

$$\frac{3\,ft}{1\,yd} = 1$$

This is a strange way to write 1, but it makes sense: 3 ft equal 1 yd, so the quantities in the numerator and denominator are the same quantity, just expressed with different units.

The expression

$$\frac{3\,ft}{1\,yd}$$

is called a conversion factor and it is used to formally change the unit of a quantity into another unit. (The process of converting units in such a formal fashion is sometimes called *dimensional analysis* or the *factor label method*.)

To see how this happens, let us start with the original quantity: 4 yd.

Now let us multiply this quantity by 1. When you multiply anything by 1, you do not change the value of the quantity. Rather than multiplying by just 1, let us write 1 as:

$$\frac{3\ ft}{1\ yd}$$

$$4\ yd \times \frac{3\ ft}{1\ yd}$$

The 4 yd term can be thought of as 4yd/1; that is, it can be thought of as a fraction with 1 in the denominator. We are essentially multiplying fractions. If the same thing appears in the numerator and denominator of a fraction, they cancel. In this case, what cancels is the unit *yard*:

$$4\ yd \times \frac{3\ ft}{1\ yd}$$

That is all that we can cancel. Now, multiply and divide all the numbers to get the final answer:

$$\frac{4 \times 3\ ft}{1} = \frac{12\ ft}{1} = 12\ ft$$

Again, we get an answer of 12 ft, just as we did originally. But in this case, we used a more formal procedure that is applicable to a variety of problems.

How many millimeters are in 14.66 m? To answer this, we need to construct a conversion factor between millimeters and meters and apply it correctly to the original quantity. We start with the definition of a millimeter, which is:

$$1\ mm = \frac{1}{1000\ m}$$

The 1/1000 is what the prefix *milli-* means. Most people are more comfortable working without fractions, so we will rewrite this equation by bringing the 1,000 into the numerator of the other side of the equation:

$$1000\ mm = 1\ m$$

Now we construct a conversion factor by dividing one quantity into both sides. But now a question arises: which quantity do we divide by? It turns out that we have two choices, and the two choices will give us different conversion factors, both of which equal 1:

$$\frac{1000\ mm}{1000\ mm} = \frac{1\ m}{1000\ mm}$$

or

$$\frac{1000\ mm}{1\ m} = \frac{1\ m}{1\ m}$$

$$1 = \frac{1\ m}{1000\ mm}$$

or

$$\frac{1000\ mm}{1\ m} = 1$$

Which conversion factor do we use? The answer is based on *what unit you want to get rid of in your initial quantity*. The original unit of our quantity is meters, which we want to convert to millimeters. Because the original unit is assumed to be in the numerator, to get rid of it, we want the meter unit in the *denominator*; then they will cancel. Therefore, we will use the second conversion factor. Canceling units and performing the mathematics, we get:

$$14.66m \times \frac{1000\,mm}{1\,m} = 14660\,mm$$

Note how m cancels, leaving mm, which is the unit of interest.

The ability to construct and apply proper conversion factors is a very powerful mathematical technique in chemistry. You need to master this technique if you are going to be successful in this and future courses.

Example 1.5.1

a. Convert 35.9 kL to liters.
b. Convert 555 nm to meters.

Solution

a. We will use the fact that 1 kL = 1,000 L. Of the two conversion factors that can be defined, the one that will work is 1000L/ 1kL. Applying this conversion factor, we get:

$$35.9\,kL \times \frac{1000\,L}{1\,kL} = 35,900\,L$$

b. We will use the fact that 1 nm = 1/1,000,000,000 m, which we will rewrite as 1,000,000,000 nm = 1 m, or 10^9 nm = 1 m. Of the two possible conversion factors, the appropriate one has the nm unit in the denominator:

$$\frac{1\,m}{10^9\,nm}$$

Applying this conversion factor, we get:

$$555\,nm \times \frac{1m}{10^9 nm} = 0.000000555\,m = 5.55 \times 10^{-7}\,m$$

In the final step, we expressed the answer in scientific notation.

Exercise 1.5.1

a. Convert 67.08 µL to liters.
b. Convert 56.8 m to kilometers.

Answer a available at the end of this section.

Answer b available at the end of this section.

What if we have a derived unit that is the product of more than one unit, such as m^2? Suppose we want to convert square meters to square centimeters? The key is to remember that m^2 means m × m, which means we have *two* meter units in our derived unit. That means we have to include *two* conversion factors, one for each unit. For example, to convert 17.6 m^2 to square centimeters, we perform the conversion as follows:

$$\begin{aligned} 17.6m^2 &= 17.6(m \times m) \times \frac{100cm}{1m} \times \frac{100cm}{1m} \\ &= 176000\,cm \times cm \\ &= 1.76 \times 10^5\,cm^2 \end{aligned} \tag{1.5.1}$$

Example 1.5.2

How many cubic centimeters are in 0.883 m^3?

Solution

With an exponent of 3, we have three length units, so by extension we need to use three conversion factors between meters and centimeters. Thus, we have:

$$0.883 m^3 \times \frac{100\,cm}{1\,m} \times \frac{100\,cm}{1\,m} \times \frac{100\,cm}{1\,m} = 883000\,cm^3 = 8.83 \times 10^5\,cm^3$$

You should demonstrate to yourself that the three meter units do indeed cancel.

Exercise 1.5.2

How many cubic millimeters are present in 0.0923 m^3?

Answer available at the end of this section.

Suppose the unit you want to convert is in the denominator of a derived unit—what then? Then, in the conversion factor, the unit you want to remove must be in the *numerator*. This will cancel with the original unit in the denominator and introduce a new unit in the denominator. The following example illustrates this situation.

Example 1.5.3

Convert 88.4 m/min to meters/second.

Solution

We want to change the unit in the denominator from minutes to seconds. Because there are 60 seconds in 1 minute (60 s = 1 min), we construct a conversion factor so that the unit we want to remove, minutes, is in the numerator: 1min/60s. Apply and perform the math:

$$\frac{88.4 m}{min} \times \frac{1\,min}{60\,s} = 1.47 \frac{m}{s}$$

Notice how the 88.4 automatically goes in the numerator. That's because any number can be thought of as being in the numerator of a fraction divided by 1.

Exercise 1.5.3

Convert 0.203 m/min to meters/second.

Answer available at the end of this section.

Sometimes there will be a need to convert from one unit with one numerical prefix to another unit with a different numerical prefix. How do we handle those conversions? Well, you could memorize the conversion factors that interrelate all numerical prefixes. Or you can go the easier route: first convert the quantity to the base unit—the unit with no numerical prefix—using the definition of the original prefix. Then, convert the quantity in the base unit to the desired unit using the definition of the second prefix. You can do the conversion in two separate steps or as one long algebraic step. For example, to convert 2.77 kg to milligrams:

$$2.77\,kg \times \frac{1000\,g}{1\,kg} = 2770\,g$$

(convert to the base units of grams)

$$2770\,g \times \frac{1000\,mg}{1\,g} = 2770000\,mg = 2.77 \times 10^6\,mg$$

(convert to desired unit)

Alternatively, it can be done in a single multi-step process:

$$2.77\,\cancel{kg} \times \frac{1000\,\cancel{g}}{1\,\cancel{kg}} \times \frac{1000\,mg}{1\,\cancel{g}} = 2770000\,mg$$
$$= 2.77 \times 10^6\,mg \tag{1.5.2}$$

You get the same answer either way.

Example 1.5.4

How many nanoseconds are in 368.09 μs?

Solution

You can either do this as a one-step conversion from microseconds to nanoseconds or convert to the base unit first and then to the final desired unit. We will use the second method here, showing the two steps in a single line. Using the definitions of the prefixes *micro-* and *nano-*,

$$368.0\,\mu s \times \frac{1\,s}{1000000\,\mu s} \times \frac{1000000000}{1\,s} = 3.6809 \times 10^5\,ns$$

Exercise 1.5.4

How many milliliters are in 607.8 kL?

Answer available at the end of this section.

When considering the significant figures of a final numerical answer in a conversion, there is one important case where a number does not impact the number of significant figures in a final answer: the so-called **exact number**. An exact number is a number from a defined relationship, not a measured one. For example, the prefix *kilo-* means 1,000-*exactly* 1,000, no more or no less. Thus, in constructing the conversion factor:

$$\frac{1000\,g}{1\,kg}$$

neither the 1,000 nor the 1 enter into our consideration of significant figures. The numbers in the numerator and denominator are defined exactly by what the prefix *kilo-* means. Another way of thinking about it is that these numbers can be thought of as having an infinite number of significant figures, such as:

$$\frac{1000.0000000000\ldots\,g}{1.0000000000\ldots\,kg}$$

The other numbers in the calculation will determine the number of significant figures in the final answer.

Example 1.5.5

A rectangular plot in a garden has the dimensions 36.7 cm by 128.8 cm. What is the area of the garden plot in square meters? Express your answer in the proper number of significant figures.

Solution

Area is defined as the product of the two dimensions, which we then have to convert to square meters, and express our final answer to the correct number of significant figures—which in this case will be three.

$$36.7\,cm \times 128.8\,cm \times \frac{1\,m}{100\,cm} \times \frac{1\,m}{100\,cm} = 0.472696\,m^2 = 0.473\,m^2$$

The 1 and 100 in the conversion factors do not affect the determination of significant figures because they are exact numbers, defined by the centi- prefix.

Exercise 1.5.5

What is the volume of a block in cubic meters with the dimensions 2.1 cm × 34.0 cm × 118 cm?

Answer available at the end of this section.

Chemistry is Everywhere: The Gimli Glider

On July 23, 1983, an Air Canada Boeing 767 jet had to glide to an emergency landing at Gimli Industrial Park Airport in Gimli, Manitoba, because it unexpectedly ran out of fuel during flight. There was no loss of life in the course of the emergency landing, only some minor injuries associated in part with the evacuation of the craft after landing. For the remainder of its operational life (the plane was retired in 2008), the aircraft was nicknamed "the Gimli Glider."



The Gimli Glider is the Boeing 767 that ran out of fuel and glided to safety at Gimli Airport. The aircraft ran out of fuel because of confusion over the units used to express the amount of fuel. Source: Photo courtesy of Will F., (CC BY-SA 2.5; Aero Icarus).

The 767 took off from Montreal on its way to Ottawa, ultimately heading for Edmonton, Canada. About halfway through the flight, all the engines on the plane began to shut down because of a lack of fuel. When the final engine cut off, all electricity (which was generated by the engines) was lost; the plane became, essentially, a powerless glider. Captain Robert Pearson was an experienced glider pilot, although he had never flown a glider the size of a 767. First Officer Maurice Quintal quickly determined that the aircraft would not be able make it to Winnipeg, the next large airport. He suggested his old Royal Air Force base at Gimli Station, one of whose runways was still being used as a community airport. Between the efforts of the pilots and the flight crew, they managed to get the airplane safely on the ground (although with buckled landing gear) and all passengers off safely.

What happened? At the time, Canada was transitioning from the older English system to the metric system. The Boeing 767s were the first aircraft whose gauges were calibrated in the metric system of units (liters and kilograms) rather than the English system of units (gallons and pounds). Thus, when the fuel gauge read 22,300, the gauge meant kilograms, but the ground crew mistakenly fueled the plane with 22,300 *pounds* of fuel. This ended up being just less than half of the fuel needed to make the trip, causing the engines to quit about halfway to Ottawa. Quick thinking and extraordinary skill saved the lives of 61 passengers and 8 crew members—an incident that would not have occurred if people were watching their units.

Key Takeaways

- Units can be converted to other units using the proper conversion factors.
- Conversion factors are constructed from equalities that relate two different units.
- Conversions can be a single step or multi-step.
- Unit conversion is a powerful mathematical technique in chemistry that must be mastered.
- Exact numbers do not affect the determination of significant figures.

Answers

Exercise 1.5.1

6.708×10^{-5} L

Exercise 1.5.1

5.68×10^{-2} km

Exercise 1.5.2

9.23×10^{7} mm^3

Exercise 1.5.3

0.00338 m/s

or

3.38×10^{-3} m/s

Exercise 1.5.4

6.078×10^{8} mL

Exercise 1.5.5

0.0084 m^3

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1.6: Atomic Theory

Learning Objectives

- State the modern atomic theory.
- Learn how atoms are constructed.

The smallest piece of an element that maintains the identity of that element is called an atom. Individual atoms are extremely small. It would take about fifty million atoms in a row to make a line that is 1 cm long. The period at the end of a printed sentence has several million atoms in it. Atoms are so small that it is difficult to believe that all matter is made from atoms—but it is.

The concept that atoms play a fundamental role in chemistry is formalized by the modern atomic theory, first stated by John Dalton, an English scientist, in 1808. It consists of three parts:

1. All matter is composed of atoms.
2. Atoms of the same element are the same; atoms of different elements are different.
3. Atoms combine in whole-number ratios to form compounds.

These concepts form the basis of chemistry. Although the word *atom* comes from a Greek word that means "indivisible," we understand now that atoms themselves are composed of smaller parts called *subatomic particles*. The first part to be discovered was the electron, a tiny subatomic particle with a negative charge. It is often represented as e^-, with the right superscript showing the negative charge. Later, two larger particles were discovered. The proton is a more massive (but still tiny) subatomic particle with a positive charge, represented as p^+. The neutron is a subatomic particle with about the same mass as a proton, but no charge. It is represented as either n or n^0. We now know that all atoms of all elements are composed of electrons, protons, and (with one exception) neutrons. Table 1.6.1 summarizes the properties of these three subatomic particles.

Table 1.6.1: Properties of the Three Subatomic Particles

Name	Symbol	Mass (approx.; kg)	Charge
Proton	p^+	1.6×10^{-27}	1+
Neutron	n, n^0	1.6×10^{-27}	none
Electron	e^-	9.1×10^{-31}	1–

How are these particles arranged in atoms? They are not arranged at random. Experiments by Ernest Rutherford in England in the 1910s pointed to a nuclear model with atoms that has the protons and neutrons in a central nucleus with the electrons in orbit about the nucleus. The relatively massive protons and neutrons are collected in the center of an atom, in a region called the nucleus of the atom (plural *nuclei*). The electrons are outside the nucleus and spend their time orbiting in space about the nucleus. (Figure 1.6.1).

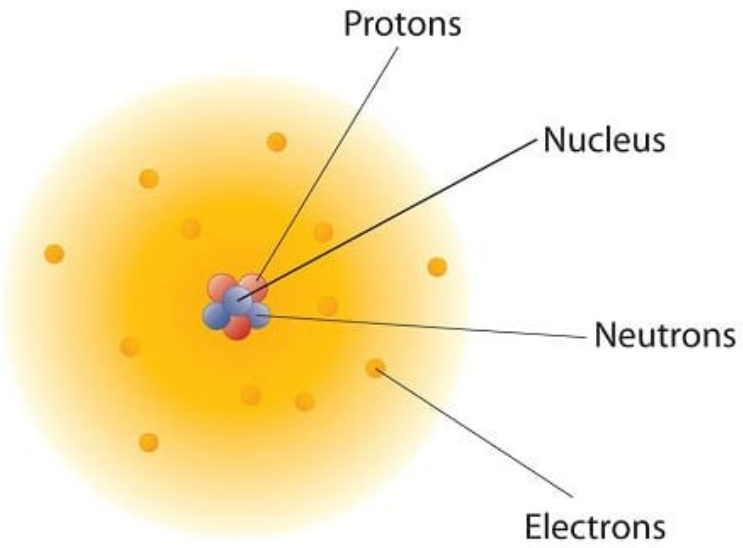


Figure 1.6.1: The Structure of the Atom. Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.

The modern atomic theory states that atoms of one element are the same, while atoms of different elements are different. What makes atoms of different elements different? The fundamental characteristic that all atoms of the same element share is the *number of protons*. All atoms of hydrogen have one and only one proton in the nucleus; all atoms of iron have 26 protons in the nucleus. This number of protons is so important to the identity of an atom that it is called the atomic number. The number of protons in an atom is the atomic number of the element. Thus, hydrogen has an atomic number of 1, while iron has an atomic number of 26. Each element has its own characteristic atomic number.

Atoms of the same element can have different numbers of neutrons, however. Atoms of the same element (i.e., atoms with the same number of protons) with different numbers of neutrons are called isotopes. Most naturally occurring elements exist as isotopes. For example, most hydrogen atoms have a single proton in their nucleus. However, a small number (about one in a million) of hydrogen atoms have a proton and a neutron in their nuclei. This particular isotope of hydrogen is called deuterium. A very rare form of hydrogen has one proton and two neutrons in the nucleus; this isotope of hydrogen is called tritium. The sum of the number of protons and neutrons in the nucleus is called the mass number of the isotope.

Neutral atoms have the same number of electrons as they have protons, so their overall charge is zero. However, as we shall see later, this will not always be the case.

Example 1.6.1

a. The most common carbon atoms have six protons and six neutrons in their nuclei. What are the atomic number and the mass number of these carbon atoms?
b. An isotope of uranium has an atomic number of 92 and a mass number of 235. What are the number of protons and neutrons in the nucleus of this atom?

Solution

a. If a carbon atom has six protons in its nucleus, its atomic number is 6. If it also has six neutrons in the nucleus, then the mass number is 6 + 6, or 12.
b. If the atomic number of uranium is 92, then that is the number of protons in the nucleus. Because the mass number is 235, then the number of neutrons in the nucleus is 235 – 92, or 143.

Exercise 1.6.1

The number of protons in the nucleus of a tin atom is 50, while the number of neutrons in the nucleus is 68. What are the atomic number and the mass number of this isotope?

Answer available at the end of this section.

When referring to an atom, we simply use the element's name: the term *sodium* refers to the element as well as an atom of sodium. But it can be unwieldy to use the name of elements all the time. Instead, chemistry defines a symbol for each element. The atomic symbol is a one- or two-letter representation of the name of an element. By convention, the first letter of an element's symbol is always capitalized, while the second letter (if present) is lowercase. Thus, the symbol for hydrogen is H, the symbol for sodium is Na, and the symbol for nickel is Ni. Most symbols come from the English name of the element, although some symbols come from an element's Latin name. (The symbol for sodium, Na, comes from its Latin name, *natrium*.) Table 1.6.2 lists some common elements and their symbols. You should memorize the symbols in Table 1.6.2, as this is how we will be representing elements throughout chemistry.

Table 1.6.2: Names and Symbols of Common Elements

Element Name	Symbol	Element Name	Symbol
Aluminum	Al	Mercury	Hg
Argon	Ar	Molybdenum	Mo
Arsenic	As	Neon	Ne
Barium	Ba	Nickel	Ni
Beryllium	Be	Nitrogen	N
Bismuth	Bi	Oxygen	O
Boron	B	Palladium	Pd
Bromine	Br	Phosphorus	P
Calcium	Ca	Platinum	Pt
Carbon	C	Potassium	K
Chlorine	Cl	Radium	Ra
Chromium	Cr	Radon	Rn
Cobalt	Co	Rubidium	Rb
Copper	Cu	Scandium	Sc
Fluorine	F	Selenium	Se
Gallium	Ga	Silicon	Si
Germanium	Ge	Silver	Ag
Gold	Au	Sodium	Na
Helium	He	Strontium	Sr
Hydrogen	H	Sulfur	S
Iodine	I	Tantalum	Ta
Iridium	Ir	Tin	Sn
Iron	Fe	Titanium	Ti
Krypton	Kr	Tungsten	W
Lead	Pb	Uranium	U

Element Name	Symbol	Element Name	Symbol
Lithium	Li	Xenon	Xe
Magnesium	Mg	Zinc	Zn
Manganese	Mn	Zirconium	Zr

The elements are grouped together in a special chart called the periodic table of all the elements. A simple periodic table is shown in Figure 1.6.2, while one may view a more extensive periodic table from another source. The elements on the periodic table are listed in order of ascending atomic number. The periodic table has a special shape that will become important to us when we consider the organization of electrons in atoms (Chapter 8). One immediate use of the periodic table helps us identify metals and nonmetals. Nonmetals are in the upper right-hand corner of the periodic table, on one side of the heavy line splitting the right-side part of the chart. All other elements are metals.

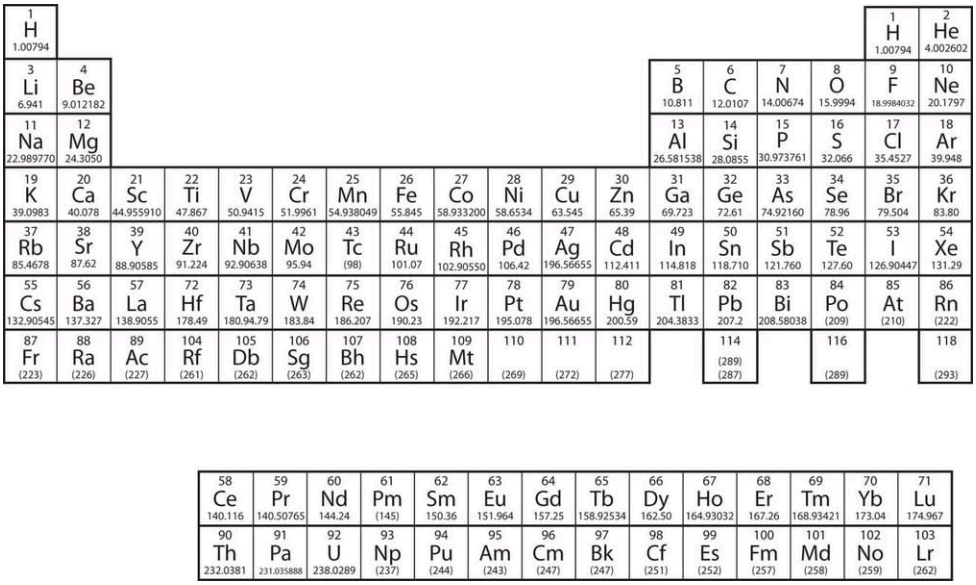


Figure 1.6.1: A Simple Periodic Table

There is an easy way to represent isotopes using the atomic symbols. We use the construction:

$$ {}^{A}_{Z}\mathrm{X} $$

where X is the symbol of the element, A is the mass number, and Z is the atomic number. Thus, for the isotope of carbon that has 6 protons and 6 neutrons, the symbol is:

$$ {}^{12}_{6}\mathrm{C} $$

where C is the symbol for the element, 6 represents the atomic number, and 12 represents the mass number.

Example 1.6.2

a. What is the symbol for an isotope of uranium that has an atomic number of 92 and a mass number of 235?
b. How many protons and neutrons are in $ {}^{56}_{26}\mathrm{Fe} $

Solution

a. The symbol for this isotope is $ {}^{235}_{92}\mathrm{U} $
b. This iron atom has 26 protons and 56 – 26 = 30 neutrons.

Exercise 1.6.2

How many protons are in $^{23}_{11}\mathrm{Na}$

Answer available at the end of this section.

It is also common to state the mass number after the name of an element to indicate a particular isotope. *Carbon-12* represents an isotope of carbon with 6 protons and 6 neutrons, while *uranium-238* is an isotope of uranium that has 146 neutrons.

Key Takeaways

- Chemistry is based on the modern atomic theory, which states that all matter is composed of atoms.
- Atoms themselves are composed of protons, neutrons, and electrons.
- Each element has its own atomic number, which is equal to the number of protons in its nucleus.
- Isotopes of an element contain different numbers of neutrons.
- Elements are represented by an atomic symbol.
- The periodic table is a chart that organizes all the elements.

Answers

Exercise 1.6.1

Atomic number = 50, mass number = 118

Exercise 1.6.2

11 protons

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1.7: 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.

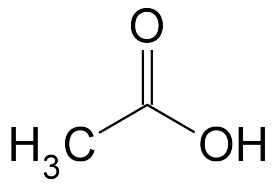


Figure 1: The structural formula of acetic acid, whose molecular formula is CH_3COOH.

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.

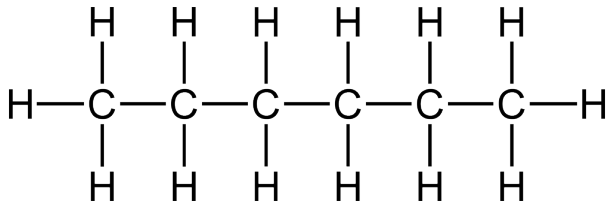
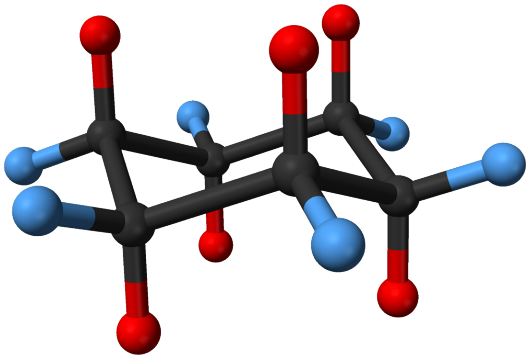
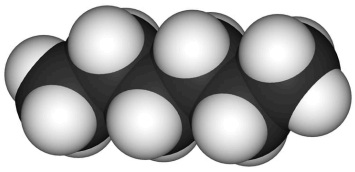


Figure 2: The structural formula of hexane. By referring to the structural formula and emphasizing where bonding occurs, one can ascertain a condensed structural formula of $CH_3CH_2CH_2CH_2CH_2CH_3$.

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.

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1.8: Polyatomic Ions

The compound NaOH has wide industrial use and is the active ingredient in drain cleaners. Based on the discussion in the previous section, we would expect NaOH to be an ionic compound because it contains sodium, a Group 1A metal. Hydrogen and oxygen, however, are nonmetals, and we would expect these to bond together covalently. This compound, called sodium hydroxide, is an example of an ionic compound formed between a metal ion (sodium) and a *polyatomic ion* (HO^-). Charged groups of atoms, like HO^-, that are bonded together covalently are called **polyatomic ions**. Within an ionic compound a polyatomic behaves as a single unit forming salts with other cations or anions.

Using the rules described in Section 3.2, we can draw a Lewis diagram for HO^-. Oxygen has six valence electrons and hydrogen has one, for a total of seven. The central atom in our structure will be hydrogen (it is to the *left* of oxygen in the periodic table). Next, because this is a polyatomic ion with a single negative charge, we add the extra electron to the central atom, pair the electrons and then draw the two atoms bonded together. Next, the six remaining electrons are distributed around the oxygen to form an octet. Finally, the polyatomic ion is enclosed in brackets with the charge as a superscript to show that the ion behaves as a single unit.

Polyatomic ions are very common in chemistry. It is *essential* that you memorize these and be able to correlate the name, the composition and the charge for each of them, as they will be discussed freely throughout the remainder of the course and you will be expected to know these in General Chemistry.

Example 1.8.1:

Construct a Lewis diagram for the polyatomic ion CO_3^{2-}.

Solution

Oxygen has six valence electrons and carbon has four; therefore in CO_3^{2-} there will be a total of 22 valence electrons, plus two additional electrons from the 2- charge. The central atom in our structure will be carbon (it is to the *left* of oxygen in the periodic table). Next, we draw the carbon (our central atom) with its' four electrons and add the additional two electrons from the charge. The three oxygens are placed around the carbon and the electrons are arranged to form the three covalent bonds. Next, the 18 remaining electrons are distributed around the oxygens so that they all have a full octet. The carbon, however, is only surrounded by six electrons. To remedy this, we move one electron pair in to form a double bond to one of the oxygen atoms. Finally, the polyatomic ion is enclosed in brackets with the charge as a superscript.

We need to understand that the process of placing electrons into a particular bond in a compound is an *artificial* aspect of building Lewis diagrams. In fact, the electrons are added to the polyatomic ion, but it is *impossible* to know exactly where they went.

Exercise 1.8.1

a. Draw Lewis diagrams for NO_2^- and NH_4^+.

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1.9: 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 1.9.1). 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.

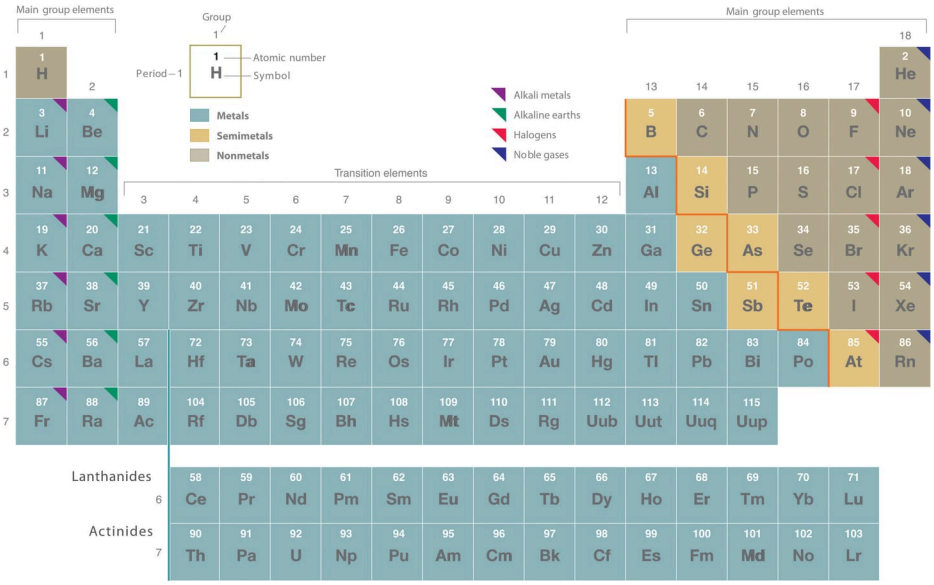


Figure 1.9.1: The Periodic Table Showing the Elements in Order of Increasing Z. The metals are on the bottom left in the periodic table, and the nonmetals are at the top right. The semimetals lie along a diagonal line separating the metals and nonmetals. An interactive Periodic table can be found Periodic 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 1.9.1 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 1.9.1: 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 1.9.1 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 1.9.1, 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 1.9.1

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

Answer available at the end of this section.

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.

Answers

Exercise 1.9.1

metal

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1.10: Measurement and Scale - The Mole Concept

One of the important concepts to grasp in chemistry is *scale*. Atoms and molecules are very small. A single atom of hydrogen has a mass of about 1.67 x 10^{-24} grams (that's 0.000000000000000000000000167 grams). One cubic centimeter of water (one mL) contains about 3.3 x 10^{22} water molecules (that's 33 sextillion molecules). Because chemists routinely use numbers that are both incredibly small and incredibly large, unique units of measurement have been developed to simplify working with these numbers. As we learned in Chapter 1, the atomic mass unit (amu) helps us talk about the mass of atoms on a scale appropriate to atoms (one grams is about 600 sextillion amu). In this chapter, we will introduce the concept of a mole to help us talk about numbers of atoms on a scale appropriate to the size of a sample we could work with in a laboratory (for example, in grams). The **mole** is defined as the number of atoms contained in *exactly* 12 grams of carbon-12 (the isotope $^{12}_{6}\mathrm{C}$). Chemist have measured this number and it turns out to be 6.0221415 x 10^{23}. We can think of the term *mole* as a number, just like the word *dozen* represents the number 12. We will use the mole to represent this very large number (a *chemist's dozen*) and we will see that there is a special relationship between a mole of a pure substance and the mass of the substance measured in amu.

The origin of the mole concept is generally attributed to the Italian chemical physicist, Amadeo Avogadro. In 1811, Avogadro published an important article that drew a distinction between atoms and molecules (although these terms were not in use at the time). As part of his explanation of the behavior of gasses, he suggested *that equal volumes of all gases at the same temperature and pressure contained the same number of molecules*. This statement is referred to as **Avogadro's Hypothesis** and today we commonly refer to the number of *things* in a mole, (6.0221415 x 10^{23}) as **Avogadro's number** (this is rounded to 6.02 x 10^{23} for most calculations). Because a mole can be thought of as a *number*, you can convert any number to moles by dividing that number by 6.02 x 10^{23}. For example, at the time of this writing, the national debt of the United States is about 7.9 trillion dollars (7.9 x 10^{12} dollars). This could be expressed as *moles of dollars* as shown below:

$$(7.9 \times 10^{12} dollars)\left(\frac{1\ mol\ dollars}{6.02 \times 10^{23} dollars}\right) = 1.3 \times 10^{-11}\ mol\ dollars$$

The ratio of any number to the number of things in a mole is often referred to as a **mole fraction**.

Exercise 1.10.1

a. It is estimated there are 7 x 10^{22} stars in the universe. How many moles of stars is this?
b. It is estimated there are 7.5 x 10^{18} grains of sand on the earth. How many moles of sand grains is this?
c. You have 0.0555 moles of jelly donuts. What number of donuts would that be?
d. You drink a small bottle of drinking water that contains 13 moles of water. What is the number of molecules of water you drank?

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1.11: Molar Mass

As we described in Section 4.1, in chemistry, the term **mole** can be used to describe a particular number. The number of things in a mole is large, *very* large (6.0221415×10^{23}). We are all familiar with common copy-machine paper that comes in 500 sheet reams. If you stacked up 6.02×10^{23} sheets of this paper, the pile would reach from the earth to the moon **80 billion times**! The mole is a *huge* number, and by appreciating this, you can also gain an understanding of how *small* molecules and atoms really are.

Chemists work simultaneously on the level of individual atoms, and on the level of samples large enough to work with in the laboratory. In order to go back and forth between these two scales, they often need to know how many atoms or molecules there are in the sample they're working with. The concept that allows us to bridge these two scales is **molar mass**. Molar mass is defined **as the mass in grams of one mole of a substance**. The units of molar mass are grams *per* mole, abbreviated as **g/mol**.

The mass of a single isotope of any given element (the **isotopic atomic mass**) is a value relating the mass of that isotope to the mass of the isotope carbon-12 ($^{12}_{6}\mathrm{C}$); a carbon atom with six proton and six neutrons in its' nucleus, surrounded by six electrons. The **atomic mass** of an element is the relative average of *all* of the naturally occurring isotopes of that element and atomic mass is the number that appears in the periodic table. We have defined a mole based on the isotopic atomic mass of carbon-12. By definition, the *molar mass* of carbon-12 is numerically the same, and is therefore *exactly* 12 grams. Generalizing this definition, **the molar mass of any substance in grams *per* mole is numerically equal to the mass of that substance expressed in atomic mass units**. For example, the *atomic mass* of an oxygen atom is 16.00 amu; that means the *molar mass* of an oxygen atom is 16.00 g/mol. Further, if you have 16.00 grams of oxygen atoms, you know from the definition of a mole that your sample contains 6.022×10^{23} oxygen atoms.

The concept of molar mass can also be applied to compounds. For a molecule (for example, nitrogen, N_2) the mass of molecule is the sum of the atomic masses of the two nitrogen atoms. For nitrogen, the mass of the N_2 molecule is simply (14.01 + 14.01) = 28.02 amu. This is referred to as the **molecular mass** and the molecular mass of any molecule is simply the sum of the atomic masses of all of the elements in that molecule. The molar mass of the N_2 molecule is therefore 28.02 g/mol. For compounds that are *not molecular* (ionic compounds), it is improper to use the term "molecular mass" and "**formula mass**" is generally substituted. This is because there are no individual molecules in ionic compounds. However when talking about a mole of an ionic compound we will still use the term molar mass. Thus, the *formula* mass of calcium hydrogen carbonate is 117.10 amu and the *molar* mass of calcium hydrogen carbonate is 117.10 grams per mole (g/mol).

Exercise 1.11.1

Find the molar mass of each of the following compounds:

- Sand - silicon dioxide (SiO_2)
- Draino - sodium hydroxide (NaOH)
- Nutrasweet - Aspartame ($C_{14}H_{18}N_2O_5$)
- Bone phosphate - calcium phosphate $Ca_3(PO_4)_2$

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1.12: Mole-Mass Conversions

As described in the previous section, molar mass is expressed as "grams *per* mole". The word *per* in this context implies a mathematical relationship between grams and mole. Think of this as a ratio. The fact that a *per* relationship, ratio, exists between grams and moles implies that you can use dimensional analysis to interconvert between the two. For example, if we wanted to know the mass of 0.50 mole of molecular hydrogen (H_2) we could set up the following equations:

The ***known*** molar mass of H_2 is:

$$\left(\frac{2.06g\ H_2}{1\ mol\ H_2}\right)$$

We are ***given*** that we have 0.50 moles of H_2 and we want to ***find*** the number of grams of H_2 that this represents. To perform the dimensional analysis, we arrange the *known* and the *given* so that the units cancel, leaving only the units of the item we want to *find*.

$$(0.5mol\ H_2) \times \left(\frac{2.06g\ H_2}{1\ mol\ H_2}\right) = x\ g\ H_2 = 1.0g\ H_2$$

Exercise 1.12.1

a. Determine the mass of 0.752 mol of H_2 gas.
b. How many *moles* of molecular hydrogen are present in 6.022 grams of H_2?
c. If you have 22.414 grams of Cl_2, how many *moles* of molecular chlorine do you have?

We can also use what is often called a *per* relationship (really just a **ratio**) to convert between number of *moles* and the number to *things* (as in 6.02 x 10^{23} *things per mole*). For example, if we wanted to know how many *molecules* of H_2 are there in 3.42 moles of H_2 gas we could set up the following equations:

The ***known*** ratio of molecules *per* mole is :

$$\left(\frac{6.02 \times 10^{23} molecules\ H_2}{1\ mol\ H_2}\right)$$

We are ***given*** that we have 3.42 moles of H_2 and we want to ***find*** the number of molecules of H_2 that this represents. To perform the dimensional analysis, we arrange the *known* and the *given* so that the units cancel, leaving only the units of the item we want to *find*.

$$(3.42mol\ H_2) \times \left(\frac{6.02 \times 10^{23} molecules\ H_2}{1\ mol\ H_2}\right) = x\ molecules\ H_2 = 2.06 \times 10^{24}\ molecules\ H_2$$

And finally, we can combine these two operations and use the *per* relationships to convert between *mass* and the *number* of atoms or molecules. For example, if we wanted to know how many *molecules* of H_2 are there in 6.022 *grams* of H_2 gas we could set up the following series of equations:

The ***known*** molar mass of H_2 is

$$\left(\frac{2.016gH_2}{1molH_2}\right)$$

The ***known*** ratio of molecules *per* mole is

$$\left(\frac{6.02 \times 10^{23} molecules\ H_2}{1\ mol\ H_2}\right)$$

We are ***given*** that we have 6.022 grams of H_2 and we want to ***find*** the number of molecules of H_2 that this represents. As always, to perform the dimensional analysis, we arrange the *known* ratios and the *given* so that the units cancel, leaving only the units of the item we want to *find*.

$$(6.022 g H_2) \times \left(\frac{1 mol H_2}{2.016 g H_2}\right) \times \left(\frac{6.02 \times 10^{23} molecules\ H_2}{1\ mol\ H_2}\right) = x\ molecules\ H_2 = 1.80 \times 10^{24}$$

Exercise 1.12.1

a. A sample of molecular chlorine is found to contain 1.0 x 10^{20} molecules of Cl_2. What is the *mass* (in grams) of this sample?
b. How many moles of sand, silicon dioxide (SiO_2), and how many molecules of sand are found in 1.00 pound (454g) of sand?
c. You add 2.64 x 10^{23} molecules of sodium hydroxide (Drano™; NaOH), to your drain. How many moles are this and how many grams?

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1.13: Concentration and Molarity

As described in the previous section, sodium chloride is quite soluble in water. At 25 ˚C (about room temperature), 359 grams of sodium chloride will dissolve in one liter of water. If you were to add more sodium chloride to the solution, it would not dissolve, because a given volume of water can only dissolve, disperse and stabilize a fixed amount of solute (the stuff that dissolves). This amount is different for every compound and it depends on the structure of the particular compound and how that structure interacts with the solvation shell. When a substance is dissolved in water to the point that no more will go into solution, we say the solution is **saturated**. For most compounds, heating the solution will allow more of the substance to dissolve, hence it is important to note the temperature when you are speaking of the solubility of a particular compound.

If we had a saturated solution of sodium chloride at 25 ˚C, we could quote the concentration as 359 grams/L, but because we know the molar mass of sodium chloride (58.44 grams/mole), we could also express our concentration as:

$$\left(\frac{(359\,g) \times \frac{1\,mole}{58.44\,g}}{1\,L} \right) = 6.14\,moles/L$$

In chemistry, the units of moles/L are called **molarity**, with the abbreviation M. Thus we could say that our saturated solution of sodium chloride was **6.14 molar**, or **6.14 M**.

The advantage of expressing concentrations in terms of molarity is that these solutions can now be used in chemical reactions of known stoichiometry because any volume of the solution corresponds directly to a known number of moles of a particular compound. For example, the molar mass of potassium bromide is 119.0 g/mole. If we dissolved 119.0 grams of KBr in 1.000 L of water, the concentration would be 1.000 mole/L, or 1.000 M. If we now took half o this solution (0.500 L) we know that we would also have 0.500 moles of KBr.

We can determine the concentration of a solution using the problem-solving algorithm we introduced back in Chapter 1. For example, if you wan to find the molarity of a solution containing 42.8 grams of KBr in 1.00 L of water, you would identify the *given* and 42.8 g, your *ratio* is the molar mass (119 g/mole) and you want to *find* molarity (or moles/L). Remembering to set the equation up so that the units of *given* appear in the denominator of the *ratio*, the number of moles is:

$$42.8\,g) \times \left(\frac{1\,mole}{119\,g} \right) = 0.360\,moles$$

and, the molarity is:

$$\left(\frac{0.360\,mole}{1.00\,L} \right) = 0.360\,moles/L\ or\ 0.360\,M$$

When you become comfortable with the simple two-step method, you can combine steps and simply divide your given mass by the given volume to get the result directly. Thus, if you had 1.73 grams of KBr in 0.0230 L of water, your concentration would be:

$$\left(\frac{(1.73\,g) \times \frac{1\,mole}{119\,g}}{0.0230\,L} \right) = 6.32\,moles/L\ or\ 0.632\,M$$

We can also solve these problems *backwards,* that is, convert molarity into mass. For example; determine the number of grams of KBr that are present in 72.5 mL of a 1.05 M solution of KBr. Here we are given a volume of 0.0725 L and our ratio is the molarity, or (1.05 moles/L). We first solve for moles,

$$0.0725\,L \times \left(\frac{1.05\,mole}{1.00\,L} \right) = 0.0761\,moles$$

and then convert to mass using:

$$0.0761\,moles \times \left(\frac{119\,grams}{1\,mole} \right) = 9.06\,grams\,of\,KBr$$

Exercise 1.13.1

A sample of 12.7 grams of sodium sulfate (Na_2SO_4) is dissolved in 672 mL of distilled water.

a. What is the molar concentration of sodium sulfate in the solution?
b. What is the concentration of sodium ion in the solution?

Exercise 1.13.1

Calculate the mass of sodium chloride required to make 125.0 mL of a 0.470 M NaCl solution. If you dissolve 5.8g of NaCl in water and then dilute to a total of 100.0 mL, what will be the molar concentration of the resulting sodium chloride solution?

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1.14: 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).

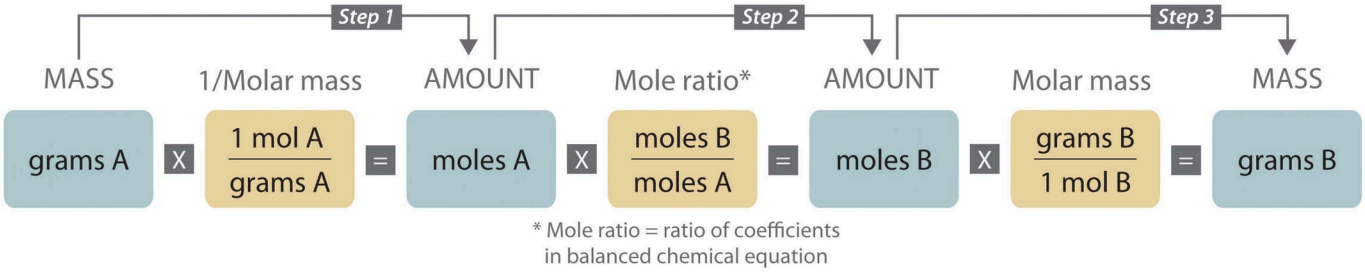


Figure 1.14.1: A Flowchart for Stoichiometric Calculations Involving Pure Substances. The molar masses of the reactants and the products are used as conversion factors so that you can calculate the mass of product from the mass of reactant and vice versa.

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:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \tag{1.14.1}$$

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

$$moles\,CO_2 = mol\,glucose \times \frac{6\,mol\,CO_2}{1\,mol\,glucose}$$

$$= 0.251\,mol\,glucose \times \frac{6\,mol\,CO_2}{1\,mol\,glucose}$$

$$= 1.51\,mol\,CO_2$$

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 1.14.1, the mass of one reactant that is required to consume a given mass of another reactant.

Example 1.14.1: 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 1.14.1: 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 available at the end of this section.

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 1.14.2. 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.

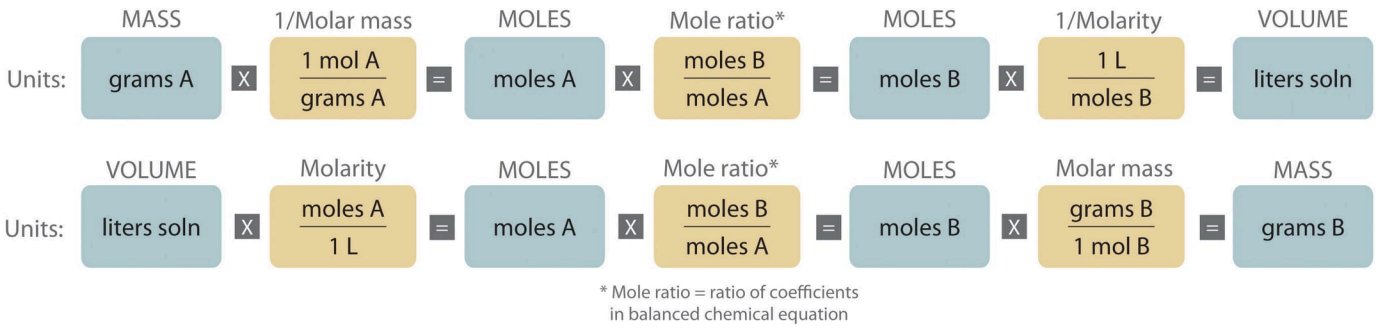


Figure 1.14.2: An Expanded Flowchart for Stoichiometric Calculations. Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in a balanced chemical equation.

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 1.14.2 : 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

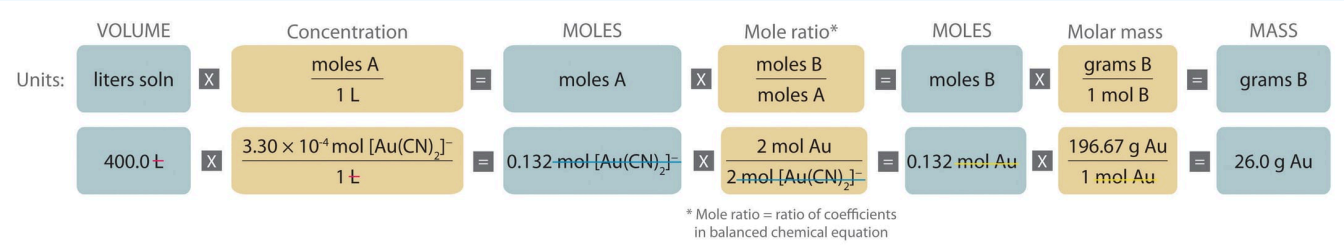
Strategy:

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 1.14.2 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:

$$moles\ [Au(CN)_2]^- = V_L M_{mol/L} \tag{1.14.2}$$

$$= 400.0\ \cancel{L}\left(\frac{3.30 \times 10^{4-}\ mol\ [Au(CN)_2]^-}{1\ \cancel{L}}\right) = 0.132\ mol\ [Au(CN)_2]^- \tag{1.14.3}$$

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:

$$mass\ of\ Au = (moles\ Au)(molar\ mass\ Au) \tag{1.14.4}$$

$$= 0.132\ \cancel{mol\ Au}\left(\frac{196.97\ g\ Au}{1\ \cancel{mol\ Au}}\right) = 26.0\ g\ Au \tag{1.14.5}$$

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

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

Exercise 1.14.2 : Lanthanum Oxalate

What mass of solid lanthanum(III) oxalate nonahydrate $[La_2(C_2O_4)_3 \bullet 9H_2O]$ 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 available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

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.

Answers

Exercise 1.14.1**: Roasting Cinnabar**

86.2 g

Exercise 1.14.2 **: Lanthanum Oxalate**

3.89 g

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1.15: 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.

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

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

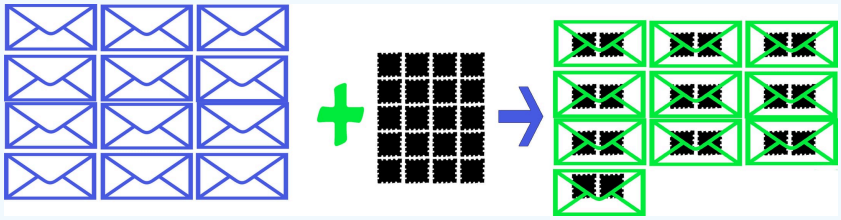
The equation for this can be written as

$$\mathrm{I} + 2\,\mathrm{S} \rightarrow \mathrm{IS}_2$$

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 I x (1IS_2/1I) = 12 IS_2 possible

20 S x (1IS_2/2S) = 10 IS_2 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:

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

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.

Volume x (Mass/Volume) = Mass

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

10 g sample x (5 g carbon/100 g sample) = 0.5 g carbon

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.

$$\mathrm{C}_x\mathrm{H}_y\mathrm{O}_z\,(\mathrm{g}) + \mathrm{O}_2\,(\mathrm{g}) \rightarrow \mathrm{CO}_2\,(\mathrm{g}) + \mathrm{H}_2\mathrm{O}\,(\mathrm{g})$$

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.

0.0333mol CO_2 (1mol C/ 1mol CO_2) = 0.0333mol C in unknown

0.599g H_2O (1mol H_2O/ 18.01528g H_2O)(2mol H/ 1mol H_2O) = 0.0665 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:

0.0333mol CO_2 (2mol O/1mol CO_2) = 0.0666 mol O

Moles of oxygen in H_2O:

0.599g H_2O (1mol H_2O/18.01528 g H_2O)(1mol O/1mol H_2O) = 0.0332 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.

0.333mol CO_2(44.0098g CO_2/ 1mol CO_2) = 1.466g CO_2

1.466g CO_2 + 0.599g H_2O - 1.000g unknown organic = 1.065g O_2

Moles of oxygen in O_2

1.065g O_2(1mol O_2/ 31.9988g O_2)(2mol O/1mol O_2) = 0.0666mol O

Moles of oxygen in unknown

(0.0666mol O + 0.0332 mol O) - 0.0666mol O = 0.0332 mol O

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

(1/0.0332)(0.0333mol C : 0.0665mol H : 0.0332 mol O) => 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.

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

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.

$$(120.056\ g/mol) / (30.026\ g/mol) = 3.9984$$

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.

$$CH_2O * 4 = ?$$

$$C: 1 * 4 = 4$$

$$H: 2 * 4 = 8$$

$$O\ 1 * 4 = 4$$

$$CH_2O * 4 = C_4H_8O_4$$

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

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

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

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

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

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

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).

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

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 = 1.203cm^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.

1.203cm^3 alloy(1liter alloy/1000cm^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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Contributors and Attributions

- Joseph Nijmeh (UCD), Mark Tye (DVC)

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1.16: 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

$$1\,\text{box mix} + 2\,\text{eggs} \rightarrow 1\,\text{batch brownies} \tag{1.16.1}$$

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.

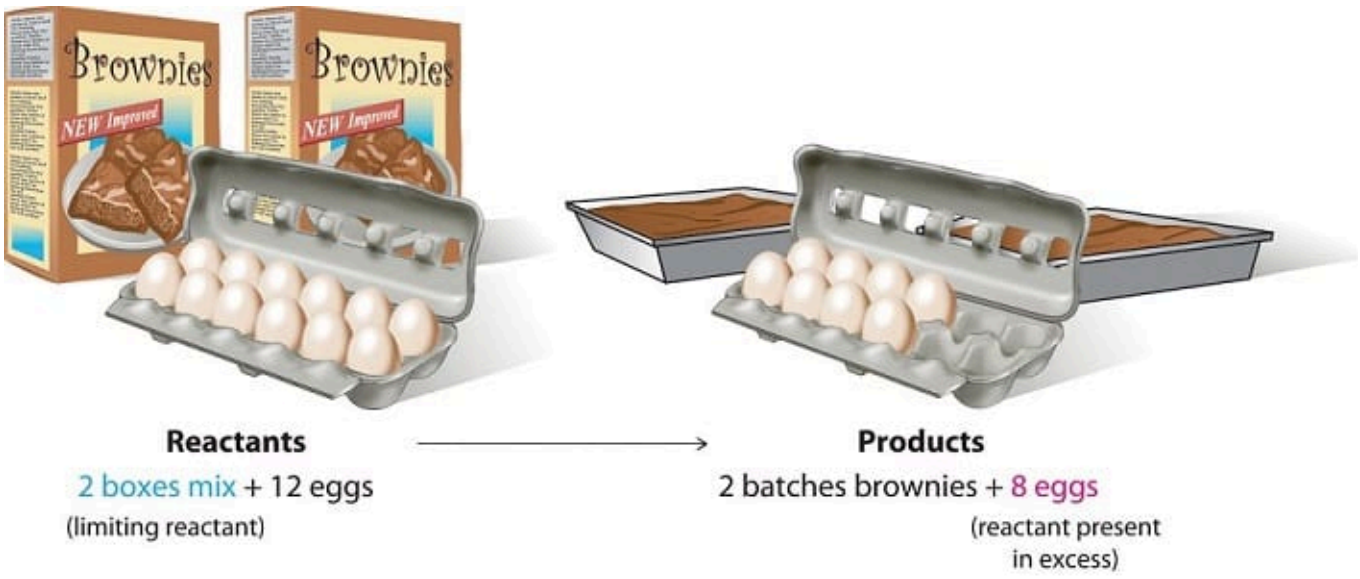


Figure 1.16.1: The Concept of a Limiting Reactant in the Preparation of Brownies

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.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

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.

$$\mathrm{TiO_2\,(s) + Cl_2\,(g)} \rightarrow \mathrm{TiCl_4\,(g) + CO_2\,(g)}$$

Titanium tetrachloride is then converted to metallic titanium by reaction with molten magnesium metal at high temperature:

$$\mathrm{TiCl_4\,(g) + 2\ Mg\,(l)} \rightarrow \mathrm{Ti\,(s) + 2\ MgCl_2\,(l)} \tag{1.16.2}$$

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 1.16.2: 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 1.16.2?

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:

$$\begin{aligned} \text{moles } \mathrm{TiCl_4} &= \frac{\text{mass } \mathrm{TiCl_4}}{\text{molar mass } \mathrm{TiCl_4}} \\ &= 1000 \cancel{g}\ \mathrm{TiCl_4} \times \frac{1\, mol\ TiCl_4}{189.679 \cancel{g}\ \mathrm{TiCl_4}} \\ &= 5.272\, mol\ \mathrm{TiCl_4} \end{aligned} \tag{1.16.3}$$

$$\begin{aligned} \text{moles } \mathrm{Mg} &= \frac{\text{mass } \mathrm{Mg}}{\text{molar mass } \mathrm{Mg}} \\ &= 200 \cancel{g}\ \mathrm{Mg} \times \frac{1\, mol\, \mathrm{Mg}}{24.305 \cancel{g}\ \mathrm{Mg}} \\ &= 8.23\, \mathrm{mol\ Mg} \end{aligned} \tag{1.16.4}$$

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:

$$TiCl_4 : \frac{5.272\,mol\,(actual)}{1\,mol\,(stoich)} = 5.272$$

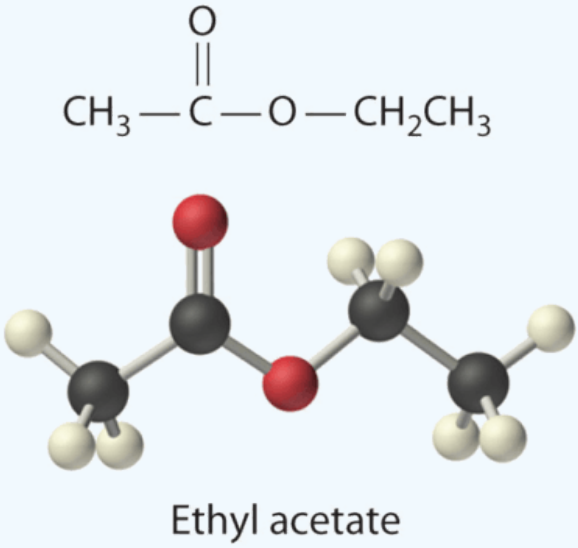
$$Mg : \frac{8.23\,mol\,(actual)}{2\,mol\,(stoich)} = 4.12$$

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 1.16.1 demonstrates.

Example 1.16.1: 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.



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):

$$\begin{aligned}
\text{moles } C_2H_5OH &= \frac{\text{mass } C_2H_5OH}{\text{molar mass } C_2H_5OH} \\
&= \frac{(\text{volume } C_2H_5OH) \times (\text{density } C_2H_5OH)}{\text{molar mass } C_2H_5OH} \\
&= 10.0 \cancel{ml}\ {}_2CH_5OH \times \frac{0.7893 \cancel{g}\ C_2H_5OH}{1 \cancel{ml}\ C_2H_5OH} \times \frac{1\,mol\ C_2H_5OH}{46.07 \cancel{g}\ C_2H_5OH} \\
&= 0.171\,mol\ {}_2CH_5OH \\
\text{moles } CH_3CO_2H &= \frac{\text{mass } CH_3CO_2H}{\text{molar mass } CH_3CO_2H} \\
&= \frac{(\text{volume } CH_3CO_2H) \times (\text{density } CH_3CO_2H)}{\text{molar mass } CH_3CO_2H} \\
&= 10.0 \cancel{ml}\ CH_3CO_2H \times \frac{1.0492 \cancel{g}\ CH_3CO_2H}{1 \cancel{ml}\ CH_3CO_2H} \times \frac{1\,mol\ CH_3CO_2H}{60.05 \cancel{g}\ CH_3CO_2H} \\
&= 0.175\,mol\ CH_3CO_2H
\end{aligned}$$

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:

$$\begin{aligned}
moles \text{ ethyl acetate} &= mol \text{ ethanol} \times \frac{1\,mol \text{ ethyl acetate}}{1\,mol \text{ ethanol}} \\
&= 0.171\,mol\ {}_2CH_5OH \times \frac{1\,mol\ CH_3CO_2C_2H_5}{1\,mol\ C_2H_5OH} \\
&= 0.171\,mol\ {}_{322}CHCOCH_5
\end{aligned}$$

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:

$$\begin{aligned}
\text{mass of ethyl acetate} &= mol \text{ ethyl acetate} \times \text{molar mass ethyl acetate} \\
&= 0.171\,mol\ {}_{322}CHCOCH_5 \times \frac{88.11\,g\,CH_3CO_2C_2H_5}{1\,mol\,CH_3CO_2C_2H_5} \\
&= 15.1\,g\,CH_3CO_2C_2H_5
\end{aligned}$$

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:

$$\text{volume of ethyl acetate} = 15.1\,g\,CH_3CO_2C_2H_5 \times \frac{1\,ml\ CH_3CO_2C_2H_5}{0.9003\,g\ CH_3CO_2C_2H_5}$$

$$= 16.8\,ml\ {}_{322}CHCOCH_5$$

Exercise 1.16.1

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 P_4 and 30.0 g of S_8?

Answer available at the end of this section.

YouTube Video

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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

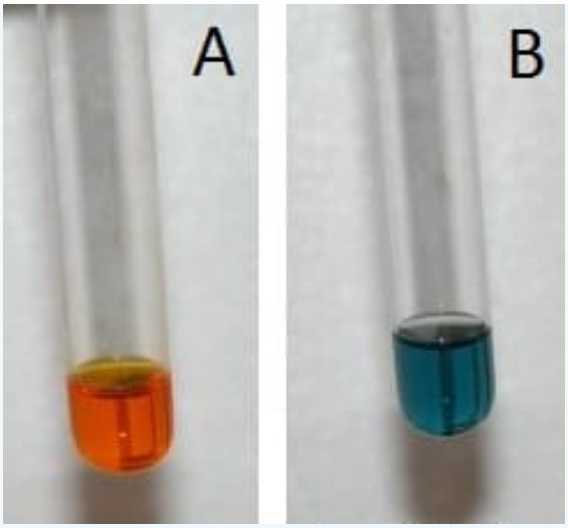
The concept of limiting reactants applies to reactions carried out in solution as well as to reactions involving pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example 1.16.2.

Example 1.16.2: 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:

$$3\,CH_3\ CH_2\ OH\,(aq) + 2\,\underset{yellow-orange}{Cr_2\ O_7{}^{2-}}(aq) + 16\,H^+\,(aq) \xrightarrow[H_2SO_4\,(aq)]{Ag^+} 3\,CH_3CO_2H\,(aq) + 4\,\underset{green}{Cr^{3+}}(aq) + 11\,H_2O\,(l)$$

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 $Cr_2O_7{}^{2-}$ 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 $Cr_2O_7{}^{2-}$ 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

$$moles\ of\ C_2H_5OH = (2.6 \times 10^{-6}\ \cancel{mol_{\ 2}CrO^{2-}}) \left(\frac{3\ mol\ C_2H_5OH}{2\ \cancel{mol_{\ 2}CrO^{2-}}} \right) = 3.9 \times 10^{-6}\ mol\ {}_2CH_5OH$$

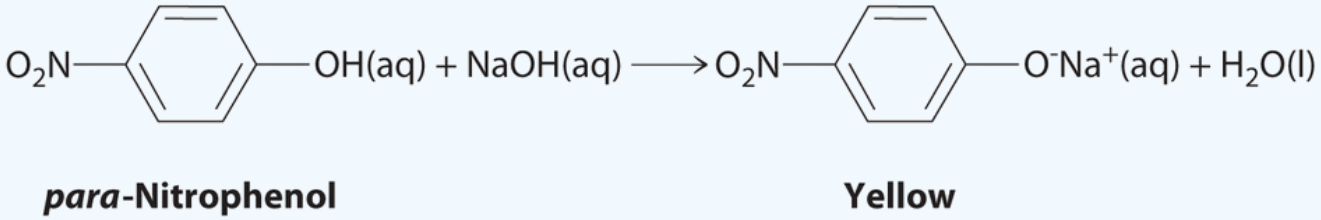
As indicated in the strategy, this number can be converted to the mass of C_2H_5OH using its molar mass:

$$mass\ {}_2CH_5OH = (3.9 \times 10^{-6}\ \cancel{mol\ {}_2CH_5OH}) \left(\frac{46.07\ g}{\cancel{mol\ {}_2CH_5OH}} \right) = 1.8 \times 10^{-4}\ g\ C_2H_5OH$$

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 1.16.2

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 available at the end of this section.

In Examples 1.16.1 and 1.16.2, 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 1.16.3.

Example 1.16.3

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:

$$2\,AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \rightarrow Ag_2Cr_2O_7\,(s) + 2\,KNO_3\,(aq)$$

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:

$$moles\ K_2Cr_2O_7 = 500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.17\ mol\ K_2Cr_2O_7}{1\ \cancel{L}}\right) = 0.085\ mol\ K_2Cr_2O_7$$

$$moles\ AgNO_3 = 250\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.57\ mol\ AgNO_3}{1\ \cancel{L}}\right) = 0.14\ mol\ AgNO_3$$

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 1.16.3

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 available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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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:

$$\text{percent yield} = \frac{\text{actual yield } (g)}{\text{theoretical yield } (g)} \times 100\% \tag{1.16.5}$$

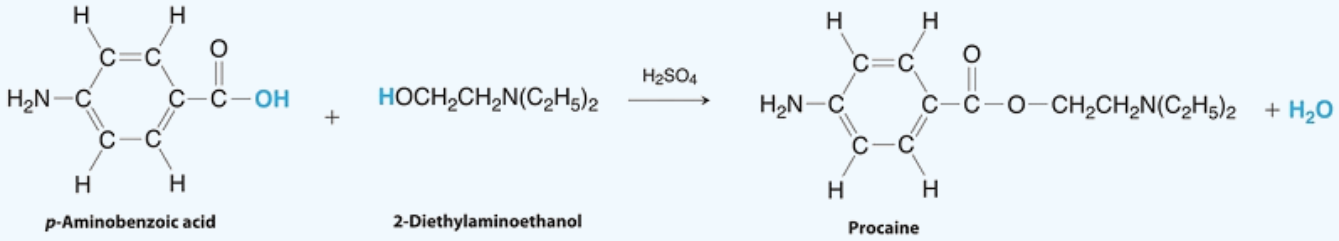
The method used to calculate the percent yield of a reaction is illustrated in Example 1.16.4.

Example 1.16.4: 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 1.16.5) 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 1.16.4: 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:

$$2\,PbS\,(s) + 3\,O_2 \rightarrow 2\,PbO\,(s) + 2\,SO_2\,(g)$$

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:

$$PbO\,(s) + C\,(s) \rightarrow Pb\,(l) + CO\,(g)$$

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 available at the end of this section.

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.

Answers

Exercise 1.16.1

35.9 g

Exercise 1.16.2

4.93×10^{-5} L or 49.3 µL

Exercise 1.16.3

3.4 g

Exercise 1.16.4**: Extraction of Lead**

89.2%

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2: ATOMIC STRUCTURE AND PERIODIC TRENDS

2.1: Electromagnetic Radiation
2.2: Quantum Theory
2.3: Atomic Spectra
2.4: The Bohr Atom
2.5: Two Ideas Leading to a New Quantum Mechanics
2.6: Wave Mechanics and Quantum Numbers
2.7: Electron Spin- A Fourth Quantum Number
2.8: Orbital Shapes and Energies
2.9: Polyelectronic Atoms
2.10: The History of the Periodic Table
2.11: Electron Configurations
2.12: Magnetic Properties
2.13: Sizes of Atoms and Ions
2.14: Ionization Energy
2.15: Electron Affinity
2.16: Electronegativity
2.17: Periodic Properties of the Elements

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2.1: Electromagnetic Radiation

Learning Objectives

- to learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves among the types of electromagnetic waves.

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.



Figure 2.1.1: A Wave in Water When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

Properties of Waves

A wave is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure 2.1.1). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

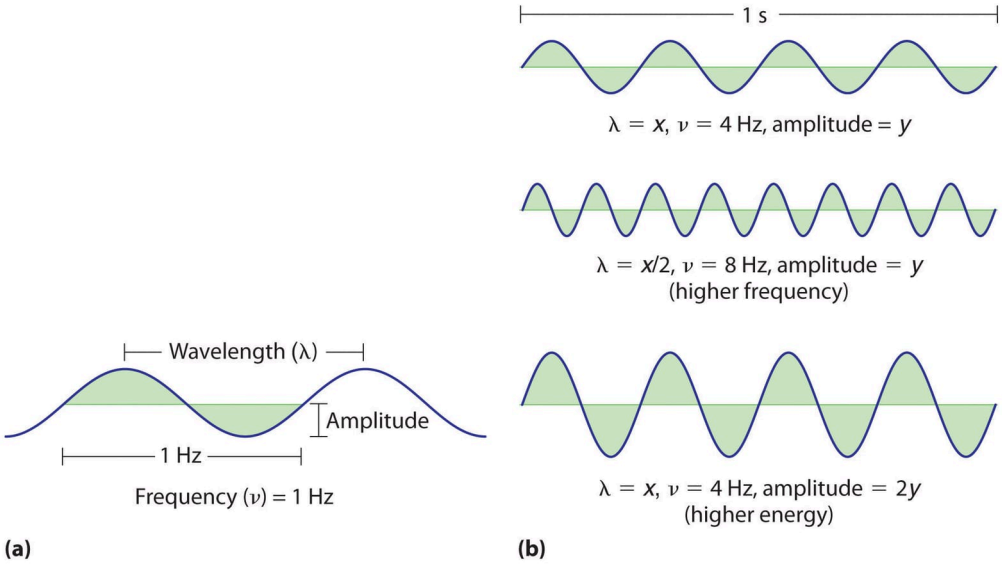


Figure 2.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 2.1.2). As you may have noticed in Figure 2.1.1, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the wavelength (λ), distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs. λ is the lowercase Greek lambda, and u is the lowercase Greek nu. Wavelengths are described by a unit of distance, typically meters. The frequency (ν), the number of oscillations (i.e., of a wave) that pass a particular point in a given period of time. of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations persecond (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894),a pioneer in the field of electromagnetic radiation. The amplitude (the vertical height of a wave, which is defined as half the peak-to-trough height), or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 2.1.2, two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), the distance traveled by a wave per unit time, which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

$$(\text{wavelength})(\text{frequency}) = speed \tag{2.1.1}$$

$$\lambda u = v \tag{2.1.2}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{wave}}{second}\right) = \frac{meters}{second} \tag{2.1.3}$$

Be careful not to confuse the symbols for the speed, v, with the frequency, u. Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as electromagnetic radiation, which is energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure 2.1.3). Some forms of electromagnetic radiation are shown in Figure 2.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which is the speed with which all forms of electromagnetic radiation travel in a vacuum, a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (which is about 3.00 ×10^8 m/s or 1.86 × 10^5 mi/s). This is about a million times faster than the speed of sound.

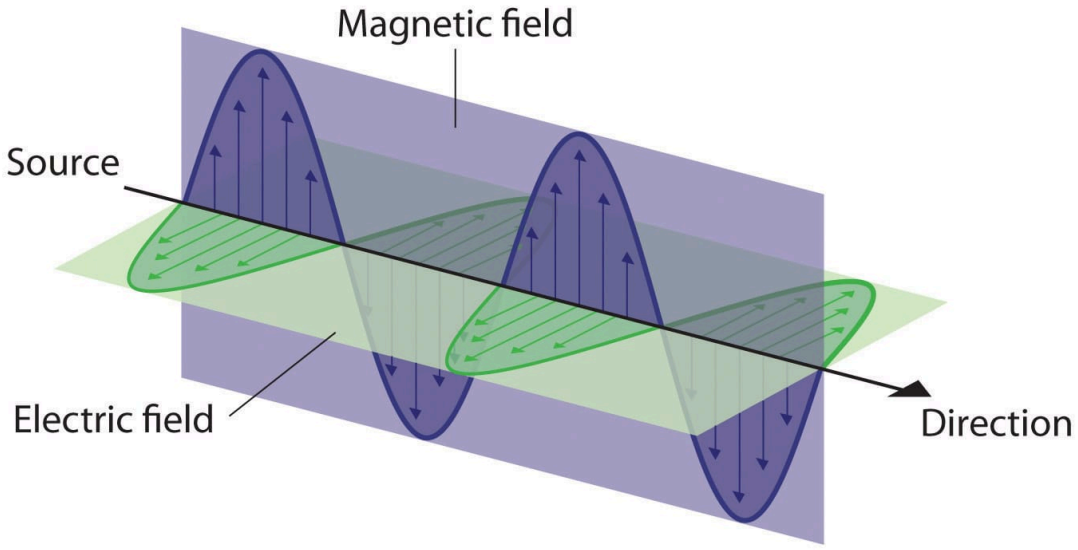


Figure 2.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (*c*), they differ in only wavelength and frequency. As shown in Figure 2.1.4 and Table 2.1.1, the wavelengths of familiar electromagnetic radiation range from 10^{1} m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing *v* with *c* in Equation 2.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda u$$
$$u = \frac{c}{\lambda} \tag{2.1.4}$$

For example, the frequency of radio waves is about 10^{8} Hz, whereas the frequency of gamma rays is about 10^{20} Hz. Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7×10^{-7} m (700 nm, or 4.3×10^{14} Hz) and 4×10^{-7} m (400 nm, or 7.5×10^{14} Hz). Note that when frequency increases, wavelength decreases; c being a constant stays the same. Similarly when frequency decreases, the wavelength increases.

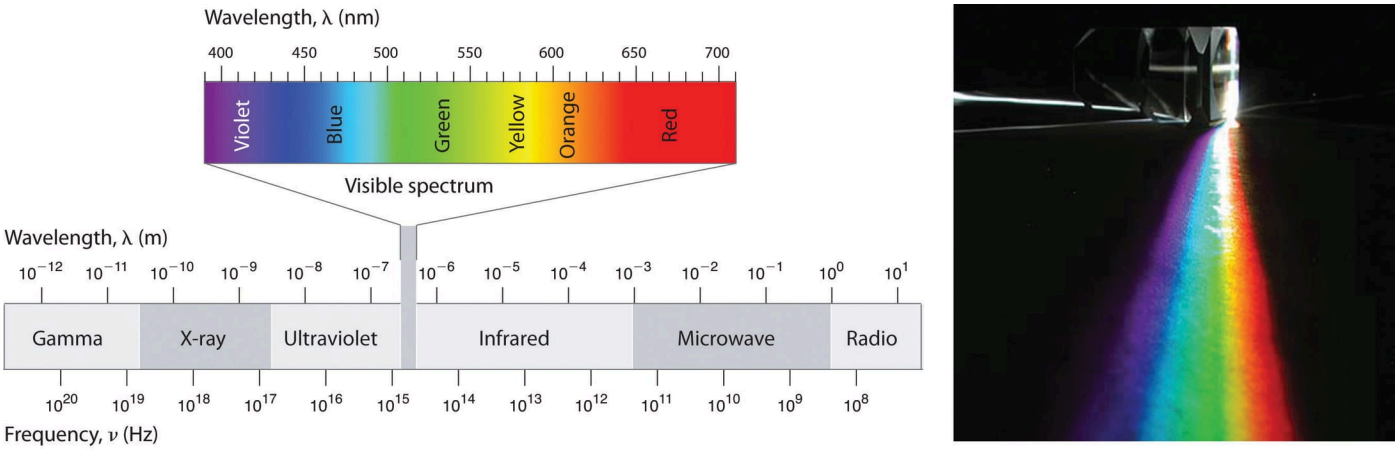


Figure 2.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum. (CC BY-NC-SA; anonymous)

Within this visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible

light—can be separated by a prism, as shown in part (b) in Figure 2.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 2.1.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	x-ray
micrometer	μm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto u \tag{2.1.5}$$

$$E \propto \frac{1}{\lambda} \tag{2.1.6}$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

> The energy of electromagnetic radiation **increases** with **increasing** frequency and **decreasing** wavelength.

Example 2.1.1

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 2.1.2 to calculate the wavelength in meters.

Solution:

From Equation 2.1.4, we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998 × 10^8 m/s:

$$\lambda\nu = c = 2.998 \times 10^8 m/s \tag{2.1.7}$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{u} = \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \cancel{MHz}}\right)\left(\frac{1\ \cancel{MHz}}{10^6\ \cancel{s^{-1}}}\right) = 2.965\ m \tag{2.1.8}$$

Exercise 2.1.1

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

Answer: 8.45 mm

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Electromagnetic Radiation: https://youtu.be/TZy7a69pP-w

Summary

Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A basic knowledge of the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A **wave** is a periodic oscillation by which energy is transmitted through space. All waves are **periodic**, repeating regularly in both space and time. Waves are characterized by several interrelated properties: **wavelength (λ)**, the distance between successive waves; **frequency (ν)**, the number of waves that pass a fixed point per unit time; **speed (*v*)**, the rate at which the wave propagates through space; and **amplitude**, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. **Electromagnetic radiation** consists of two perpendicular waves, one electric and one magnetic, propagating at the **speed of light (*c*)**. Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ in their frequencies and wavelengths.

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2.2: Quantum Theory

Learning Objectives

- To understand how energy is quantized.

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could *not* be explained by the theories available at the time.

Blackbody Radiation

One phenomenon that seemed to contradict the theories of classical physics was blackbody radiation, which is electromagnetic radiation whose wavelength and color that depends on the temperature of the object. The wavelength of energy emitted by an object depends on only its temperature, not its surface or composition. Hence an electric stove burner or the filament of a space heater glows dull red or orange when heated, whereas the much hotter tungsten wire in an incandescent light bulb gives off a yellowish light.



Figure 2.2.1: Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

The *intensity* of radiation is a measure of the energy emitted per unit area. A plot of the intensity of blackbody radiation as a function of wavelength for an object at various temperatures is shown in Figure 2.2.2. One of the major assumptions of classical physics was that energy increased or decreased in a smooth, continuous manner. For example, classical physics predicted that as wavelength decreased, the intensity of the radiation an object emits should increase in a smooth curve without limit at *all* temperatures, as shown by the broken line for 6000 K in Figure 2.2.2. Thus classical physics could not explain the sharp *decrease* in the intensity of radiation emitted at shorter wavelengths (primarily in the ultraviolet region of the spectrum), which was referred to as the "ultraviolet catastrophe." In 1900, however, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 2.2.2, so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum..

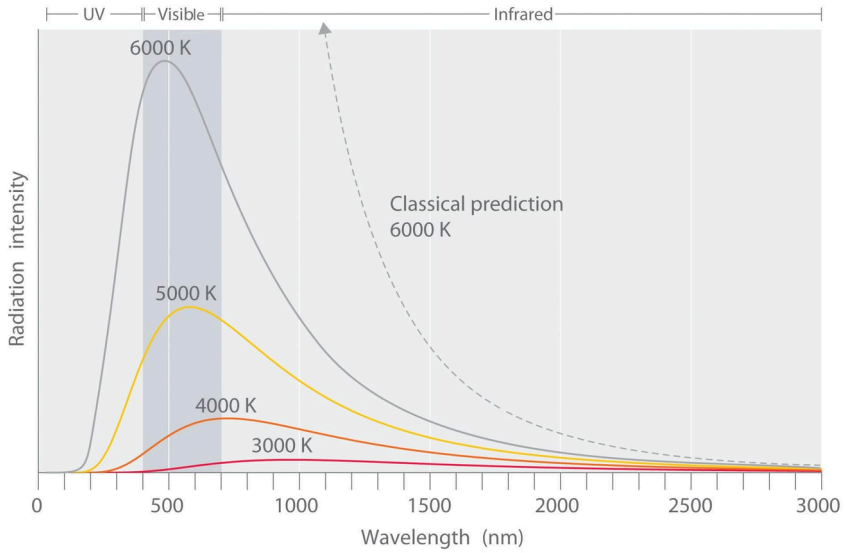
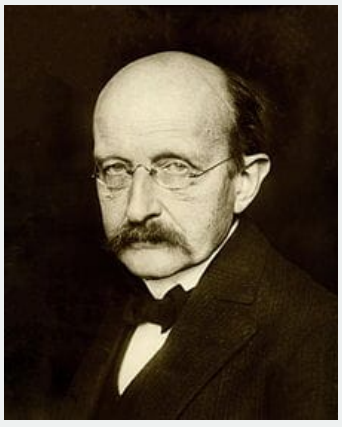


Figure 2.2.2: Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure 2.2.1 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun (Figure 2.2.1). Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity.

Max Planck (1858–1947)

In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.



One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler, and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

Although quantization may seem to be an unfamiliar concept, we encounter it frequently. For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. Even electrical charge is quantized: an ion may have a charge of –1 or –2 but *not* –1.33 electron charges.

Planck postulated that the energy of a particular quantum of radiant energy could be described Max Planck (1858–1947) by the

equation

$$E = hu \tag{2.2.1}$$

where the proportionality constant *h* is called Planck's constant, one of the most accurately known fundamental constants in science. For our purposes, its value to four significant figures is generally sufficient:

$$h = 6.626 \times 10^{-34} \text{ J•s (joule-seconds)}$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of *h*ν, Planck devised an equation that fit the experimental data shown in Figure 2.2.2. We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 2.2.2, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

The Photoelectric Effect

Only five years after he proposed it, Planck's quantization hypothesis was used to explain a second phenomenon that conflicted with the accepted laws of classical physics. When certain metals are exposed to light, electrons are ejected from their surface (Figure 2.2.3). Classical physics predicted that the number of electrons emitted and their kinetic energy should depend on only the intensity of the light, not its frequency. In fact, however, each metal was found to have a characteristic threshold frequency of light; below that frequency, no electrons are emitted regardless of the light's intensity. Above the threshold frequency, the number of electrons emitted was found to be proportional to the intensity of the light, and their kinetic energy was proportional to the frequency. This phenomenon was called the photoelectric effect (A phenomenon in which electrons are ejected from the surface of a metal that has been exposed to light).

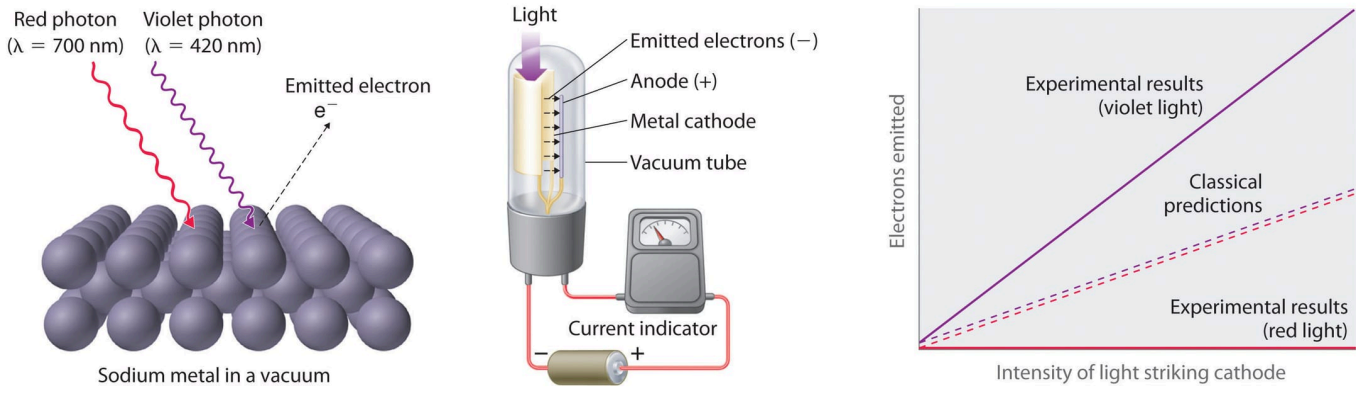


Figure 2.2.3: The Photoelectric Effect *(a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons are emitted and attracted to the anode, resulting in a flow of electrical current. If the incoming light is interrupted by, for example, a passing person, the current drops to zero. (c) In contrast to predictions using classical physics, no electrons are emitted when photons of light with energy less than E_0, such as red light, strike the cathode. The energy of violet light is above the threshold frequency, so the number of emitted photons is proportional to the light's intensity.*

Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) quickly realized that Planck's hypothesis about the quantization of radiant energy could also explain the photoelectric effect. The key feature of Einstein's hypothesis was the assumption that radiant

energy arrives at the metal surface in particles that we now call photons (a quantum of radiant energy, each of which possesses a particular energy energy *E* given by Equation 8.3.1 Einstein postulated that each metal has a particular electrostatic attraction for its electrons that must be overcome before an electron can be emitted from its surface ($E_o = h\nu_o$). If photons of light with energy less than E_o strike a metal surface, no single photon has enough energy to eject an electron, so no electrons are emitted regardless of the intensity of the light. If a photon with energy greater than E_o strikes the metal, then part of its energy is used to overcome the forces that hold the electron to the metal surface, and the excess energy appears as the kinetic energy of the ejected electron:

$$kinetic\ energy\ of\ ejected\ electron = E - E_o = hu - hu_o = h\,(u - u_o) \tag{2.2.2}$$

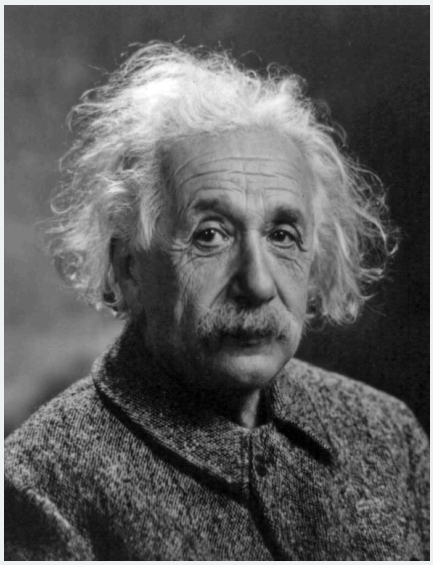
When a metal is struck by light with energy above the threshold energy E_o, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the number of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *frequency* of the light. Thus Einstein showed that the energy of the emitted electrons depended on the frequency of the light, contrary to the prediction of classical physics.



Figure 2.2.4: A Beam of Red Light Emitted by a Helium Neon laser reads a bar code. Originally Helium neon lasers, which emit red light at a wavelength of 632.8 nm, were used to read bar codes. Today, smaller, inexpensive diode lasers are used.

Albert Einstein (1879–1955)

In 1900, Einstein was working in the Swiss patent office in Bern. He was born in Germany and throughout his childhood his parents and teachers had worried that he might be developmentally disabled. The patent office job was a low-level civil service position that was not very demanding, but it did allow Einstein to spend a great deal of time reading and thinking about physics.



In 1905, his "miracle year" he published four papers that revolutionized physics. One was on the special theory of relativity, a second on the equivalence of mass and energy, a third on Brownian motion, and the fourth on the photoelectric effect, for which he received the Nobel Prize in 1921, the theory of relativity and energy-matter equivalence being still controversial at the time

Planck's and Einstein's postulate that energy is quantized is in many ways similar to Dalton's description of atoms. Both theories

are based on the existence of simple building blocks, atoms in one case and quanta of energy in the other. The work of Planck and Einstein thus suggested a connection between the quantized nature of energy and the properties of individual atoms.

Example 2.2.1

A ruby laser, a device that produces light in a narrow range of wavelengths emits red light at a wavelength of 694.3 nm (Figure 2.2.4). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

A. Use Equation 6.1.2 and Equation 8.3.1 to calculate the energy in joules.

Solution:

The energy of a single photon is given by $E = h\nu = hc/\lambda$.

Exercise 2.2.1

An x-ray generator, such as those used in hospitals, emits radiation with a wavelength of 1.544 Å.

a. What is the energy in joules of a single photon?
b. How many times more energetic is a single x-ray photon of this wavelength than a photon emitted by a ruby laser?

Answer

a. $1.287 \times 10^{-15}\ J/photon$
b. 4497 times

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The Photoelectric Effect: https://youtu.be/mxBMxJLauQk

Summary

- The fundamental building blocks of energy are quanta and of matter are atoms.

The properties of **blackbody radiation**, the radiation emitted by hot objects, could not be explained with classical physics. Max Planck postulated that energy was quantized and could be emitted or absorbed only in integral multiples of a small unit of energy, known as a **quantum**. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant h is a fundamental constant (Planck's constant). Albert Einstein used Planck's concept of the quantization of energy to explain the **photoelectric effect**, the ejection of electrons from certain metals when exposed to light. Einstein postulated the existence of what today we call **photons**, particles of light with a particular energy, $E = h\nu$. Both energy and matter have fundamental building blocks: quanta and atoms, respectively.

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2.3: Atomic Spectra

Learning Objectives

- To know the relationship between atomic spectra and the electronic structure of atoms.

The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. The concept of the photon, however, emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. More direct evidence was needed to verify the quantized nature of electromagnetic radiation. In this section, we describe how experimentation with visible light provided this evidence.

Line Spectra

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation, a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines, called a line spectrum, which is a spectrum in which light of only a certain wavelength is emitted or absorbed, rather than a continuous range of wavelengths (Figure 2.3.1), rather than a continuous range of colors. The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.





Figure 2.3.1: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm.

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge because classical physics was unable to explain them. Part of the explanation is provided by the observation of only a few values of λ (or ν) in the line spectrum meant that only a few values of *E* were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

In 1885, a Swiss mathematics teacher, Johann Balmer (1825–1898), showed that the frequencies of the lines observed in the visible region of the spectrum of hydrogen fit a simple equation that can be expressed as follows:

$$u = constant\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{2.3.1}$$

where *n* = 3, 4, 5, 6. As a result, these lines are known as the *Balmer series*. The Swedish physicist Johannes Rydberg (1854–1919) subsequently restated and expanded Balmer's result in the *Rydberg equation*:

$$\frac{1}{\lambda} = \Re\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{2.3.2}$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and $\Re$ the *Rydberg constant*, has a value of 1.09737 × 10^7 m^{-1}.

Johann Balmer (1825–1898)

A mathematics teacher at a secondary school for girls in Switzerland, Balmer was 60 years old when he wrote the paper on the spectral lines of hydrogen that made him famous.



Balmer published only one other paper on the topic, which appeared when he was 72 years old.

Like Balmer's equation, Rydberg's simple equation described the wavelengths of the visible lines in the emission spectrum of hydrogen (with n_1 = 2, n_2 = 3, 4, 5,...). More important, Rydberg's equation also described the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet (n_1 = 1, n_2 = 2, 3, 4,...) and one in the infrared (n_1 = 3, n_2 = 4, 5, 6). Unfortunately, scientists had not yet developed any theoretical justification for an equation of this form.

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The Bohr Atom: https://youtu.be/GuFQEOzFOgA

Summary

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Most light is polychromatic and contains light of many wavelengths. Light that has only a single wavelength is monochromatic and is produced by devices called lasers, which use transitions between two atomic energy levels to produce light in a very narrow range of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element.

Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Bohr's model could not, however, explain the spectra of atoms heavier than hydrogen.

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Modified by Joshua Halpern (Howard University)

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2.4: The Bohr Atom

Learning Objectives

- To know the relationship between atomic spectra and the electronic structure of atoms.

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required only one assumption: *The electron moves around the nucleus in circular orbits that can have only certain allowed radii.* Rutherford's earlier model of the atom had also assumed that electrons moved in circular orbits around the nucleus and that the atom was held together by the electrostatic attraction between the positively charged nucleus and the negatively charged electron. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space*.

Using classical physics, Niels Bohr showed that the energy of an electron in a particular orbit is given by

$$E_n = \frac{-\Re hc}{n^2} \tag{2.4.1}$$

where $\Re$ is the Rydberg constant, h is Planck's constant, c is the speed of light, and n is a positive integer corresponding to the number assigned to the orbit, with $n = 1$ corresponding to the orbit closest to the nucleus. In this model $n = \infty$ corresponds to the level where the energy holding the electron and the nucleus together is zero. In that level, the electron is unbound from the nucleus and the atom has been separated into a negatively charged (the electron) and a positively charged (the nucleus) ion. In this state the radius of the orbit is also infinite. The atom has been ionized.

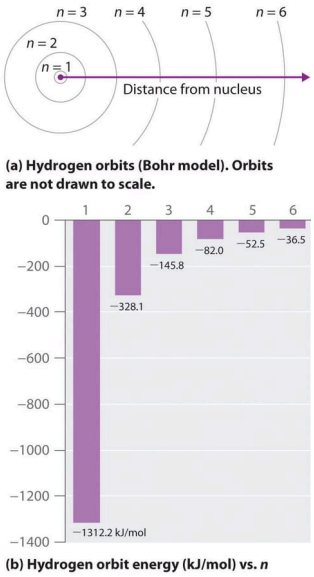
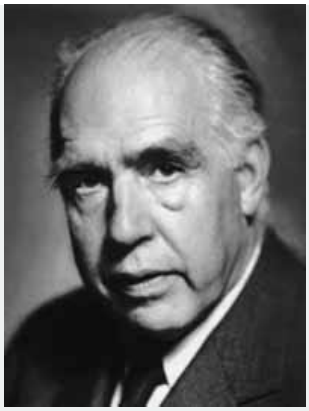


Figure 2.4.2 The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing *n*. (b) The energy of the orbit becomes increasingly less negative with increasing *n*.

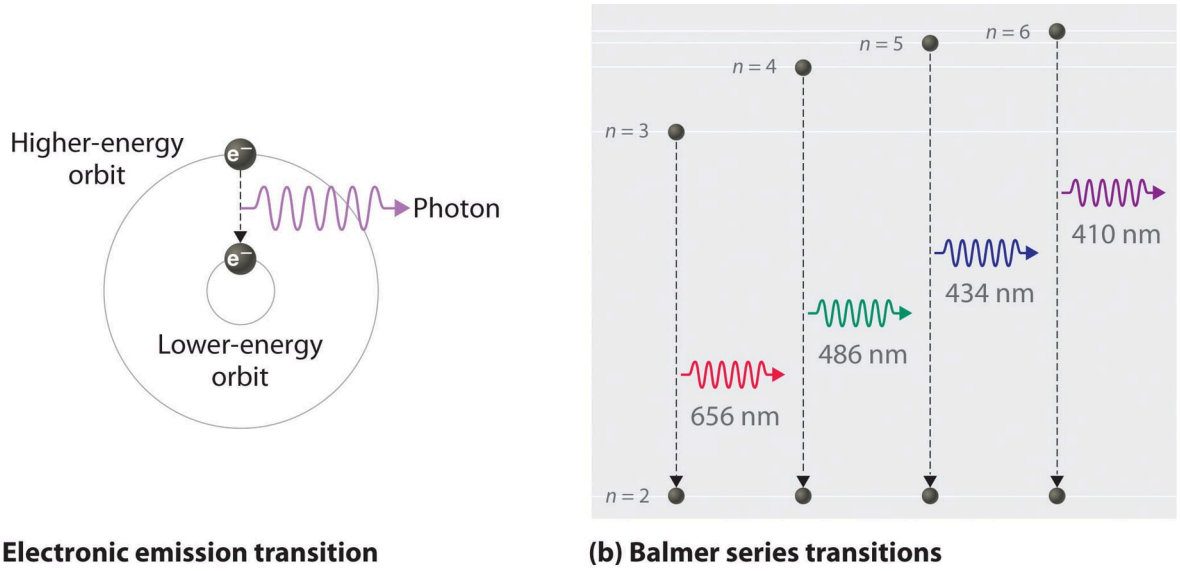
Niels Bohr (1885–1962)

During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project.



In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative, the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with n = 1 is the lowest lying and most tightly bound. The negative sign in Equation 2.4.3 indicates that the electron-nucleus pair is more tightly bound when they are near each other than when they are far apart. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the ground state (the most stable arrangement of electrons for an element or a compound), the most stable arrangement for a hydrogen atom. As n increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy (Figure 2.10). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an excited state. Any arrangement of electrons that is higher in energy than the ground state.: its energy is higher than the energy of the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called decay, it loses energy by emitting a photon whose energy corresponds to the difference in energy between the two states (Figure 2.4.1).



(a) Electronic emission transition **(b) Balmer series transitions**

Figure 2.4.3: The Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of *n* (at a higher energy) to an orbit with a lower value of *n* (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with *n* ≥ 3 to the orbit with *n* = 2. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.

So the difference in energy (Δ*E*) between any two orbits or energy levels is given by $\Delta E = E_{n_1} - E_{n_2}$ where n_1 is the final orbit and n_2 the initial orbit. Substituting from Bohr's equation (Equation 2.4.3) for each energy value gives

$$\Delta E = E_{final} - E_{initial} = -\frac{\Re hc}{n_2^2} - \left(-\frac{\Re hc}{n_1^2}\right) = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{2.4.2}$$

If $n_2 > n_1$, the transition is from a higher energy state (larger-radius orbit) to a lower energy state (smaller-radius orbit), as shown by the dashed arrow in part (a) in Figure 2.4.3. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{2.4.3}$$

Canceling hc on both sides gives

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{2.4.4}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equation 2.4.5 and Equation 2.4.6 indicates that energy is released as the electron moves from orbit n_2 to orbit n_1 because orbit n_2 is at a higher energy than orbit n_1. Bohr calculated the value of $\Re$ from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of 1.0974×10^7 m^{-1}, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (part (b) in Figure 2.9). As shown in part (b) in Figure 2.4.3, the lines in this series correspond to transitions from higher-energy orbits (n > 2) to the second orbit (n = 2). Thus the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state (n > 2) to a lower-energy state (n = 2) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the difference in energy between the two states (part (a) in Figure 2.4.3). The n = 3 to n = 2 transition gives rise to the line at 656 nm (red), the n = 4 to n = 2 transition to the line at 486 nm (green), the n = 5 to n = 2 transition to the line at 434 nm (blue), and the n = 6 to n = 2 transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the n = 3 than the n ≥ 4 levels. Consequently, the n = 3 to n = 2 transition is the most intense line, producing the characteristic red color of a hydrogen discharge (part (a) in Figure 2.4.1). Other families of lines are produced by transitions from excited states with n > 1 to the orbit with n = 1 or to orbits with n ≥ 3. These transitions are shown schematically in Figure 2.4.4

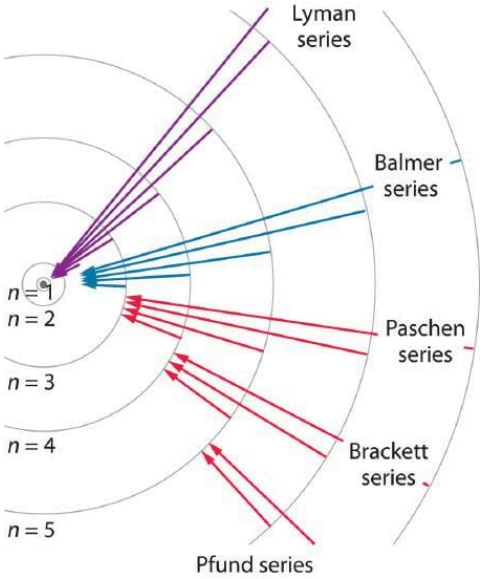


Figure 2.4.4: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to 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.)

In contemporary applications, electron transitions are used in timekeeping that needs to be exact. Telecommunications systems, such as cell phones, depend on timing signals that are accurate to within a millionth of a second per day, as are the devices that control the US power grid. Global positioning system (GPS) signals must be accurate to within a billionth of a second per day,

which is equivalent to gaining or losing no more than one second in 1,400,000 years. Quantifying time requires finding an event with an interval that repeats on a regular basis. To achieve the accuracy required for modern purposes, physicists have turned to the atom. The current standard used to calibrate clocks is the cesium atom. Supercooled cesium atoms are placed in a vacuum chamber and bombarded with microwaves whose frequencies are carefully controlled. When the frequency is exactly right, the atoms absorb enough energy to undergo an electronic transition to a higher-energy state. Decay to a lower-energy state emits radiation. The microwave frequency is continually adjusted, serving as the clock's pendulum. In 1967, the second was defined as the duration of 9,192,631,770 oscillations of the resonant frequency of a cesium atom, called the *cesium clock*. Research is currently under way to develop the next generation of atomic clocks that promise to be even more accurate. Such devices would allow scientists to monitor vanishingly faint electromagnetic signals produced by nerve pathways in the brain and geologists to measure variations in gravitational fields, which cause fluctuations in time, that would aid in the discovery of oil or minerals.

Example 2.4.1: The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the n = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

A. Substitute the appropriate values into Equation 2.4.2 (the Rydberg equation) and solve for λ.
B. Use Figure 2.4.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{2.4.5}$$

A For the Lyman series, n_1 = 1. The lowest-energy line is due to a transition from the n = 2 to n = 1 orbit because they are the closest in energy.

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1} \tag{2.4.6}$$

It turns out that spectroscopists (the people who study spectroscopy) use cm^{-1} rather than m^{-1} as a common unit. Wavelength is inversely proportional to energy but frequency is directly proportional as shown by Planck's formula, E=hu.

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly 200 - 5,000 cm^{-1}, the visible from 11,000 to 25.000 cm^{-1} and the UV between 25,000 and 100,000 cm^{-1}. The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1}.

$$\varpi = \frac{1}{\lambda} = 8.228 \times 10^6\ \cancel{m}^{-1}\left(\frac{\cancel{m}}{100\ cm}\right) = 82,280\ cm^{-1} \tag{2.4.7}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm \tag{2.4.8}$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone

B This wavelength is in the ultraviolet region of the spectrum.

Exercise 2.4.1: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $n = 5$ orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer: 4.65×10^3 nm; infrared

Bohr's model of the hydrogen atom gave an exact explanation for its observed emission spectrum. The following are his key contributions to our understanding of atomic structure:

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of tinkering, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element other than hydrogen (Figure 2.4.5). In fact, Bohr's model worked only for species that contained just one electron: H, He^+, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

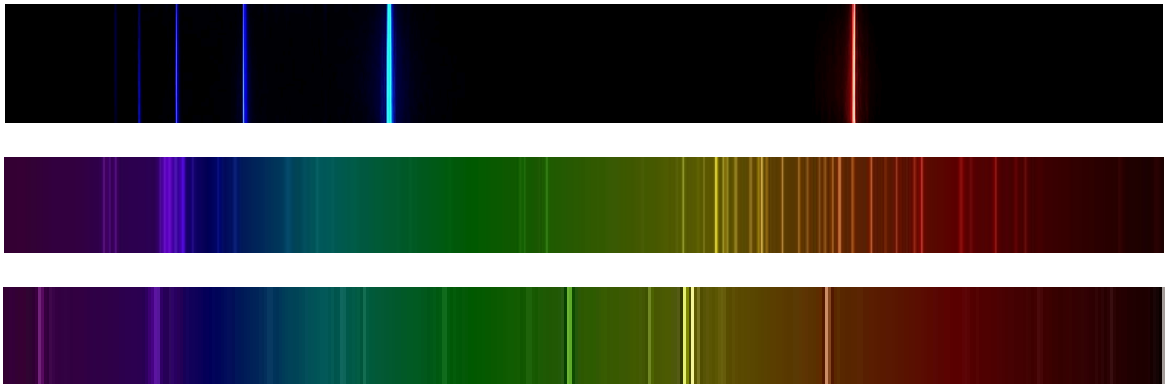


Figure 2.4.5: The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown.

Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrum (a spectrum produced by the emission of light by atoms in excited states). The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrum (a spectrum produced by the absorption of light by ground-state atoms). Because each element has characteristic emission and absorption spectra, scientists can use such spectra to analyze the composition of matter.

When an atom emits light, it decays to a lower energy state; when an atom absorbs light, it is excited to a higher energy state.

The Energy States of the Hydrogen Atom

If white light is passed through a sample of hydrogen, hydrogen atoms absorb energy as an electron is excited to higher energy levels (orbits with $n \geq 2$). If the light that emerges is passed through a prism, it forms a continuous spectrum with *black* lines (corresponding to no light passing through the sample) at 656, 468, 434, and 410 nm. These wavelengths correspond to the $n = 2$ to $n = 3$, $n = 2$ to $n = 4$, $n = 2$ to $n = 5$, and $n = 2$ to $n = 6$ transitions. Any given element therefore has both a characteristic emission spectrum and a characteristic absorption spectrum, which are essentially complementary images.

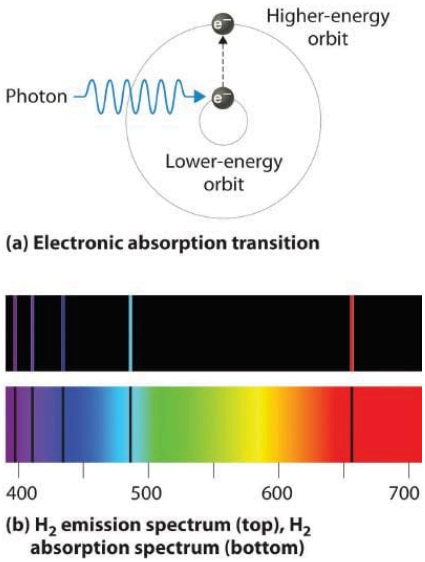


Figure 2.4.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 2.4.7 Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning “sun.” Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium, pick up electrons from the rocks to form helium atoms.

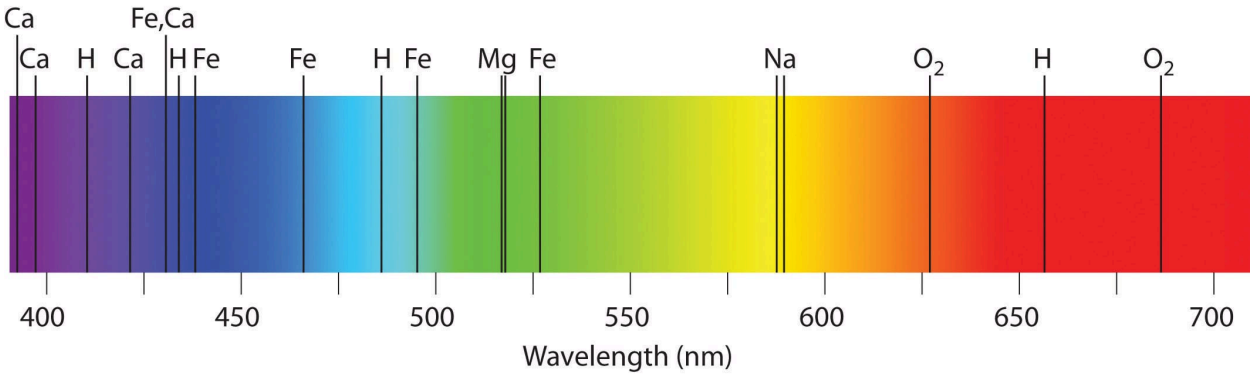


Figure 2.4.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere.

The familiar red color of "neon" signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 2.4.5. Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure 2.4.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

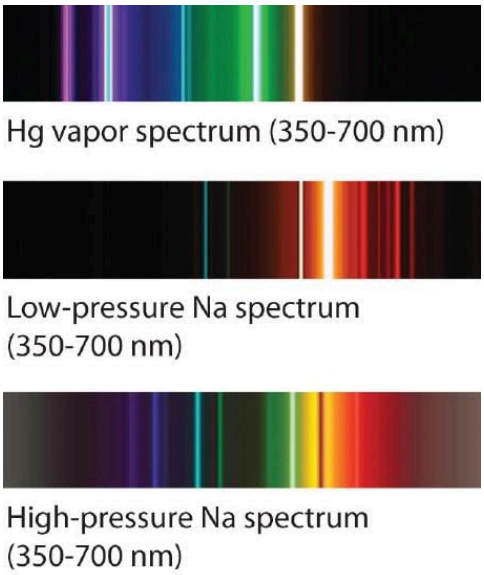


Figure 2.4.8: The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is cause by absorption of light in the cooler outer part of the lamp.

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The Chemistry of Fireworks

The colors of fireworks are also due to atomic emission spectra. As shown in part (a) in Figure 2.4.9, a typical shell used in a fireworks display contains gunpowder to propel the shell into the air and a fuse to initiate a variety of reactions that produce heat and small explosions. Thermal energy excites the atoms to higher energy states; as they decay to lower energy states, the atoms emit light that gives the familiar colors.



Figure 2.4.9 :The Chemistry of Fireworks *(a) In the "multibreak" shell used for fireworks, the chambers contain mixtures of fuels and oxidizers plus compounds for special effects ("stars") connected by time-delay fuses so that the chambers explode in stages. (b) The finale of a fireworks display usually consists of many shells fired simultaneously to give a dazzling multicolor display. The labels indicate the substances that are responsible for the colors of some of the fireworks shown.*

When oxidant/reductant mixtures listed in Table 2.4.1 are ignited, a flash of white or yellow light is produced along with a loud bang. Achieving the colors shown in part (b) in Figure 2.4.9 requires adding a small amount of a substance that has an emission spectrum in the desired portion of the visible spectrum. For example, sodium is used for yellow because of its 589 nm emission lines. The intense yellow color of sodium would mask most other colors, so potassium and ammonium salts, rather than sodium salts, are usually used as oxidants to produce other colors, which explains the preponderance of such salts in Table 2.4.1 . Strontium salts, which are also used in highway flares, emit red light, whereas barium gives a green color. Blue is one of the most difficult colors to achieve. Copper(II) salts emit a pale blue light, but copper is dangerous to use because it forms highly unstable explosive compounds with anions such as chlorate. As you might guess, preparing fireworks with the desired properties is a complex, challenging, and potentially hazardous process. If you have the time here is a NOVA program about how fireworks are made.

*Table 2.4.1: Common Chemicals Used in the Manufacture of Fireworks**

Oxidizers	Fuels (reductants)	Special effects
ammonium perchlorate	aluminum	*blue flame*: copper carbonate, copper sulfate, or copper oxide
barium chlorate	antimony sulfide	*red flame*: strontium nitrate or strontium carbonate
barium nitrate	charcoal	*white flame*: magnesium or aluminum
potassium chlorate	magnesium	*yellow flame*: sodium oxalate or cryolite (Na_3AlF_6)
potassium nitrate	sulfur	*green flame*: barium nitrate or barium chlorate
potassium perchlorate	titanium	*white smoke*: potassium nitrate plus sulfur
strontium nitrate		*colored smoke*: potassium chlorate and sulfur, plus organic dye
***Almost any combination of an oxidizer and a fuel may be used along with the compounds needed to produce a desired special effect.**		

Oxidizers	Fuels (reductants)	Special effects
		whistling noise: potassium benzoate or sodium salicylate
		white sparks: aluminum, magnesium, or titanium
		gold sparks: iron fillings or charcoal
***Almost any combination of an oxidizer and a fuel may be used along with the compounds needed to produce a desired special effect.**		

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Summary

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Bohr's model could not, however, explain the spectra of atoms heavier than hydrogen.

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2.5: Two Ideas Leading to a New Quantum Mechanics

Learning Objectives

- To understand the wave–particle duality of matter.

Einstein's photons of light were individual packets of energy having many of the characteristics of particles. Recall that the collision of an electron (a particle) with a sufficiently energetic photon can eject a *photoelectron* from the surface of a metal. Any excess energy is transferred to the electron and is converted to the kinetic energy of the ejected electron. Einstein's hypothesis that energy is concentrated in localized bundles, however, was in sharp contrast to the classical notion that energy is spread out uniformly in a wave. We now describe Einstein's theory of the relationship between energy and mass, a theory that others built on to develop our current model of the atom.

The Wave Character of Matter

Einstein initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his special theory of relativity, which related energy and mass according to the following equation:

$$E = h\nu = h\frac{c}{\lambda} = mc^2 \tag{2.5.1}$$

According to this theory, a photon of wavelength λ and frequency ν has a nonzero mass, which is given as follows:

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2} = \frac{h}{\lambda c} \tag{2.5.2}$$

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle duality (a principle that matter and energy have properties typical of both waves and particles). Depending on conditions, light could be viewed as either a wave or a particle.

In 1922, the American physicist Arthur Compton (1892–1962) reported the results of experiments involving the collision of x-rays and electrons that supported the particle nature of light. At about the same time, a young French physics student, Louis de Broglie (1892–1972), began to wonder whether the converse was true: Could particles exhibit the properties of waves? In his PhD dissertation submitted to the Sorbonne in 1924, de Broglie proposed that a particle such as an electron could be described by a wave whose wavelength is given by

$$\lambda = \frac{h}{mv} \tag{2.5.3}$$

where

- is Planck's constant,
- *m* is the mass of the particle, and
- *v* is the velocity of the particle.

This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie's equation, which is an extremely small number. As you will calculate in Example 2.5.1, Planck's constant (6.63×10^{-34} J•s) is so small that the wavelength of a particle with a large mass is too short (less than the diameter of an atomic nucleus) to be noticeable.

Example 2.5.1

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

Given: mass and speed of object

Asked for: wavelength

Strategy:

A. Convert the speed of the baseball to the appropriate SI units: meters per second.
B. Substitute values into Equation 8.5.3 and solve for the wavelength.

Solution:

The wavelength of a particle is given by λ = *h*/*mv*. We know that *m* = 0.149 kg, so all we need to find is the speed of the baseball:

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right)$$

B Recall that the joule is a derived unit, whose units are (kg•m^2)/s^2. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} = \frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}^{\cancel{-2}} \cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m} \cdot \cancel{s^{-1}}\right)} = 9.95 \times 10^{-35}\ m \tag{2.5.4}$$

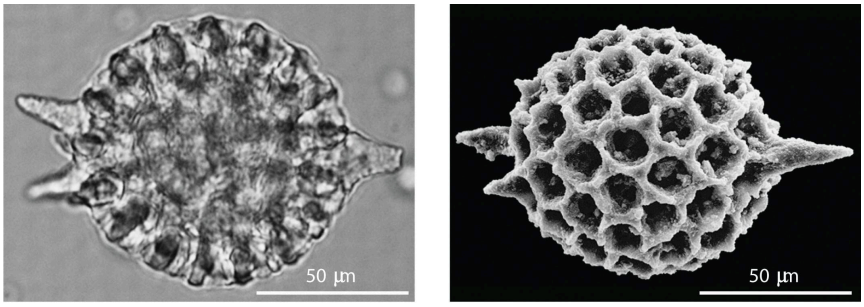
(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

Exercise 2.5.1

Calculate the wavelength of a neutron that is moving at 3.00 × 10^3 m/s.

Answer: 1.32 Å, or 132 pm

As you calculated in Example 2.5.1, objects such as a baseball or a neutron have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, such as electrons, exhibit the properties of both particles and waves. Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can (Figure 2.5.1).



(a) Radiolarian under light microscope **(b) Radiolarian under electron microscope**

Figure 2.5.1: A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope**.** Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). (Radiolaria, which are shown here, are unicellular planktonic organisms.)

An Important Wave Property: Phase

A wave is a disturbance that travels in space. The magnitude of the wave at any point in space and time varies sinusoidally. While the absolute value of the magnitude of one wave at any point is not very important, the **relative** displacement of two waves called the phase difference, is vitally important because it determines whether the waves reinforce or interfere with each other. Figure 2.5.2a, on the right shows an arbitrary phase difference between two wave. Figure 2.5.2b shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 2.5.2c shows what happens when the two lines are in phase, exactly superimposed on each other. Again, the green line is the sum of the intensities.

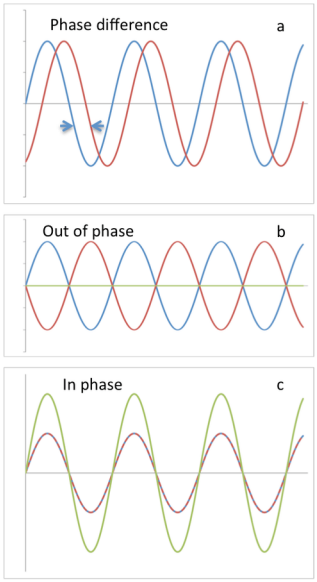


Figure 2.5.2: Phase. Two waves traveling together are displaced by a phase difference. If the phase difference is 0 then they lay on top of each other and reinforce. If the phase difference is 180 they completely cancel each other out.

Standing Waves

De Broglie also investigated why only certain orbits were allowed in Bohr's model of the hydrogen atom. He hypothesized that the electron behaves like a standing wave (a wave that does not travel in space). An example of a standing wave is the motion of a string of a violin or guitar. When the string is plucked, it vibrates at certain fixed frequencies because it is fastened at both ends (Figure 2.5.3). If the length of the string is *L*, then the lowest-energy vibration (the fundamental (the lowest-energy standing wave) has wavelength

$$\begin{aligned} \frac{\lambda}{2} &= L \\ \lambda &= 2L \end{aligned} \tag{2.5.5}$$

Higher-energy vibrations are called overtones (the vibration of a standing wave that is higher in energy than the fundamental vibration) and are produced when the string is plucked more strongly; they have wavelengths given by

$$\lambda = \frac{2L}{n} \tag{2.5.6}$$

where *n* has any integral value. Thus the resonant vibrational energies of the string are quantized. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. By analogy we can think of the resonant frequencies as being quantized. Notice in Figure 2.5.3 that all overtones have one or more nodes (the points where the amplitude of a wave is zero), points where the string does not move. The amplitude of the wave at a node is zero.

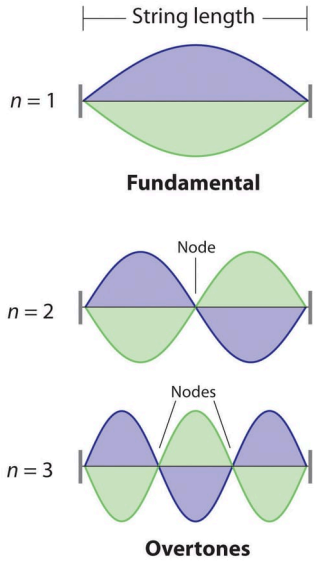


Figure 2.5.3 Standing Waves on a Vibrating String. The vibration with *n* = 1 is the fundamental and contains no nodes. Vibrations with higher values of *n* are called overtones; they contain *n* – 1 nodes.

Quantized vibrations and overtones containing nodes are not restricted to one-dimensional systems, such as strings. A two-dimensional surface, such as a drumhead, also has quantized vibrations. Similarly, when the ends of a string are joined to form a circle, the only allowed vibrations are those with wavelength

$$2\pi r = n\lambda \tag{2.5.7}$$

where *r* is the radius of the circle. De Broglie argued that Bohr's allowed orbits could be understood if the electron behaved like a *standing circular wave* (Figure 2.5.4). The standing wave could exist only if the circumference of the circle was an integral multiple of the wavelength such that the propagated waves were all in phase, thereby increasing the net amplitudes and causing *constructive interference*. Otherwise, the propagated waves would be out of phase, resulting in a net decrease in amplitude and causing *destructive interference*. The non resonant waves interfere with themselves! De Broglie's idea explained Bohr's allowed orbits and energy levels nicely: in the lowest energy level, corresponding to *n* = 1 in Equation 8.5.2, one complete wavelength would close the circle. Higher energy levels would have successively higher values of *n* with a corresponding number of nodes.

Standing waves are often observed on rivers, reservoirs, ponds, and lakes when seismic waves from an earthquake travel through the area. The waves are called *seismic seiches*, a term first used in 1955 when lake levels in England and Norway oscillated from side to side as a result of the Assam earthquake of 1950 in Tibet. They were first described in the Proceedings of the Royal Society in 1755 when they were seen in English harbors and ponds after a large earthquake in Lisbon, Portugal. Seismic seiches were also observed in many places in North America after the Alaska earthquake of March 28, 1964. Those occurring in western reservoirs lasted for two hours or longer, and amplitudes reached as high as nearly 6 ft along the Gulf Coast. The height of seiches is approximately proportional to the thickness of surface sediments; a deeper channel will produce a higher seiche.

Still, as all analogies, although the standing wave model helps us understand much about why Bohr's theory worked, it also, if pushed too far can mislead.

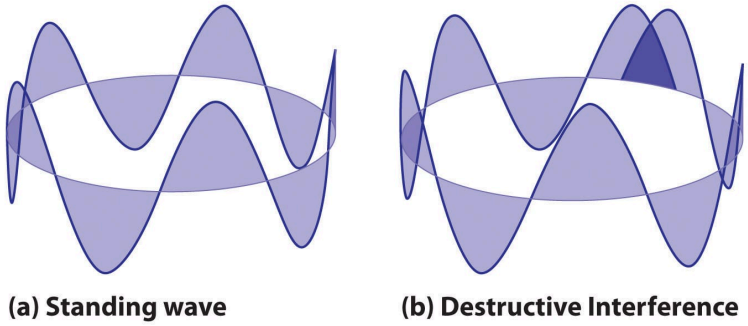


Figure 2.5.4 Standing Circular Wave and Destructive Interference.(a) In a standing circular wave with n = 5, the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of the circle is not equal to an integral multiple of wavelengths, then the wave does not overlap exactly with itself, and the resulting destructive interference will result in cancellation of the wave. Consequently, a standing wave cannot exist under these conditions.

As you will see, some of de Broglie's ideas are retained in the modern theory of the electronic structure of the atom: the wave behavior of the electron and the presence of nodes that increase in number as the energy level increases. Unfortunately, his (and Bohr's) explanation also contains one major feature that we know to be incorrect: in the currently accepted model, the electron in a given orbit is *not* always at the same distance from the nucleus.

YouTube Video

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The de Broglie Equation: https://youtu.be/pz0zMHWtK7Q

The Heisenberg Uncertainty Principle

Because a wave is a disturbance that travels in space, it has no fixed position. One might therefore expect that it would also be hard to specify the exact position of a *particle* that exhibits wavelike behavior. A characteristic of light is that is can be bent or spread out by passing through a narrow slit as shown in the video below. You can literally see this by half closing your eyes and looking through your eye lashes. This reduces the brightness of what you are seeing and somewhat fuzzes out the image, but the light bends around your lashes to provide a complete image rather than a bunch of bars across the image. This is called diffraction.

This behavior of waves is captured in Maxwell's equations (1870 or so) for electromagnetic waves and was and is well understood. Heisenberg's uncertainty principle for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. DeBroglie's idea of wave particle duality means that particles such as electrons which all exhibit wave like characteristics, will also undergo diffraction from slits whose size is of the order of the electron wavelength.

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This situation was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that "at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty relation." Mathematically, the Heisenberg uncertainty principle is greater than or equal to Planck's constant *h* divided by 4π: states that the uncertainty in the position of a particle (Δ*x*) multiplied by the uncertainty in its momentum [Δ(*mv*)] is greater than or equal to Planck's constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{2.5.8}$$

Because Planck's constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie's equation to have measurable wavelengths.

If the precise position *x* of a particle is known absolutely (Δ*x* = 0), then the uncertainty in its momentum must be infinite:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{2.5.9}$$

Because the mass of the electron at rest (*m*) is both constant and accurately known, the uncertainty in Δ(*mv*) must be due to the Δ*v* term, which would have to be infinitely large for Δ(*mv*) to equal infinity. That is, according to Equation 8.5.8, the more accurately we know the exact position of the electron (as Δ*x* → 0), the less accurately we know the speed and the kinetic energy of the electron (1/2 mv^2) because Δ(*mv*) → ∞. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as Δ(*mv*) → 0], then Δ*x* → ∞ and we have no idea where the electron is.

Bohr's model of the hydrogen atom violated the Heisenberg uncertainty principle by trying to specify **simultaneously** both the position (an orbit of a particular radius) and the energy (a quantity related to the momentum) of the electron. Moreover, given its mass and wavelike nature, the electron in the hydrogen atom could not possibly orbit the nucleus in a well-defined circular path as predicted by Bohr. You will see, however, that the *most probable radius* of the electron in the hydrogen atom is exactly the one predicted by Bohr's model.

Example 2.5.2

Calculate the minimum uncertainty in the position of the pitched baseball from Example 2.5.1 that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

Given: mass and speed of object

Asked for: minimum uncertainty in its position

Strategy:

A. Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 8.5.7) to solve for the minimum uncertainty in the position of an object (Δ*x*).
B. Find Δ*v* by converting the velocity of the baseball to the appropriate SI units: meters per second.
C. Substitute the appropriate values into the expression for the inequality and solve for Δ*x*.

Solution:

A The Heisenberg uncertainty principle tells us that (Δ*x*)[Δ(*mv*)] = *h*/4π. Rearranging the inequality gives

$$\Delta x \geq \left(\frac{h}{4\pi}\right)\left(\frac{1}{\Delta(mv)}\right)$$

B We know that *h* = 6.626 × 10^{-34} J•s and *m* = 0.149 kg. Because there is no uncertainty in the mass of the baseball, Δ(*mv*) = *m*Δ*v* and Δ*v* = ±1 mi/h. We have

$$\Delta\nu = \left(\frac{1\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 0.4469\ \ m/s$$

C Therefore,

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ J \cdot s}{4\,(3.1416)}\right)\left(\frac{1}{(0.149\ kg)\,(0.4469\ m \cdot s^{-1})}\right)$$

Inserting the definition of a joule (1 J = 1 kg•m^2/s^2) gives

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot s}{4\,(3.1416)\left(\cancel{s^2}\right)}\right)\left(\frac{1\ \cancel{s}}{\left(0.149\ \cancel{kg}\right)(0.4469\ \cancel{m})}\right)$$

$$\Delta x \geqslant 7.92 \pm \times 10^{-34}\ \ m$$

This is equal to 3.12 × 10^{-32} inches. We can safely say that if a batter misjudges the speed of a fastball by 1 mi/h (about 1%), he will not be able to blame Heisenberg's uncertainty principle for striking out.

Exercise 2.5.2

Calculate the minimum uncertainty in the position of an electron traveling at one-third the speed of light, if the uncertainty in its speed is ±0.1%. Assume its mass to be equal to its mass at rest.

Answer: 6 × 10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

Videos and Examples

- de Broglie Waves - Sixty Symbols - a bit of history and explanation (as well as wave particle duality can be explained)
- Calculating the wavelength of a proton - Josh Samson
- Calculating the wavelength of a small car - Prof. Heath
- What is the Uncertainty Principle? - Minute Physics
- AP Chem Heisenberg Uncertainty Principle - Mind Bite
- deBroglie Example - about education
- Heisenberg uncertainty principle quiz worked out - C Craig
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek

Answers for these quizzes are included.

Summary

- An electron possesses both particle and wave properties.

The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called **wave–particle duality**. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle.

$$\lambda = \frac{h}{mv} \tag{8.5.3}$$

The electron in Bohr's circular orbits could thus be described as a **standing wave**, one that does not move through space. Standing waves are familiar from music: the lowest-energy standing wave is the **fundamental** vibration, and higher-energy vibrations are **overtones** and have successively more **nodes**, points where the amplitude of the wave is always zero. Werner

Heisenberg's **uncertainty principle** states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{8.5.7}$$

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

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2.6: Wave Mechanics and Quantum Numbers

Learning Objectives

- To apply the results of quantum mechanics to chemistry.

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies. In doing so, Schrödinger developed the theory of quantum mechanics, which is used today to describe the energies and spatial distributions of electrons in atoms and molecules.

Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wave functions* that are the solutions of Schrödinger's equations.

Wave Functions

A wave function (Ψ) is a mathematical function that relates the location of an electron at a given point in space (identified by x, y, and z coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wave function is associated with a particular energy E. The properties of wave functions derived from quantum mechanics are summarized here:

- **A wave function uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates x, y, and z), and one specifies the time at which the object is at the specified location. For example, if you wanted to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure 2.6.1). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

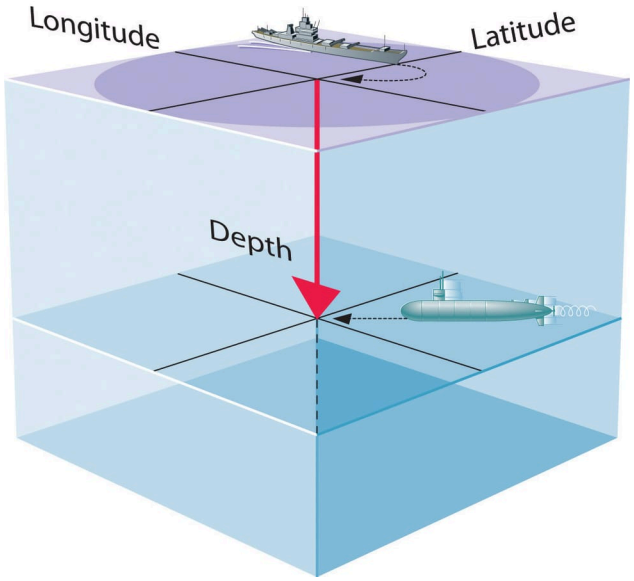


Figure 2.6.1: The Four Variables (Latitude, Longitude, Depth, and Time) Required to Precisely Locate an Object

If you are the captain of a ship trying to intercept an enemy submarine, you need to deliver your depth charge to the right location at the right time.

- **The magnitude of the wave function at a particular point in space is proportional to the amplitude of the wave at that point.** Many wave functions are complex functions, which is a mathematical term indicating that they contain $\sqrt{-1}$, represented as i. Hence the amplitude of the wave has no real physical significance. In contrast, the sign of the wave function (either positive or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding. The sign of the wave function should *not* be confused with a positive or negative electrical charge.
- **The square of the wave function at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The square of the wave function (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wave function Ψ and its complex conjugate Ψ*, in which all terms that contain *i* are replaced by $-i$. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 2.6.2.

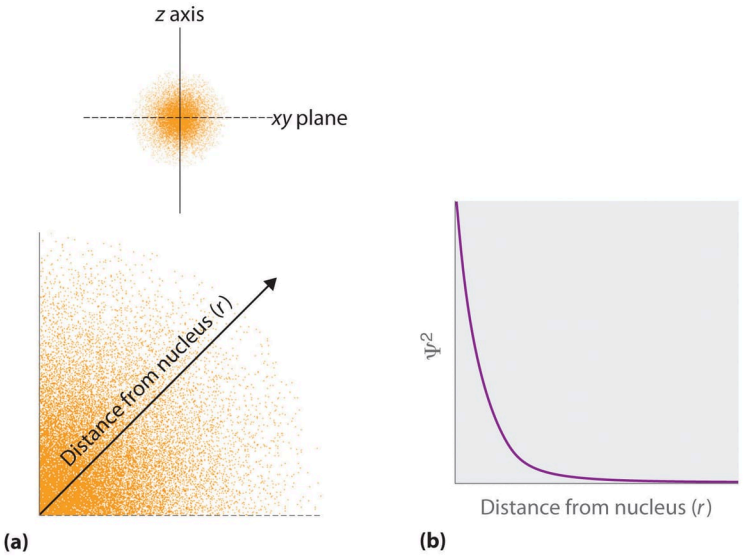


Figure 2.6.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at $r = 0$ (the nucleus) and falls off with increasing r. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but *not* zero.

- **Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wave function.** From the patterns of one- and two-dimensional standing waves shown in Figure 6.18 and Figure 6.19, you might expect (correctly) that the patterns of three-dimensional standing waves would be complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a flooded planet. Schrödinger incorporated Legendre's equations into his wave functions. The requirement that the waves must be in phase with one another to avoid cancellation and produce a standing wave results in a limited number of solutions (wave functions), each of which is specified by a set of numbers called quantum numbers.
- **Each wave function is associated with a particular energy.** As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.

Quantum Numbers

Schrödinger's approach uses three quantum numbers (n, l, and m_l) to specify any wave function. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer, only certain values of l and m_l are allowed for a given value of n.

YouTube Video

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Introduction to Quantum Numbers: https://youtu.be/07JpBeaPxL8

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \ldots \tag{2.6.1}$$

As *n* increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of *n* are easier to remove from an atom. All wave functions that have the same value of *n* are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number *n* corresponds to the *n* used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the azimuthal quantum number (*l*). The value of *l* describes the *shape* of the region of space occupied by the electron. The allowed values of *l* depend on the value of *n* and can range from 0 to *n* − 1:

$$l = 0, 1, 2, \ldots, n - 1 \tag{2.6.2}$$

For example, if *n* = 1, *l* can be only 0; if *n* = 2, *l* can be 0 or 1; and so forth. For a given atom, all wave functions that have the same values of both *n* and *l* form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

YouTube Video

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Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell: https://youtu.be/ms7WR149fAY

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of *l*: m_l can range from –*l* to *l* in integral steps:

$$m_l = -l, -l + 1, \ldots, 0, \ldots, l - 1, l \tag{2.6.3}$$

For example, if $l = 0$, m_l can be only 0; if *l* = 1, m_l can be –1, 0, or +1; and if *l* = 2, m_l can be –2, –1, 0, +1, or +2.

Each wave function with an allowed combination of *n*, *l*, and m_l values describes an atomic orbital, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Example 2.6.1: n=4 Shell Structure

How many subshells and orbitals are contained within the principal shell with *n* = 4?

Given: value of *n*

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given $n = 4$, calculate the allowed values of l. From these allowed values, count the number of subshells.
B. For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to $n - 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l.

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to n^2:

Exercise 2.6.1: n=3 Shell Structure

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer: three subshells; nine orbitals

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

l =	0	1	2	3
Designation	*s*	*p*	*d*	*f*

The principal quantum number is named first, followed by the letter s, *p*, *d*, or *f* as appropriate. These orbital designations are derived from corresponding spectroscopic characteristics: sharp, *p*rinciple, *d*iffuse, and *f*undamental. A 1s orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = -1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = -2$, -1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 2.6.1):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible (1s); for $n = 2$, there are two subshells (2*s* and 2*p*); for $n = 3$, there are three subshells (3s, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with $n \geq 2$ also has an *np* subshell, and any shell with $n \geq 3$ also has an *nd* subshell. Because a 2*d* subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2*d* subshell does not exist.
- Each subshell has $2l + 1$ orbitals. This means that all *ns* subshells contain a single *s* orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

Note

Each principal shell has n subshells, and each subshell has $2l + 1$ orbitals.

Table 2.6.1 Values of n, l, and ml through n = 4

n	*l*	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	–1, 0, 1	3	
3	0	3s	0	1	9
	1	3p	–1, 0, 1	3	
	2	3d	–2, –1, 0, 1, 2	5	
4	0	4s	0	1	16
	1	4p	–1, 0, 1	3	
	2	4d	–2, –1, 0, 1, 2	5	
	3	4f	–3, –2, –1, 0, 1, 2, 3	7	

YouTube Video

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View this YouTube Video online

Magnetic Quantum Number (m_l) & Spin Quantum Number (m_s): https://youtu.be/gbmGVUXBOBk

Summary

- There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics.

Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wave functions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wave functions have five important properties:

1. the wave function uses three variables (Cartesian axes *x*, *y*, and *z*) to describe the position of an electron;
2. the magnitude of the wave function is proportional to the intensity of the wave;
3. the probability of finding an electron at a given point is proportional to the square of the wave function at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot;
4. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wave function; and
5. each spatial distribution of the electron described by a wave function with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** *n* can be any positive integer; as *n* increases for an atom, the average distance of the electron from the nucleus also increases. All wave functions with the same value of *n* constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** *l* can have integral values between 0 and *n* – 1; it describes the shape of the electron distribution. Wave functions that have the same values of both *n* and *l* constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic**

quantum number m_l can have $2l + 1$ integral values, ranging from $-l$ to $+l$, and describes the orientation of the electron distribution. Each wave function with a given set of values of n, l, and m_l describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

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2.7: Electron Spin- A Fourth Quantum Number

Learning Objectives

- To introduce the concept of electron spin and demonstrated it is quantized

The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table. All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion. Before demonstrating how to do this, however, we must introduce the concept of electron spin.

The Stern-Gerlach Experiment

The quantum numbers $n,\ l,\ m$ are not sufficient to fully characterize the physical state of the electrons in an atom. In 1926, Otto Stern and Walther Gerlach carried out an experiment that could not be explained in terms of the three quantum numbers $n,\ l,\ m$ and showed that there is, in fact, another quantum-mechanical degree of freedom that needs to be included in the theory. The experiment is illustrated in the figure 8.9.1. A beam of atoms (e.g. hydrogen or silver atoms) is sent through a spatially inhomogeneous magnetic field with a definite field gradient toward one of the poles. It is observed that the beam splits into two beams as it passes through the field region.

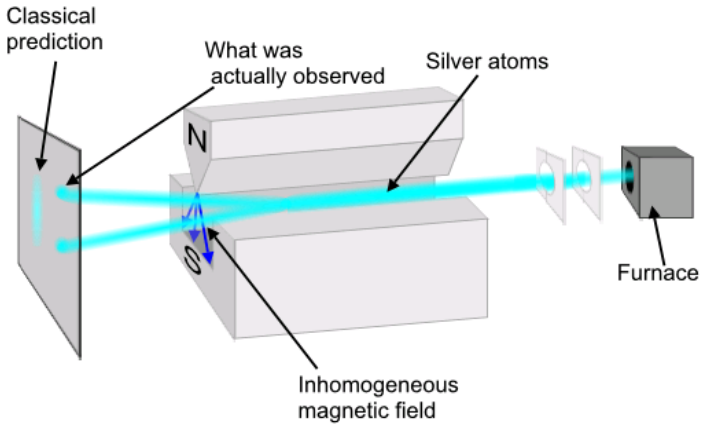


Figure 2.7.1: The Stern-Gerlach apparatus. from Wikipedia

The fact that the beam splits into 2 beams suggests that the electrons in the atoms have a degree of freedom capable of coupling to the magnetic field. That is, an electron has an *intrinsic magnetic moment* M arising from a degree of freedom that has no classical analog. The magnetic moment must take on only 2 values according to the Stern-Gerlach experiment. The intrinsic property that gives rise to the magnetic moment must have some analog to a *spin*, S; unlike position and momentum, which have clear classical analogs, spin does not.

The implication of the Stern-Gerlach experiment is that we need to include a fourth quantum number, m_s in our description of the physical state of the electron. That is, in addition to give its principle, angular, and magnetic quantum numbers, we also need to say if it is a spin-up electron or a spin-down electron.

Electron Spin

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers *n*, *l*, and m_l. Scientists also discovered that applying a magnetic field caused

the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called electron spin.

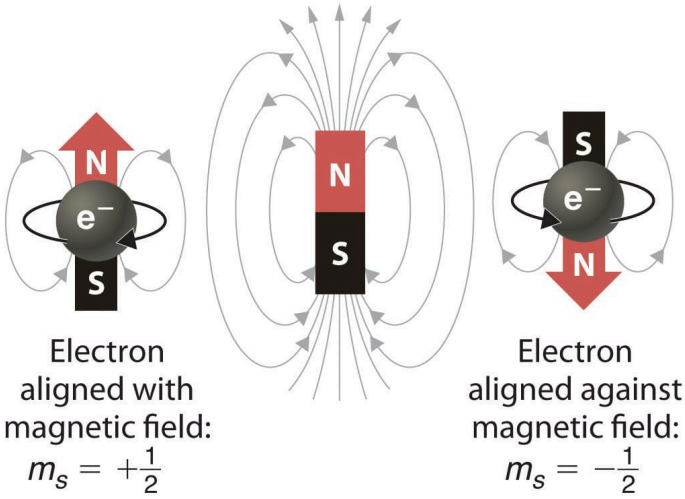


Figure 2.7.2: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure 2.7.2). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated +½ (up) and –½ (down) to indicate that the two orientations are opposites; the subscript s is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion principle: *No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).*

By giving the values of *n*, *l*, and m_l, we also specify a particular orbital (e.g., 1s with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values (+½ or –½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which was originally based on the physical and chemical properties of the known elements.

Example 2.7.2

List all the allowed combinations of the four quantum numbers (*n*, *l*, m_l, m_s) for electrons in a 2*p* orbital and predict the maximum number of electrons the 2*p* subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A. List the quantum numbers (*n*, *l*, m_l) that correspond to an $n = 2p$ orbital. List all allowed combinations of (*n*, *l*, m_l).
B. Build on these combinations to list all the allowed combinations of (*n*, *l*, m_l, m_s).
C. Add together the number of combinations to predict the maximum number of electrons the 2*p* subshell can accommodate.

Solution:

A For a 2*p* orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l, (-l + 1), \ldots, (l - 1), l$. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, –1).

B Because m_s is independent of the other quantum numbers and can have values of only +½ and –½, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, +½), (2, 1, 1, –½), (2, 1, 0, +½), (2, 1, 0, –½), (2, 1, –1, +½), and (2, 1, –1, –½).

C Hence the 2*p* subshell, which consists of three 2*p* orbitals ($2p_x$, $2p_y$, and $2p_z$), can contain a total of six electrons, two in each orbital.

Exercise 2.7.2

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a 6s orbital, and predict the total number of electrons it can contain.

Answer: (6, 0, 0, +½), (6, 0, 0, –½); two electrons

Summary

In addition to the three quantum numbers (n, l, m_l) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the **electron spin** quantum number (m_s), which can have values of +½ or –½ for any electron, corresponding to the two possible orientations of an electron in a magnetic field. The concept of electron spin has important consequences for chemistry because the **Pauli exclusion principle** implies that no orbital can contain more than two electrons (with opposite spin).

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2.8: 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
ℓ = 0	ℓ = 1	ℓ = 2	ℓ = 3
m_ℓ = 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 2.8.1.

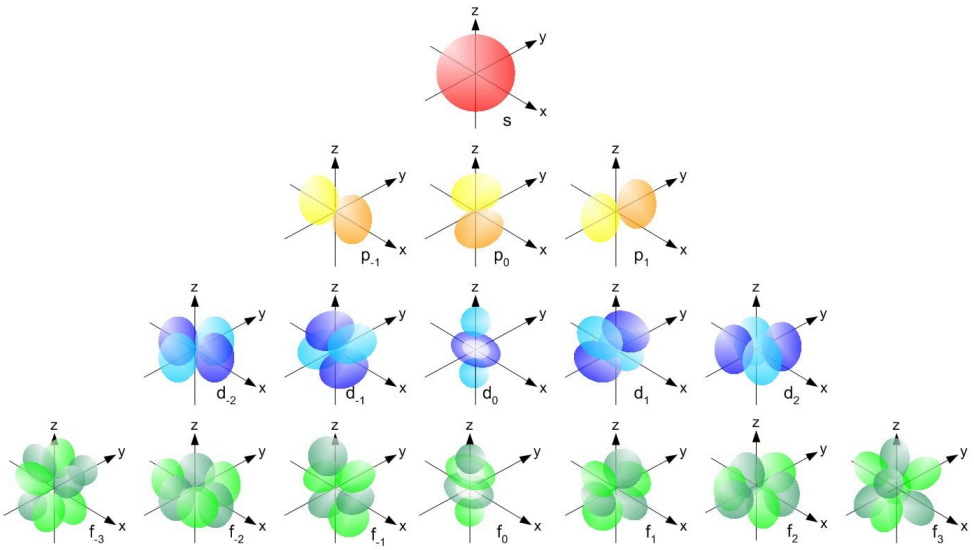


Figure 2.8.1: The 1s orbital (red), the 2p orbitals (yellow), the 3d orbitals (blue) and the 4f orbitals (green) are contrasted.

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:

$$N = n - l - 1 \tag{2.8.1}$$

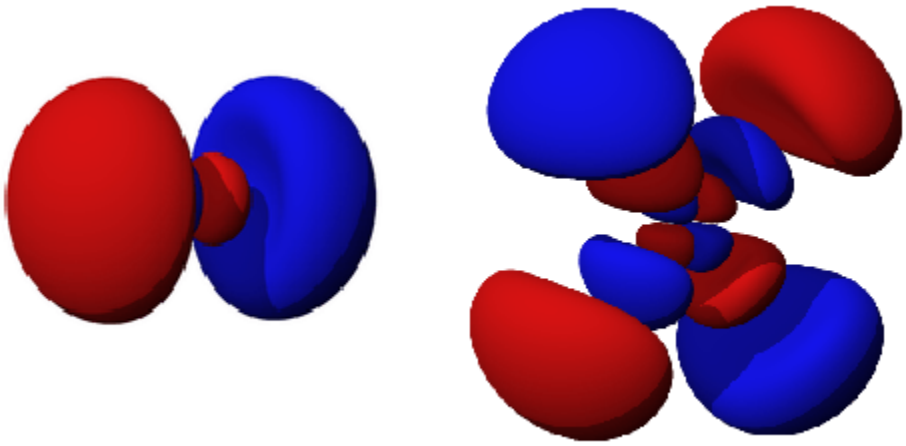


Figure 2.8.2: Two orbitals. (left) The $3p_x$ orbital has one radial node and one angular node. (right) The $5d_{xz}$ orbital has two radial nodes and two angular nodes. Images used with permission from Wikipedia

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**.

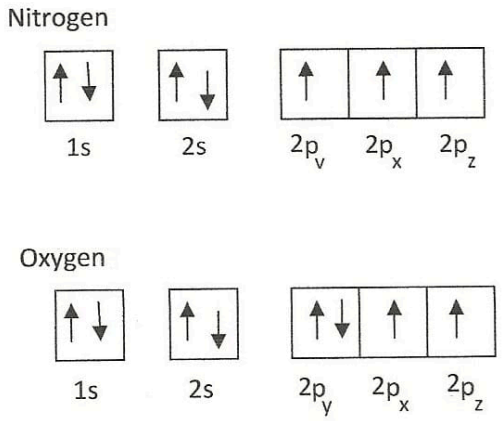


Figure 2.8.3: Electron configuration of nitrogen and oxygen atoms

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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2.9: 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.

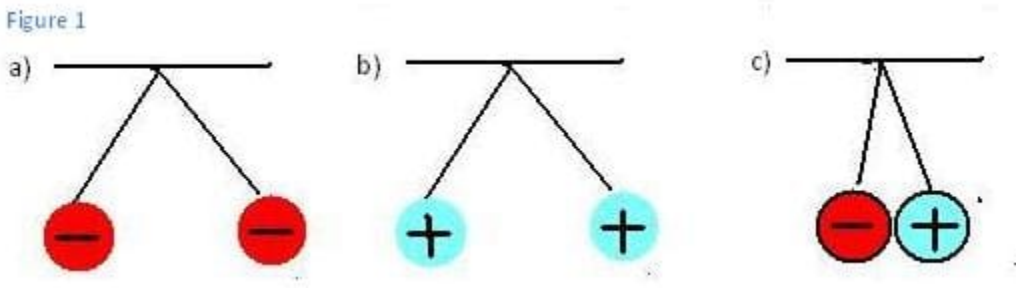


Figure 1: a) The two electrons are placed together and repel each other because of the same charge. b) The two protons are repelling each other for the same reason. c) When oppositely charged particles, an electron and a proton, are placed together, they attract each other.

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.

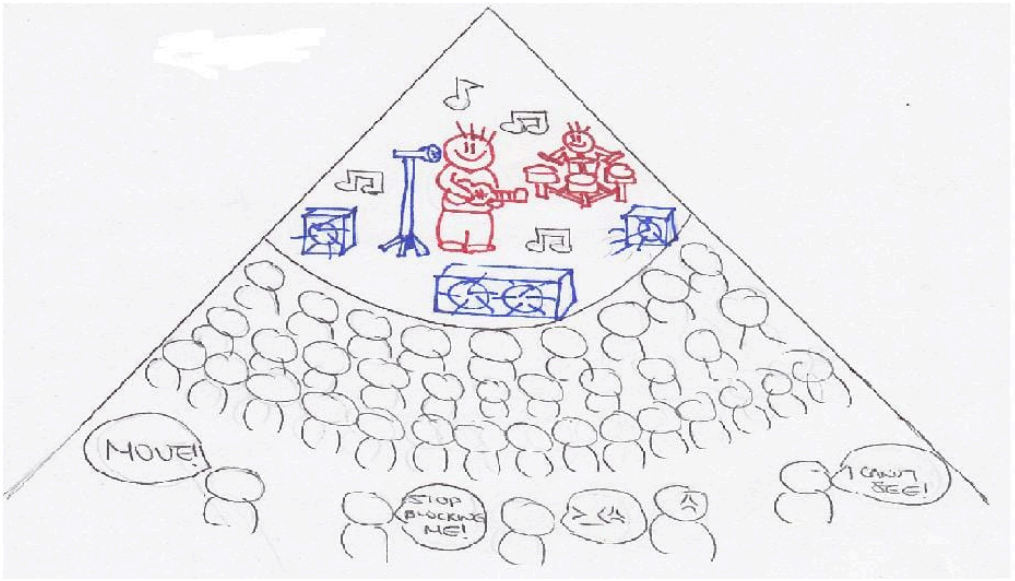


Figure 2.1

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 = $4\pi r^2$ X $R^2(r)$

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.

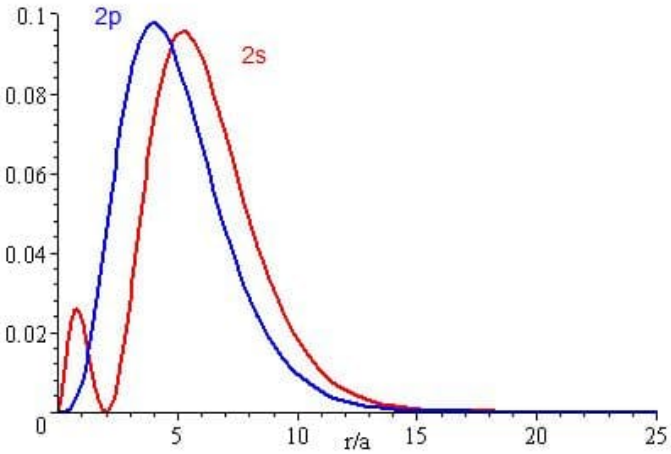


Figure 3.3

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

- Mixue (Michelle) Xie (UCD)

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2.10: 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.

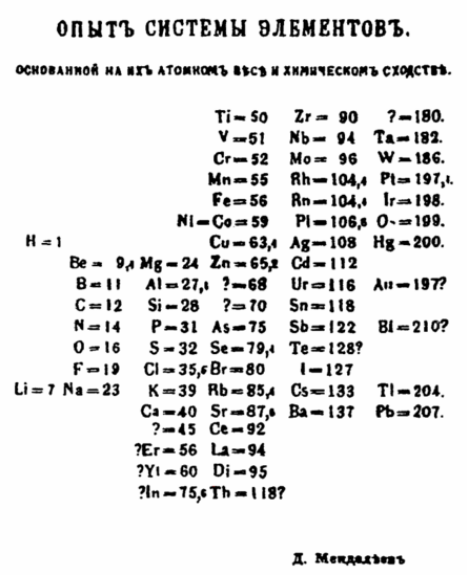
The Periodic Law

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**.

$$\text{Atomic (molar) volume } (\text{cm}^3/\text{mol}) = \frac{\text{molar mass (g/ mol)}}{\rho\ (\text{cm}^3/\text{g})}$$

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 = 197,1.	
			Fe = 56	Ru = 104,4	Ir = 198.	
			Ni = Co = 59	Pl = 106,6	O = 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 = 35,6	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:

$$\text{Li (174 }^{\circ}\text{C)} > \text{Na (97.8 }^{\circ}\text{C)} > \text{K (63.7 }^{\circ}\text{C)} > \text{Rb (38.9 }^{\circ}\text{C)} > \text{Cs (28.5 }^{\circ}\text{C)}$$

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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1. Petrucci, Ralph H., William S. Harwood, F. G. Herring, and Jeffrey D. Madura. General Chemistry: Principles and Modern Applications. 9th ed. Upper Saddle River: Pearson Education, Inc., 2007.
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3. Petrucci, Ralph H., Carey Bissonnette, F. G. Herring, and Jeffrey D. Madura. General Chemistry: Principles and Modern Applications. Custom Edition for CHEM 2. Pearson Learning Solutions, 2010.
4. Mendeleev's 1869 Periodic Table. In *Wikimedia Commons*. Retrieved 4 December 2010, from commons.wikimedia.org/wiki/Fi...odic_table.png.
5. Periodic Table of Elements. In *Wikimedia Commons*. Retrieved 4 December 2010, from commons.wikimedia.org/wiki/Pe...le_of_Elements.

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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2.11: Electron Configurations

Learning Objectives

- To understand the basics of adding electrons to atomic orbitals
- To understand the basics of the Aufbau principle

The electron configuration of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

The Aufbau Principle

We construct the periodic table by following the aufbau principle (from German, meaning "building up"). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 6.29, recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to $m_S = +½$, which is arbitrarily written first, and one with spin down ↓, corresponding to $m_S = –½$. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

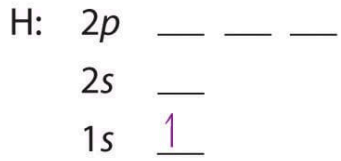
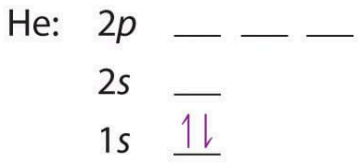


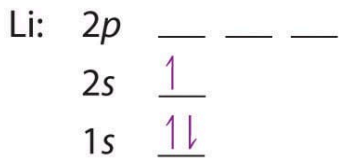
Figure 6.29"), and the electron configuration is written as $1s^1$ and read as "one-s-one."

A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the 1s orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



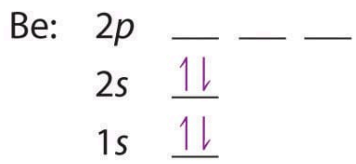
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the 1s orbital can hold two of the electrons with their spins paired. Figure 6.29 tells us that the next lowest energy orbital is 2s, so the orbital diagram for lithium is

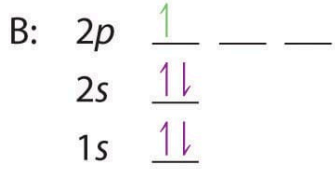


This electron configuration is written as $1s^2 2s^1$.

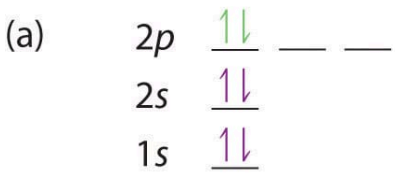
The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1s and 2s orbitals to achieve a $1s^2 2s^2$ electron configuration:

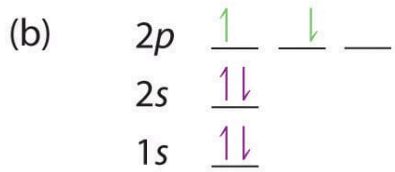


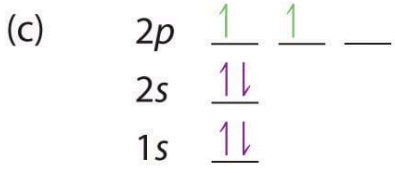
When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Because all three 2*p* orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2 2s^2 2p^1$:



At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2*p* orbital that already has an electron, or should it go in one of the empty 2*p* orbitals? If it goes in an empty 2*p* orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the 2*p* orbitals are degenerate?

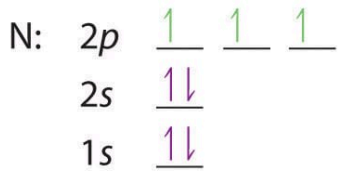






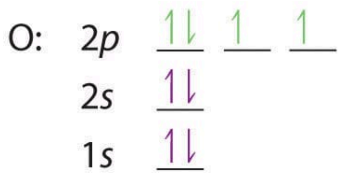
Because of electron-electron repulsions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates Hund's rule (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

When we get to nitrogen (Z = 7, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

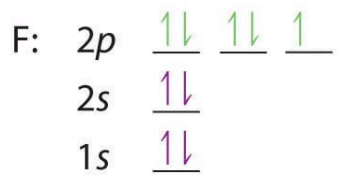


with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

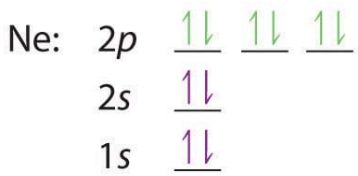
At oxygen, with Z = 8 and eight electrons, we have no choice. One electron must be paired with another in one of the 2*p* orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration. Because all the 2*p* orbitals are degenerate, it doesn't matter which one has the pair of electrons.



Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:



When we reach neon, with Z = 10, we have filled the 2*p* subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:



Notice that for neon, as for helium, all the orbitals through the 2*p* level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

YouTube Video

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Electron Configuration of Atoms: https://youtu.be/LlY-O3-bfnk

Valence Electrons

As we continue through the periodic table in this way, writing the electron configurations of larger and larger atoms, it becomes tedious to keep copying the configurations of the filled inner subshells. In practice, chemists simplify the notation by using a bracketed noble gas symbol to represent the configuration of the noble gas from the preceding row because all the orbitals in a noble gas are filled. For example, [Ne] represents the $1s^2 2s^2 2p^6$ electron configuration of neon (Z = 10), so the electron configuration of sodium, with Z = 11, which is $1s^2 2s^2 2p^6 3s^1$, is written as [Ne]$3s^1$:

Neon	Z = 10	$1s^2 2s^2 2p^6$
Sodium	Z = 11	$1s^2 2s^2 2p^6 \mathbf{3}s^1$ = [Ne]$\mathbf{3}s^1$

Because electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, they are rarely involved in chemical reactions. This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, which are called the valence electrons. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium and lithium, we have:

Sodium	$1s^2 2s^2 2p^6 3s^1$ = [Ne]$3s^1$
Lithium	$1s^2 2s^1$ = [He]$2s^1$

It is readily apparent that both sodium and lithium have one *s* electron in their valence shell. We would therefore predict that sodium and lithium have very similar chemistry, which is indeed the case.

As we continue to build the eight elements of period 3, the 3*s* and 3*p* orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration [Ne]$3s^2 3p^6$, corresponding to a filled valence shell.

Example 2.11.2

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, Z = 15. What is its valence electron configuration?

Given: atomic number

Asked for: orbital diagram and valence electron configuration for phosphorus

Strategy:

A. Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.
B. Referring to Figure 6.29, draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.
C. Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

Solution:

A Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

B The additional five electrons are placed in the next available orbitals, which Figure 6.29 tells us are the 3*s* and 3*p* orbitals:

P: [Ne] 3*p* ___ ___ ___
3*s* ___

Because the 3s orbital is lower in energy than the 3*p* orbitals, we fill it first:

P: [Ne] 3*p* ___ ___ ___
3*s* ⇅

Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:

P: [Ne] 3*p* 1 1 1
3*s* ⇅

The electron configuration is $[Ne]3s^2 3p^3$.

C We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^2 3p^3$.

Exercise 2.11.2

Draw an orbital diagram and use it to derive the electron configuration of chlorine, $Z = 17$. What is its valence electron configuration?

Answer: $[Ne]3s^2 3p^5$; $3s^2 3p^5$

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Definition of Valence Electrons: https://youtu.be/_ldxOYwM2VM

The general order in which orbitals are filled is depicted in Figure 2.11.1. Subshells corresponding to each value of *n* are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4s orbital is filled prior to the 3*d* orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is $[Ar]4s^1$, and the configuration of calcium is $[Ar]4s^2$. Five 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* orbitals. Notice that the last member of this row is the noble gas krypton ($Z = 36$), $[Ar]4s^2 3d^{10} 4p^6 = [Kr]$, which has filled 4s, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5s, 4*d*, and 5*p* orbitals are filled sequentially.

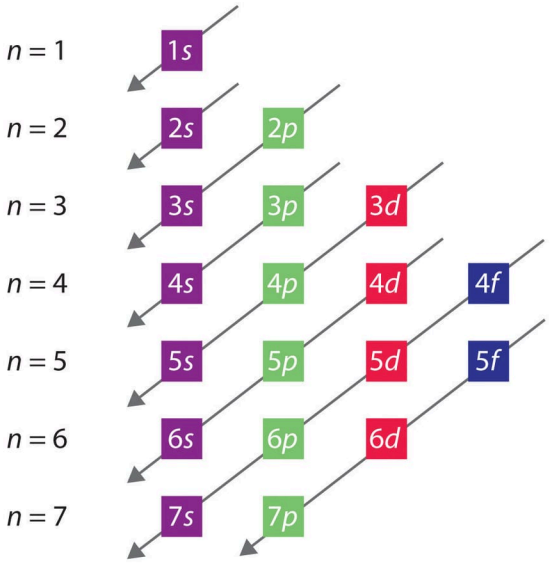


Figure 2.11.1 Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.

The sixth row of the periodic table will be different from the preceding two because the 4*f* orbitals, which can hold 14 electrons, are filled between the 6*s* and the 5*d* orbitals. The elements that contain 4*f* orbitals in their valence shell are the lanthanides. When the 6*p* orbitals are finally filled, we have reached the next (and last known) noble gas, radon (Z = 86), [Xe]$6s^2 4f^{14} 5d^{10} 6p^6$ = [Rn]. In the last row, the 5*f* orbitals are filled between the 7*s* and the 6*d* orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

Example 2.11.3

Write the electron configuration of mercury (Z = 80), showing all the inner orbitals.

Given: atomic number

Asked for: complete electron configuration

Strategy:

Using the orbital diagram in Figure 2.11.1 and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

Solution:

By placing the electrons in orbitals following the order shown in Figure 2.11.1 and using the periodic table as a guide, we obtain

$1s^2$	row 1	2 electrons
$2s^2 2p^6$	row 2	8 electrons
$3s^2 3p^6$	row 3	8 electrons
$4s^2 3d^{10} 4p^6$	row 4	18 electrons
$5s^2 4d^{10} 5p^6$	row 5	18 electrons
	row 1–5	54 electrons

After filling the first five rows, we still have 80 – 54 = 26 more electrons to accommodate. According to Figure 2.11.2, we need to fill the 6s (2 electrons), 4*f* (14 electrons), and 5*d* (10 electrons) orbitals. The result is mercury's electron configuration:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} = Hg = [Xe]6s^2 4f^{14} 5d^{10}$$

with a filled 5*d* subshell, a $6s^2 4f^{14} 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

Exercise 2.11.3

Although element 114 is not stable enough to occur in nature, two isotopes of element 114 were created for the first time in a nuclear reactor in 1999 by a team of Russian and American scientists. Write the complete electron configuration for element 114.

Answer: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^2$

The electron configurations of the elements are presented in Figure 2.11.3, which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted by Figure 2.11.1. Some of these anomalies occur as the 3*d* orbitals are filled. For example, the observed ground state electron configuration of chromium is $[Ar]4s^1 3d^5$ rather than the predicted $[Ar]4s^2 3d^4$. Similarly, the observed electron configuration of copper is $[Ar]4s^1 3d^{10}$ instead of $[Ar]s^2 3d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled (ns^1, np^3, nd^5, nf^7) or filled (ns^2, np^6, nd^{10}, nf^{14}) subshell. Given the small differences between higher energy levels, this added stability is enough to shift an electron from one orbital to another. In heavier elements, other more complex effects can also be important, leading to some of the additional anomalies indicated in Figure 2.11.3. For example, cerium has an electron configuration of $[Xe]6s^2 4f^1 5d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

Note

Additional stability is associated with half-filled or filled subshells.

Summary

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**.

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2.12: Magnetic Properties

Learning Objectives

- To predict the magnetic properties of atoms and molecules based on their electronic configurations.

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism. Only paramagnetism, and diamagnetism are discussed here.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can orient in either direction, they exhibit magnetic moments that can align with a magnet. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (that is best understood with molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:

YouTube Video

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Video $2.12.1$***:*** *A chemical demonstration of the paramagnetism of molecular oxygen, as shown by the attraction of liquid oxygen to magnets.*

As shown in Video $2.12.1$, since molecular oxygen (O_2 is paramagnetic, it is attracted to the magnet. In contrast, molecular nitrogen, N_2, has no unpaired electrons and it is diamagnetic (discussed below); it is therefore unaffected by the magnet.

Note

Paramagnetism is a form of magnetism whereby materials are **attracted** by an externally applied magnetic field.

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include Sc^{3+}, Ti^{4+}, Zn^{2+}, and Cu^{+}. These metals are the not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals,

there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 2.12.1.

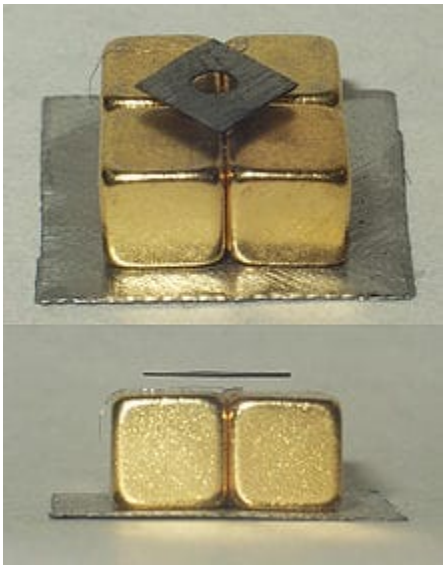


Figure 2.12.1: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

Note

Diamagnetic materials are **repelled** by the applied magnetic field.

Diamagnetism, to a greater or lesser degree, is a property of all materials and always makes a weak contribution to the material's response to a magnetic field. For materials that show some other form of magnetism (such paramagntism), the diamagnetic contribution becomes negligible.

How to tell if a substance is paramagnetic or diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration
2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic (one or more electrons unpaired) or diamagnetic (all electrons paired)

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Determining Magnetic Properties from Orbital Diagrams: https://youtu.be/lun_w5VKD8k

Example 2.12.1: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

Solution

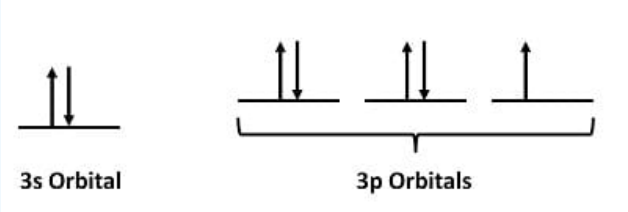
Follow the four steps outlines above.

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Since there is an unpaired electron, Cl atoms are paramagnetic (but weakly since only one electron is unpaired).

Exercise 2.12.1

Indicate whether boron atoms are paramagnetic or diamagnetic.

Answer:

The B atom has $2s^2 2p^1$ as the electron configuration. Because it has one unpaired electron, it is paramagnetic.

Example 2.12.2: Zinc Atoms

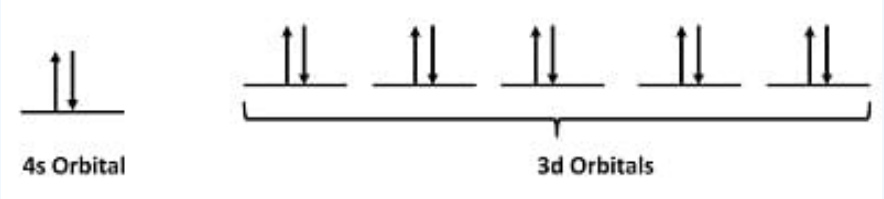
Are zinc atoms paramagnetic or diamagnetic?

Solution

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^2 3d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

Exercise 2.12.2

Indicate whether F^- ions are paramagnetic or diamagnetic.

Answer

The F^- ion has $2s^2 2p^6$ has the electron configuration. Because it has no unpaired electrons, it is diamagnetic.

Problems

1. How many unpaired electrons are found in oxygen atoms ?
2. How many unpaired electrons are found in bromine atoms?
3. Indicate whether Fe^{2+} ions are paramagnetic or diamagnetic.

Answers

1. The O atom has $2s^2 2p^4$ as the electron configuration. Therefore, O has 2 unpaired electrons.
2. The Br atom has $4s^2 3d^{10} 4p^5$ as the electron configuration. Therefore, Br has 1 unpaired electron.
3. The Fe^{2+} ion has $3d^6$ has the electron configuration. Because it has 4 unpaired electrons, it is paramagnetic.

References

1. Pettrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007

2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

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2.13: Sizes of Atoms and Ions

Learning Objectives

- To understand periodic trends in atomic radii.
- To predict relative ionic sizes within an isoelectronic series.

Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes. In this section, we discuss how atomic and ion "sizes" are defined and obtained.

Atomic Radii

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure 2.13.1 which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

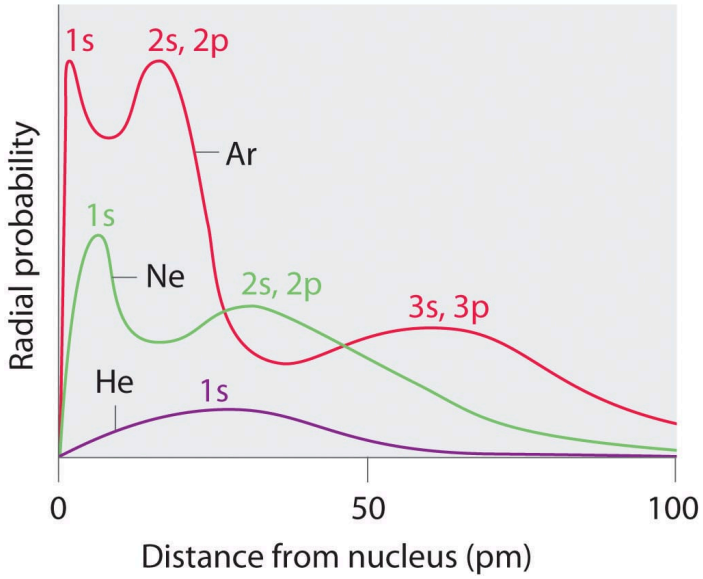


Figure 2.13.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1s electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈8 pm, and the 2s and 2p electrons combine to form another maximum at ≈35 pm (the n = 2 shell). In Ar, the 1s electrons have a maximum at ≈2 pm, the 2s and 2p electrons combine to form a maximum at ≈18 pm, and the 3s and 3p electrons combine to form a maximum at ≈70 pm.

Figure 2.13.1 also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell (n = 1), it shows only a single peak. In contrast, neon, with filled n = 1 and 2 principal shells, has two peaks. Argon, with filled n = 1, 2, and 3 principal shells, has three peaks. The peak for the filled n = 1 shell occurs at successively shorter distances for neon (Z = 10) and argon (Z = 18) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n. Consequently, the two electrons in the n = 1 shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the n = 1 shell also decreases tremendously (the filled 1s orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled n = 2 shell in argon is located closer to the nucleus and has a lower energy than the n = 2 shell in neon.

Figure 2.13.1 illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a covalent atomic radius (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (part (a) in Figure 2.13.2). Atomic radii are often measured in angstroms (Å), a non-SI unit: 1 Å = 1×10^{-10} m = 100 pm.

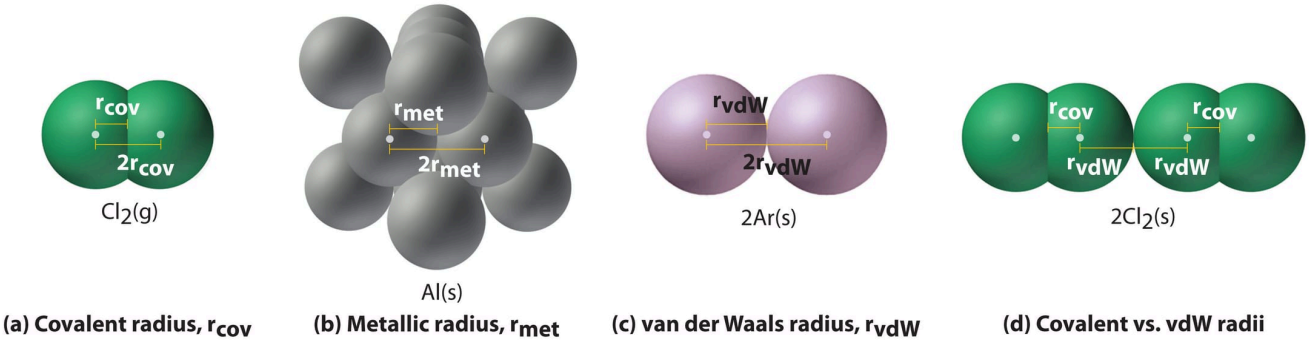


Figure 2.13.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?

In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds.A similar approach for measuring the size of ions is discussed later in this section.

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the metallic atomic radius (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms (part (b) in Figure 2.13.2). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the van der Waals atomic radius (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (part (c) in Figure 2.13.2). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $Cl_{2(s)}$ at low temperatures). These radii are generally not the same (part (d) in Figure 2.13.2).

Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 2.13.3).

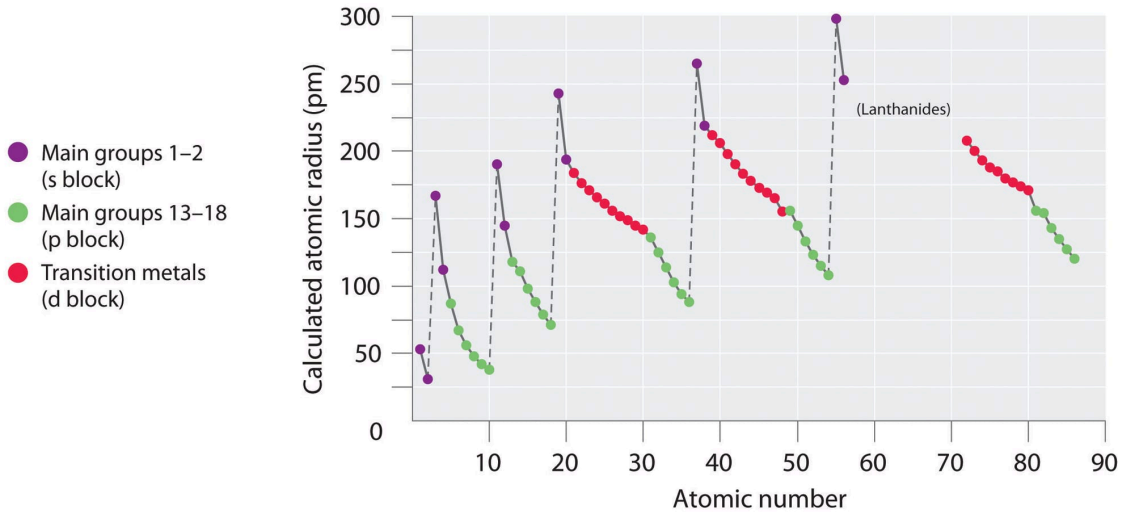


Figure 2.13.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table.

In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 2.13.4).

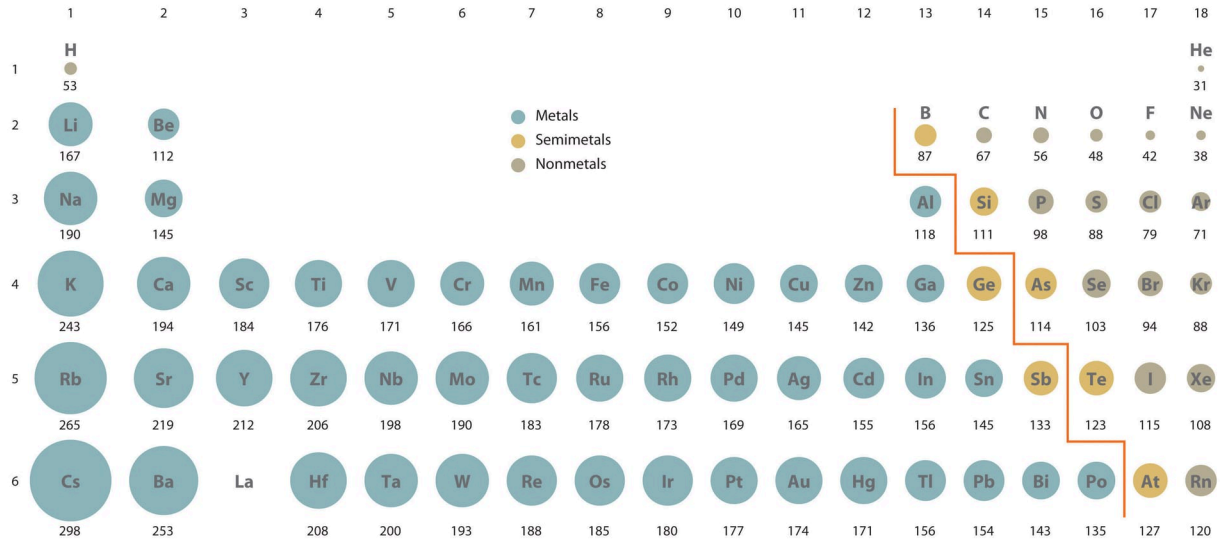


Figure 2.13.4 *Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: http://www.webelements.com. Web Elements is an excellent on line source for looking up atomic properties.*

Note

Atomic radii decrease from left to right across a row and increase from top to bottom down a column.

Trends in atomic size result from differences in the **effective nuclear charges (Z_{eff})** experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always *less* than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are

being added to the 2*s* and 2*p* orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2*s* electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.) In contrast, the two 2*s* electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2*s* electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2*s* and 2*p* orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size.

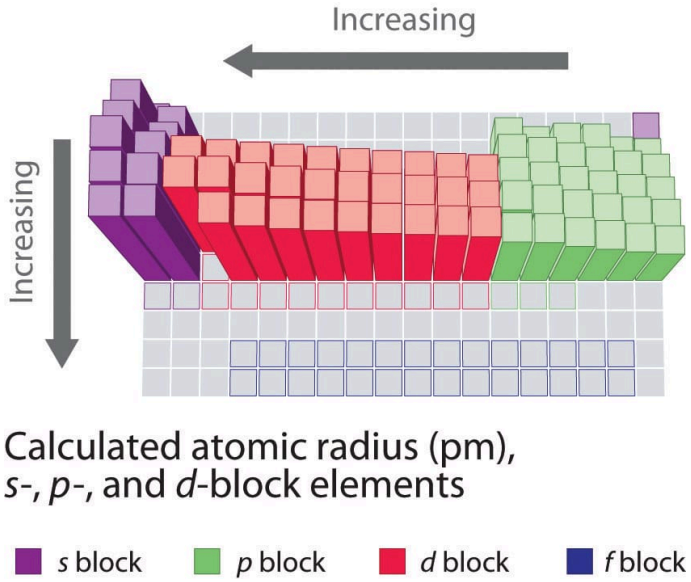


Figure 2.13.5: *The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.*

The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number *n* is not constant. As we saw in Chapter 2, the size of the orbitals increases as *n* increases, *provided the nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to *ns* orbitals with increasing values of *n*. However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number *n* increases from 2 to 6, but the nuclear charge increases from +3 to +55!

As a consequence the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the the inner electrons. If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration. The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ shells, abbreviated as $[Xe]5s^2 4d^{10} 5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

Note

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

Example 2.13.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing atomic radius: aluminum, carbon, and silicon.

Given: three elements

Asked for: arrange in order of increasing atomic radius

Strategy:

A. Identify the location of the elements in the periodic table. Determine the relative sizes of elements located in the same column from their principal quantum number *n*. Then determine the order of elements in the same row from their effective nuclear charges. If the elements are not in the same column or row, use pairwise comparisons.
B. List the elements in order of increasing atomic radius.

Solution:

A These elements are not all in the same column or row, so we must use pairwise comparisons. Carbon and silicon are both in group 14 with carbon lying above, so carbon is smaller than silicon (C < Si). Aluminum and silicon are both in the third row with aluminum lying to the left, so silicon is smaller than aluminum (Si < Al) because its effective nuclear charge is greater. **B** Combining the two inequalities gives the overall order: C < Si < Al.

Exercise 2.13.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

Answer: O < S < P < K

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Atomic Radius: https://youtu.be/ZYKB8SNrGVY

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom (cations) to form a positive ion or when additional electrons attach themselves to neutral atoms (anions) to form a negative one. The designations cation or anion come from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charges anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it *is* possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius (the radius of a cation or anion) of one or both. As illustrated in Figure 2.13.6, the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of

ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na^+ ion is essentially the same in NaCl and Na_2S, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

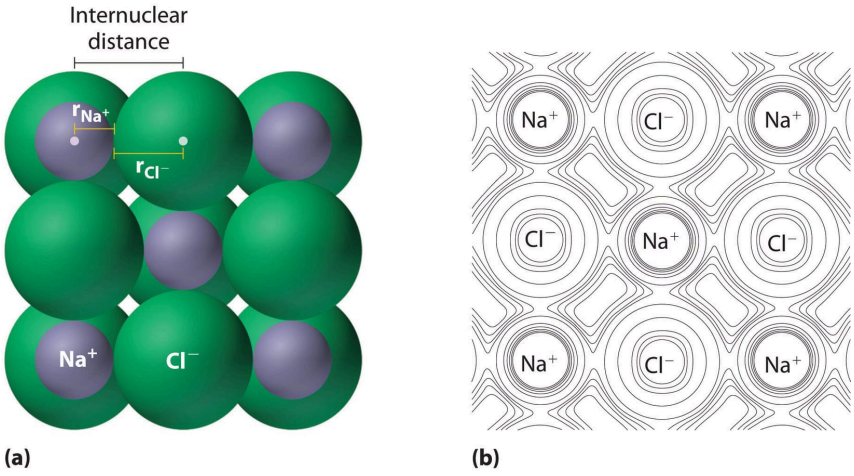


Figure 2.13.6: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl^- and Na^+.

A comparison of ionic radii with atomic radii (Figure 2.13.7) *cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom*. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases (compare Li at 167 pm with Li^+ at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe^{2+} at 78 pm with Fe^{3+} at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases (compare F at 42 pm with F^- at 133 pm).

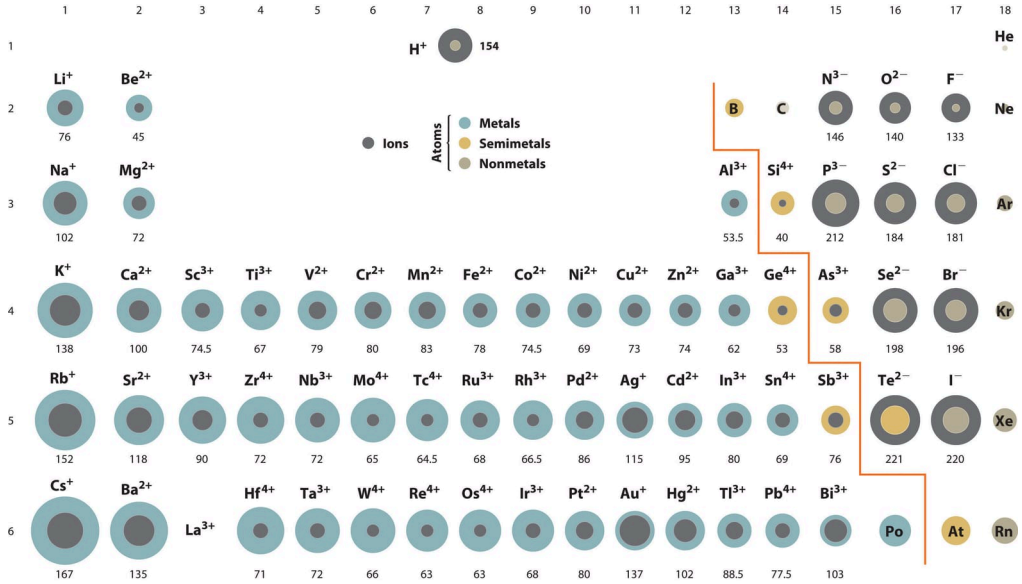


Figure 3.7. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

Note

Cations are **always** smaller than the neutral atom, and anions are **always** larger.

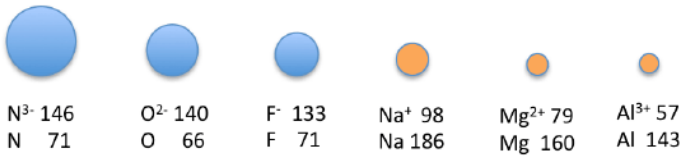
Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table 2.13.1. All three species have a nuclear charge of +11, but they contain 10 (Na^+), 11 (Na^0), and 12 (Na^-) electrons. The Na^+ ion is significantly smaller than the neutral Na atom because the $3s^1$ electron has been removed to give a closed shell with $n = 2$. The Na^- ion is larger than the parent Na atom because the additional electron produces a $3s^2$ valence electron configuration, while the nuclear charge remains the same.

Table 2.13.1: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6 3s^2$
Radius (pm)	102	154*	202†
***The metallic radius measured for Na(s).**			
†Source: M. J. Wagner and J. L. Dye, "Alkalides, Electrides, and Expanded Metals," Annual Review of Materials Science 23 (1993): 225–253.			

Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of n lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an isoelectronic series. For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^2 2s^2 2p^6$) is shown in Table 7.3



The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+}. All six of the ions contain 10 electrons in the 1s, 2s, and 2p orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. The neon atom in this isoelectronic series is not listed in Table 2.13.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table 9.3.3 Radius of Ions with the Neon Closed-Shell Electron Configuration. Source: R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallographica 32, no. 5 (1976): 751–767.

Ion	Radius (pm)	Atomic Number
N^{3-}	146	7

O^{2-}	140	8
F^-	133	9
Na^+	98	11
Mg^{2+}	79	12
Al^{3+}	57	13

Example 2.13.2

Based on their positions in the periodic table, arrange these ions in order of increasing radius: Cl^-, K^+, S^{2-}, and Se^{2-}.

Given: four ions

Asked for: order by increasing radius

Strategy:

A. Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.
B. Determine the relative sizes of the ions based on their principal quantum numbers *n* and their locations within a row.

Solution:

A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. K^+, Cl^-, and S^{2-} form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because K^+ has the greatest nuclear charge (Z = 19), its radius is smallest, and S^{2-} with Z = 16 has the largest radius. Because selenium is directly below sulfur, we expect the Se^{2-} ion to be even larger than S^{2-}. **B** The order must therefore be $K^+ < Cl^- < S^{2-} < Se^{2-}$.

Exercise 2.13.2

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br^-, Ca^{2+}, Rb^+, and Sr^{2+}.

Answer: $Ca^{2+} < Sr^{2+} < Rb^+ < Br^-$

Summary

- Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges.

A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius (r_{cov})** is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius (r_{met})** is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius (r_{vdW})** of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

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2.14: Ionization Energy

Learning Objectives

- To correlate ionization energies with the chemistry of the elements

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy (I) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad \text{energy required=I} \tag{2.14.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 9.4.1. Larger values of I mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol \tag{2.14.2}$$

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily. We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an nth ionization energy (I_n) according to the following reactions:

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad I_1 = \text{1st ionization energy} \tag{2.14.3}$$

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad I_2 = \text{2nd ionization energy} \tag{2.14.4}$$

$$E^+_{(g)} \rightarrow E^{2+}_{(g)} + e^- \qquad I_3 = \text{3rd ionization energy} \tag{2.14.5}$$

Values for the ionization energies of Li and Be listed in Table 2.14.1 show that successive ionization energies for an element increase steadily; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

Note

Successive ionization energies for an element **increase** steadily.

Table 2.14.1: Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of

Reaction	Electronic Transition	I
$Li_{(g)} \rightarrow Li^+_{(g)} + e^-$	$1s^2 2s^1 \rightarrow 1s^2$	I_1 = 520.2

Reaction	Electronic Transition	I
$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^-$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2
$Li^{2+}_{(g)} \rightarrow Li^{3+}_{(g)} + e^-$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0

The most important consequence of the values listed in Table 2.14.1 is that the chemistry of Li is dominated by the Li^+ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li

$$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^- \tag{2.14.8}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be

$$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^- \tag{2.14.9}$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both Li^+ and Be^{2+} have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 2s valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the 1+ ion but not the 2+ or 3+ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the 2+ ion but not the 3+ or 4+ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

Note

The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.

Ionization Energies of *s*- and *p*-Block Elements

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of Li and Be (Table 2.14.2): successive ionization energies increase steadily as electrons are removed from the valence orbitals (3s or 3*p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table 2.14.2. Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from Al, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.

Table 2.14.2: Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table.Source: Data from CRC Handbook of Chemistry and Physics (2004).

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	579.4.4	1816.7	2744.8	**11,579.4.4**	—	—	—
***Inner-shell electron**							

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1909.4.4	2914.1	4963.6	6274.0	**21,269.4.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,109.4.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3
***Inner-shell electron**							

Example 2.14.1: Highest Fourth Ionization Energy

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

a. List the electron configuration of each element.
b. Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

- B: [He]$2s^2 2p^1$
- C: [He]$2s^2 2p^2$
- N: [He]$2s^2 2p^3$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:

$$E^{3+}_{(g)} \rightarrow E^{4+}_{(g)} + e^- \tag{2.14.10}$$

Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

Exercise 2.14.1: Lowest Second Ionization Energy

From their locations in the periodic table, predict which of these elements has the lowest second ionization energy: Sr, Rb, or Ar.

Answer: Sr

The first column of data in Table 2.14.2 shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects represent two sides of the same coin: stronger electrostatic interactions between the

electrons and the nucleus further increase the energy required to remove the electrons.

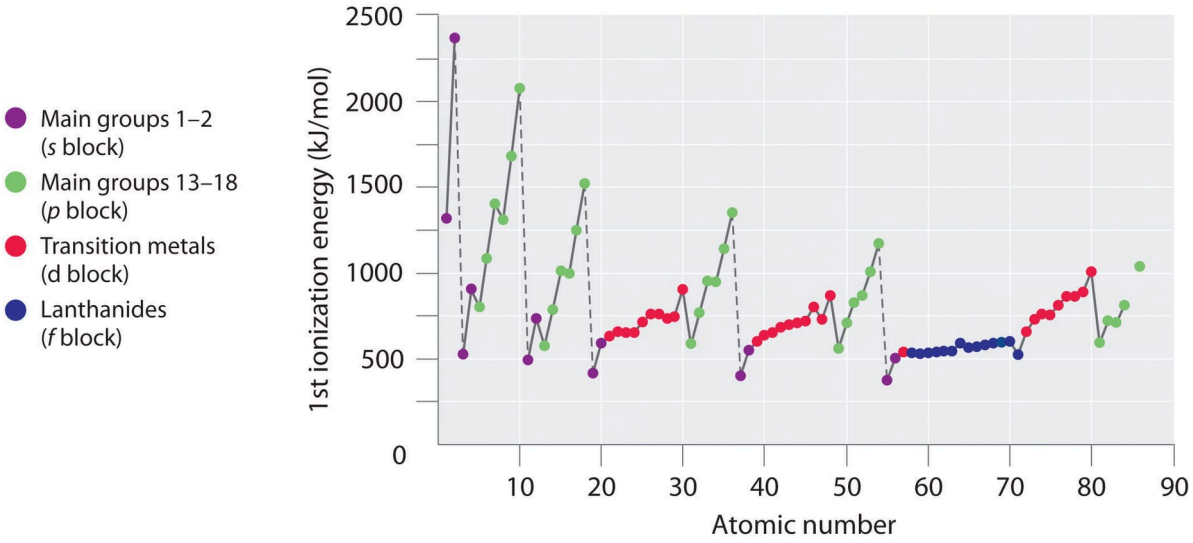


Figure 2.14.1: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electrons in aluminum's filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the s electrons penetrate closer to the nucleus than the *p* electron does. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

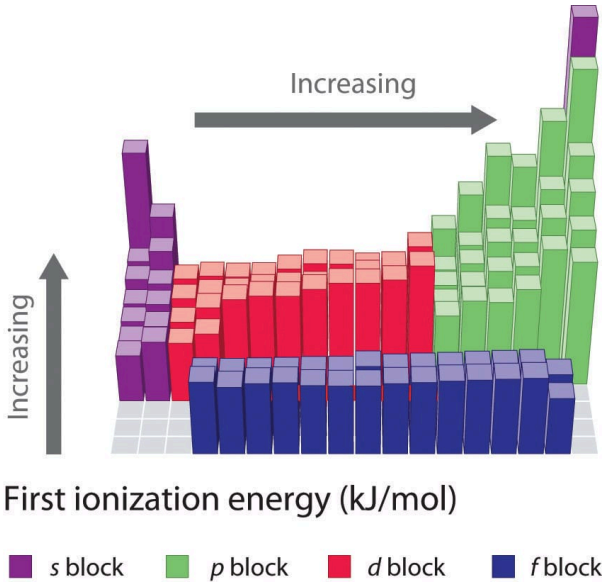


Figure 2.14.2***:*** *First Ionization Energies of the s-, p-, d-, and f-Block Elements*

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 2.14.1 and are presented numerically and graphically in Figure 2.14.2. These figures illustrate three important trends:

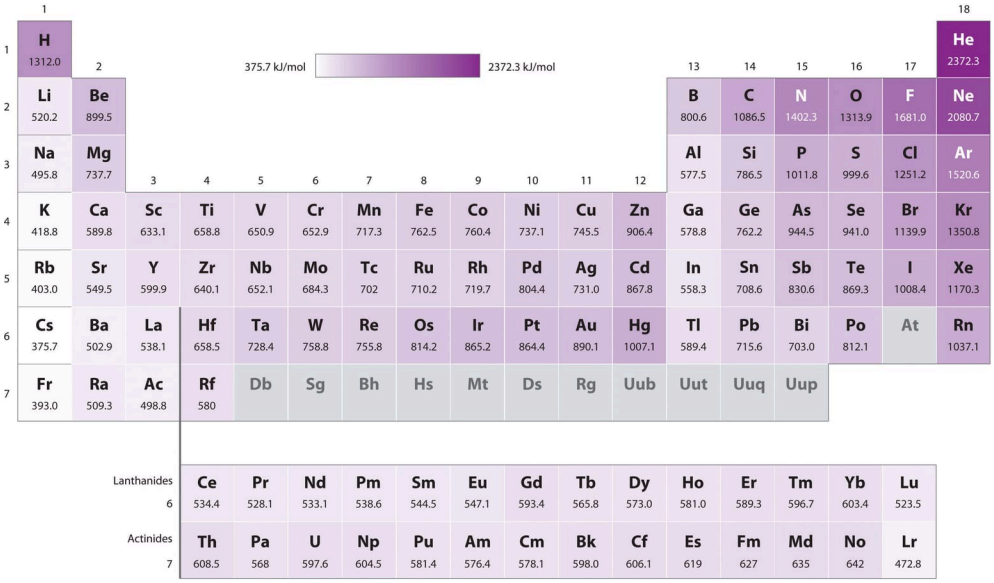
1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the s and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of

the transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12) electron configurations.

2. First ionization energies generally decrease down a column. Although the principal quantum number n increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius corresponds to a lower ionization energy.*
3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).

Note

Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.



The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Gallium (Ga), which is the first element following the first row of transition metals, has the following electron configuration: $[Ar]4s^23d^{10}4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the 4*p* subshell, screening the single 4*p* electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its $[Ar]3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier *p*-block elements. They are sometimes referred to as pseudo noble gas configurations. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the $(n-1)d^{10}$ filled subshell.*

Ionization Energies of Transition Metals & Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the *s*- and *p*-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the *ns* electrons before the $(n-1)d$ or $(n-2)f$ electrons, respectively. This means that transition metal cations have $(n-1)d^n$

valence electron configurations, and lanthanide cations have $(n - 2)f^n$ valence electron configurations. Because the $(n - 1)d$ and $(n - 2)f$ shells are closer to the nucleus than the ns shell, the $(n - 1)d$ and $(n - 2)f$ electrons screen the ns electrons quite effectively, reducing the effective nuclear charge felt by the ns electrons. As Z increases, the increasing positive charge is largely canceled by the electrons added to the $(n - 1)d$ or $(n - 2)f$ orbitals.

That the ns electrons are removed before the $(n - 1)d$ or $(n - 2)f$ electrons may surprise you because the orbitals were filled in the reverse order. In fact, the ns, the $(n - 1)d$, and the $(n - 2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the d orbitals are filled, the effective nuclear charge causes the $3d$ orbitals to be slightly lower in energy than the $4s$ orbitals. The $[Ar]3d^2$ electron configuration of Ti^{2+} tells us that the $4s$ electrons of titanium are lost before the $3d$ electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n - 2)f^n$ valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

Example 2.14.2: Lowest First Ionization Energy

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

Exercise 2.14.2: Highest First Ionization Energy

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer: As

YouTube Video

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Ionization Energy: https://youtu.be/k7j-u02ifzo

Summary

- Generally, the first ionization energy and electronegativity values increase diagonally from the lower left of the periodic table to the upper right, and electron affinities become more negative across a row.

The tendency of an element to lose is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (I)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting ion.

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2.15: Electron Affinity

Learning Objectives

- To master the concept of electron affinity as a measure of the energy required to adding an electron to an atom or ion.
- To recognize the inverse relationship of ionization energies and electron affinities

The electron affinity (EA) of an element E is defined as the energy change that occurs when an electron is added to a gaseous atom:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change}=EA \tag{2.15.1}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released.

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \qquad EA = -346\ kJ/mol \tag{2.15.2}$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$Be_{(g)} + e^- \rightarrow Be^-_{(g)} \qquad EA \geq 0 \tag{2.15.3}$$

Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy:

$$N_{(g)} + e^- \rightarrow N^-_{(g)} \qquad EA \approx 0 \tag{2.15.4}$$

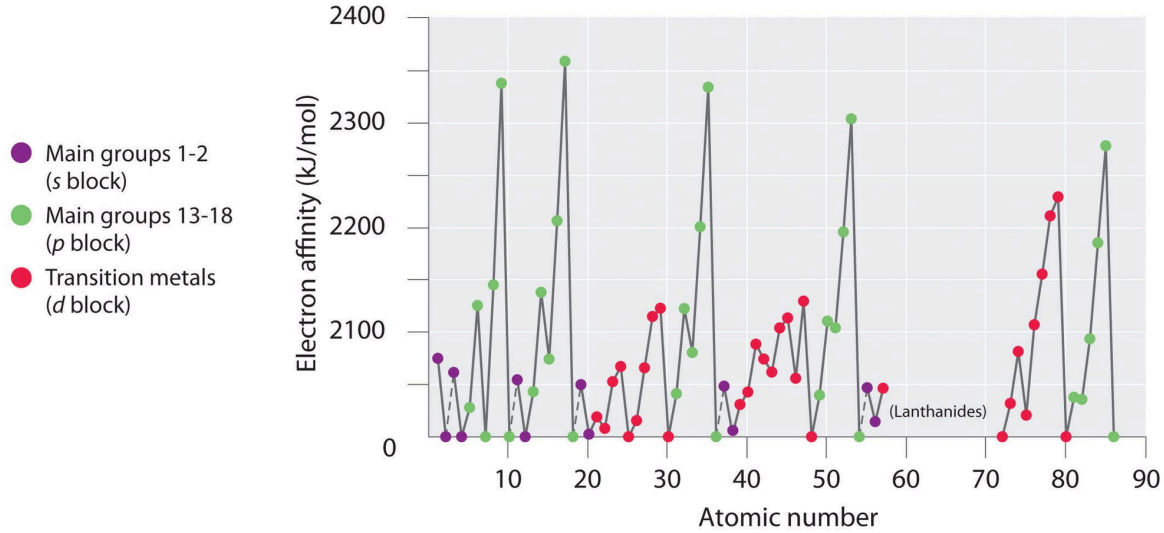


Figure 2.15.1: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table

Note

Generally, electron affinities become more negative across a row of the periodic table.

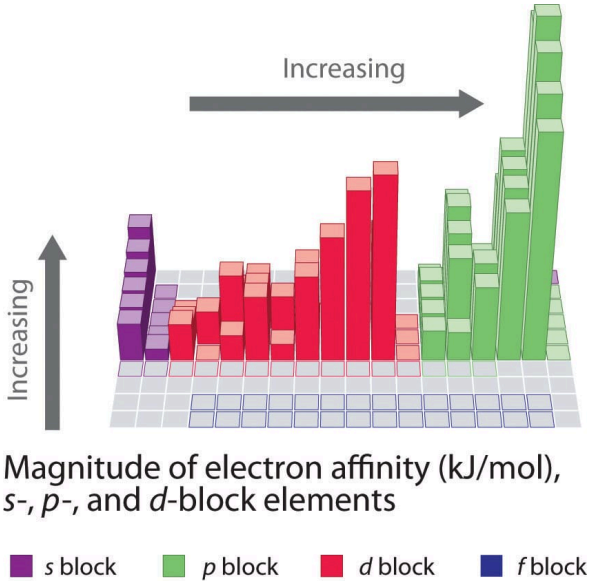
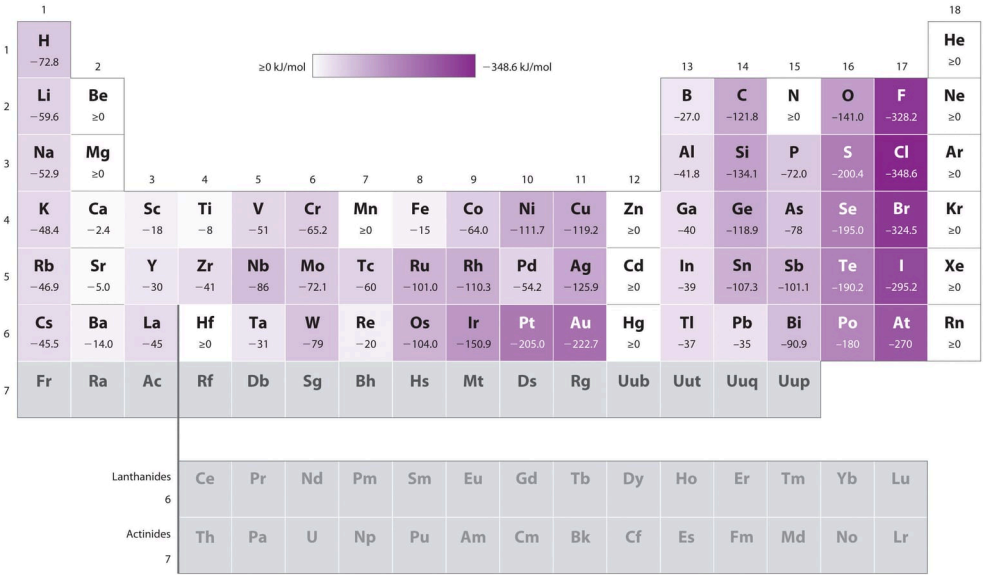


Figure 2.15.2 Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as *n* increases, the extra electrons enter orbitals that are increasingly far from the nucleus. Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* negative than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small 2*p* orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row ($n = 3$) have the most negative electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.
2. The electron affinities of the alkaline earth metals become more negative from Be to Ba. The energy separation between the filled ns^2 and the empty *np* subshells decreases with increasing *n*, so that formation of an anion from the heavier elements becomes energetically more favorable.



There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from Journal of Physical and Chemical Reference Data 28, no. 6 (1999).

Note

In general, electron affinities become more negative across a row and less negative down a column.

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change}=EA_1 \tag{2.15.5}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change}=EA_2 \tag{2.15.6}$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is –141 kJ/mol, but the second electron affinity is +744 kJ/mol:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{2.15.7}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{2.15.8}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{2.15.9}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

Note

While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.

If energy is required to form both positively charged ions and monatomic polyanions, why do ionic compounds such as MgO, Na_2S, and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt*.

Example 2.15.1: Contrasting Electron Affinities of Sb, Se, and Te

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.
B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

A We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

Exercise 2.15.1: Contrasting Electron Affinities of Rb, Sr, and Xe

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer: Rb

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Electron Affinity: https://youtu.be/M5MsRM2Xtds

Summary

The **electron affinity** (*EA*) of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table.

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2.16: 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?

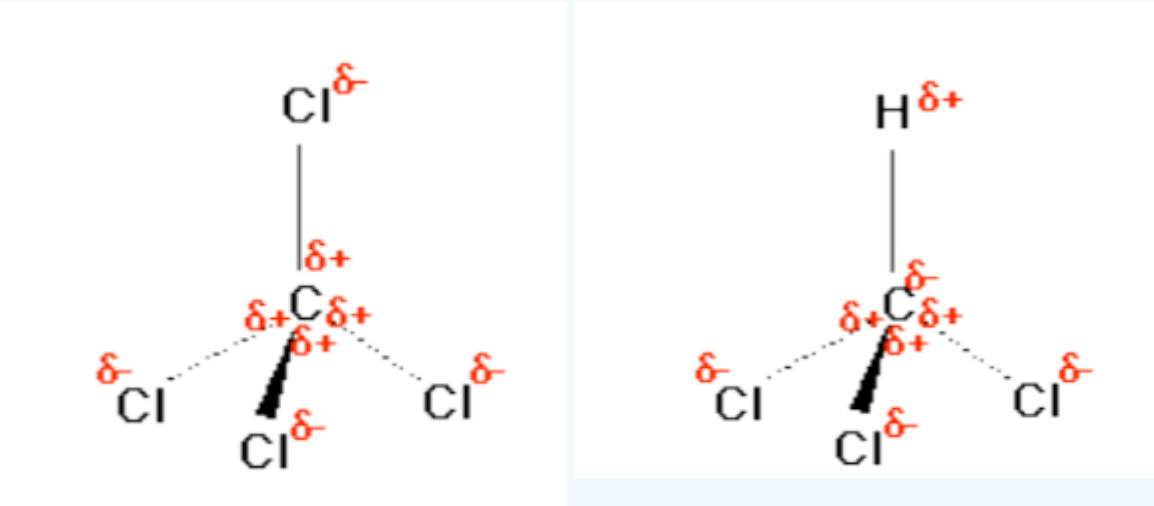


Figure 2.16.1: (left) CCl_4 (right) $CHCl_3$

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.

$$F = k\frac{Q_1 Q_2}{r^2} \tag{2.16.1}$$

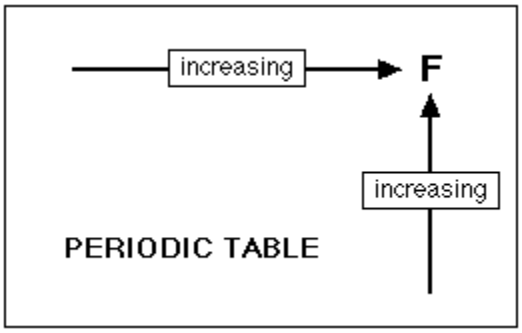
In this expression, Q represents a charge, k represents a constant and r is the distance between the charges. When r = 2, then r^2= 4. When r = 3, then r^2 = 9. When r = 4, then r^2 = 16. It is readily seen from these numbers that, as the distance between the charges increases, the force decreases very 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.

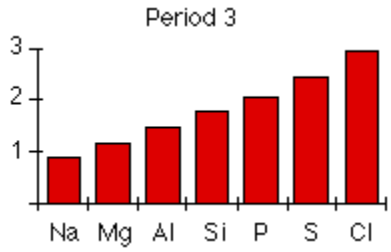


Note

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.

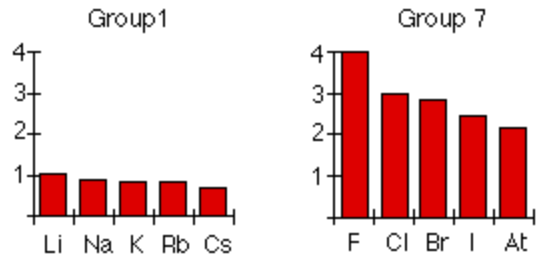
Trends in electronegativity across a period

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.



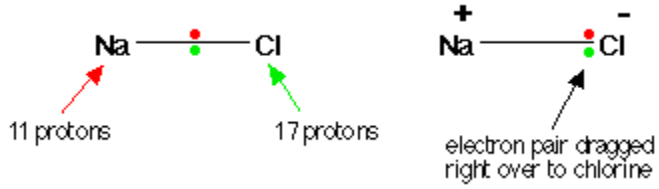
Explaining the patterns in electronegativity

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?

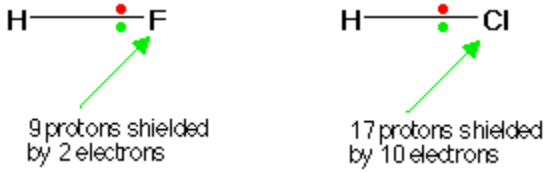
Consider sodium at the beginning of period 3 and chlorine at the end (ignoring the noble gas, argon). Think of sodium chloride as if it were covalently bonded.



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:

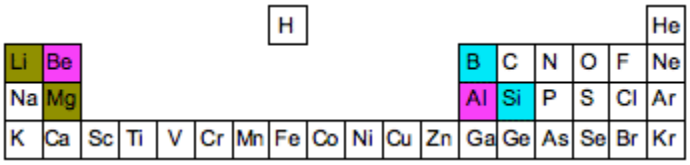


The bonding pair is shielded from the fluorine's nucleus only by the $1s^2$ electrons. In the chlorine case it is shielded by all the $1s^2 2s^2 2p^6$ electrons. In each case there is a net pull from the center of the fluorine or chlorine of +7. But fluorine has the bonding pair in the 2-level rather 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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2.17: Periodic Properties of the Elements

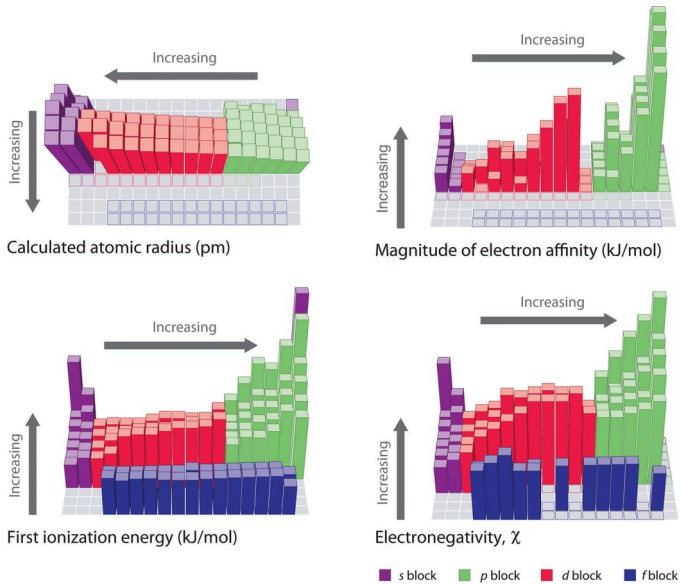


Figure 2.17.1 Summary of Major Periodic Trends. The general trends for the first ionization energy, electron affinity, and electronegativity are opposite to the general trend for covalent atomic radius.

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3: LEWIS STRUCTURES AND MOLECULAR SHAPES

3.1: Prelude to Chemical Bonding and Molecular Geometry

3.2: Ionic Bonding

3.3: Covalent Bonding

3.4: Lewis Theory- An Overview

3.5: Writing Lewis Structures

3.6: Resonance

3.7: Exceptions to the Octet Rule

3.8: Shapes of Molecules

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3.1: Prelude to Chemical Bonding and Molecular Geometry

It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene, commonly known as a “buckyball.” This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula, C_{60}, and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.



Figure 3.1.1: Nicknamed “buckyballs,” buckminsterfullerene molecules (C_{60}) contain only carbon atoms. Here they are shown in a ball-and-stick model (left). These molecules have single and double carbon-carbon bonds arranged to form a geometric framework of hexagons and pentagons, similar to the pattern on a soccer ball (center). This unconventional molecular structure is named after architect R. Buckminster Fuller, whose innovative designs combined simple geometric shapes to create large, strong structures such as this weather radar dome near Tucson, Arizona (right). (credit middle: modification of work by “Petey21”/Wikimedia Commons; credit right: modification of work by Bill Morrow).

Three figures are shown. The left figure is a many-sides spherical ball composed of hexagonal rings which have carbon atoms at each corner. The center picture shows a soccer ball. The right picture shown as water tower with sides shaped like hexagonal rings.

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3.2: Ionic Bonding

Learning Objectives

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure Figure 3.2.1). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure 3.2.1: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons)

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3, indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, (2 × +3) + (3 × –2) = 0].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure Figure 3.2.2).

Two diagrams are shown and labeled "a" and "b." Diagram a shows a cube made up of twenty-seven alternating purple and green spheres. The purple spheres are smaller than the green spheres. Diagram b shows the same spheres, but this time, they are spread out and connected in three dimensions by white rods. The purple spheres are labeled "N superscript postive sign" while the green are labeled "C l superscript negative sign."

Figure 3.2.2: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \quad \Delta H = 769\ \mathrm{kJ} \tag{3.2.1}$$

Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

Glossary

inert pair effect
: tendency of heavy atoms to form ions in which their valence s electrons are not lost

ionic bond
: strong electrostatic force of attraction between cations and anions in an ionic compound

Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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3.3: Covalent Bonding

Learning Objectives

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

In ionic compounds, electrons are transferred between atoms of different elements to form ions. But this is not the only way that compounds can be formed. Atoms can also make chemical bonds by sharing electrons between each other. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds, being electrically neutral, are poor conductors of electricity in any state.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure 3.3.1 illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1s) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

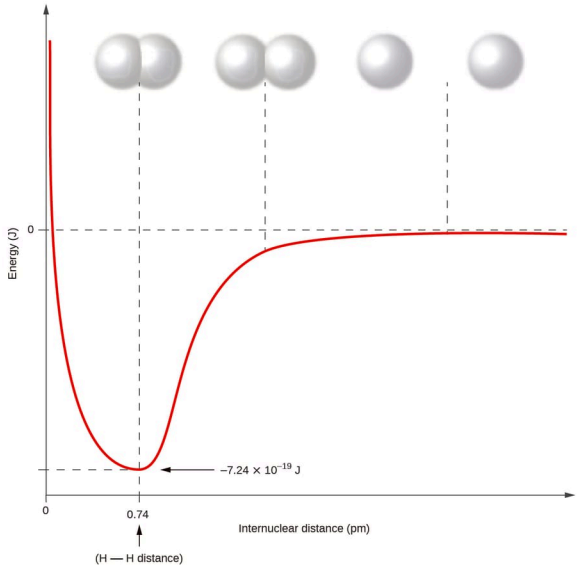


Figure 3.3.1: *The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.*

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H}(g) \quad \Delta H = 436\ \mathrm{kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$2\,\mathrm{H}(g) \longrightarrow \mathrm{H_2}(g) \quad \Delta H = -436\ \mathrm{kJ}$$

Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus. In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl} + \mathrm{Cl} \longrightarrow \mathrm{Cl_2}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 3.3.2 shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure 3.3.1, which shows the even distribution of electrons in the H_2 nonpolar bond.

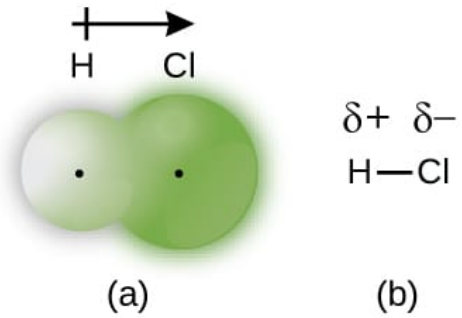


Figure 3.3.2: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,” δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure 3.3.2*b*.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom;

thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 3.3.3 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

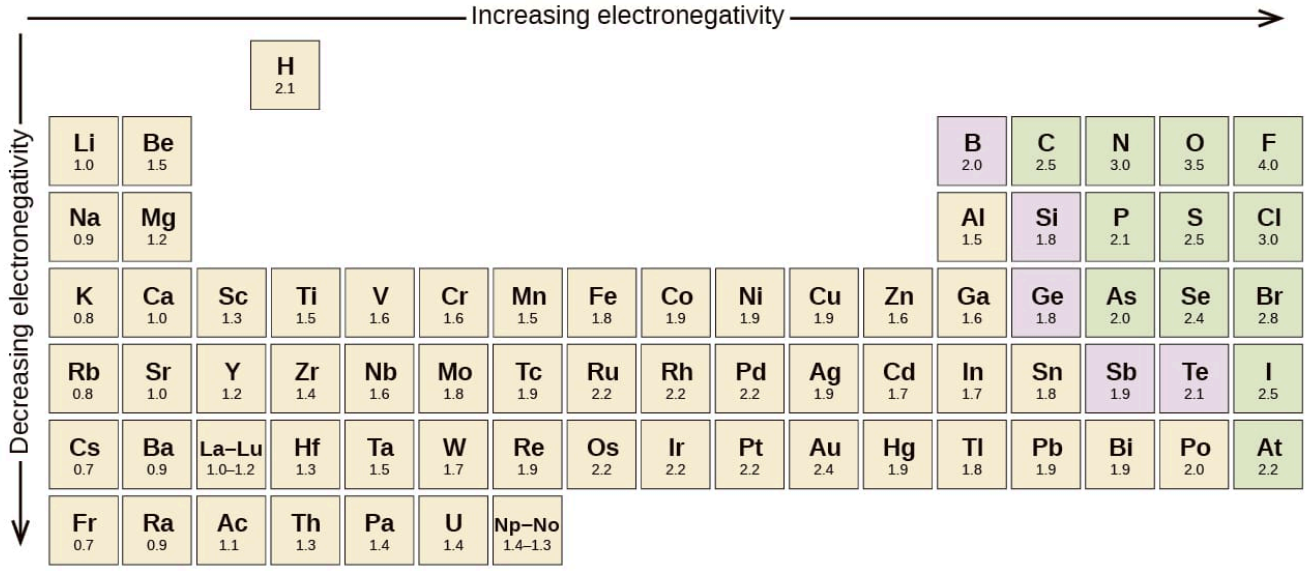


Figure 3.3.3: The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

Linus Pauling

Linus Pauling is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.



Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

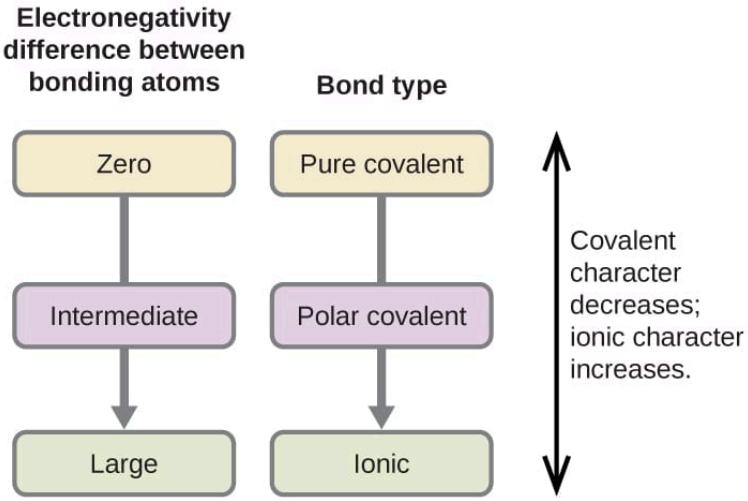
Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 3.3.4 shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 3.3.4: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 3.3.4. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, NO_3^-, and NH_4^+, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic NO_3^- anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and NO_3^-, as well as covalent between the nitrogen

and oxygen atoms in NO_3^-.

Example 3.3.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Table A2, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 3.3.1 shows these bonds in order of increasing polarity.

Table 3.3.1: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	$\overset{\delta-}{\mathrm{C}}-\overset{\delta+}{\mathrm{H}}$
S–H	0.4	$\overset{\delta-}{\mathrm{S}}-\overset{\delta+}{\mathrm{H}}$
C–N	0.5	$\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{N}}$
N–H	0.9	$\overset{\delta-}{\mathrm{N}}-\overset{\delta+}{\mathrm{H}}$
C–O	1.0	$\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{O}}$
O–H	1.4	$\overset{\delta-}{\mathrm{O}}-\overset{\delta+}{\mathrm{H}}$

Exercise 3.3.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 3.3.3, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Answer to Exercise 7.2.1

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\overset{\delta-}{\mathrm{C}}-\overset{\delta+}{\mathrm{H}}$
Si–C	0.7	$\overset{\delta+}{\mathrm{Si}}-\overset{\delta-}{\mathrm{C}}$
Si–O	1.7	$\overset{\delta+}{\mathrm{Si}}-\overset{\delta-}{\mathrm{O}}$

Summary

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic

molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

Glossary

bond length
: distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

covalent bond
: bond formed when electrons are shared between atoms

electronegativity
: tendency of an atom to attract electrons in a bond to itself

polar covalent bond
: covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

pure covalent bond
: (also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

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3.4: Lewis Theory- An Overview

Learning Objectives

- To use Lewis electron dot symbols to predict the number of bonds an element will form.

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond wil be discussed and the general properties found in typical substances in which the bond type occurs

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involves a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involves one nonmetallic element with another
3. Metallic bonds These bonds are found in solid metals (copper, iron, aluminum) with each metal bonded to several neighboring groups and bonding electrons free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

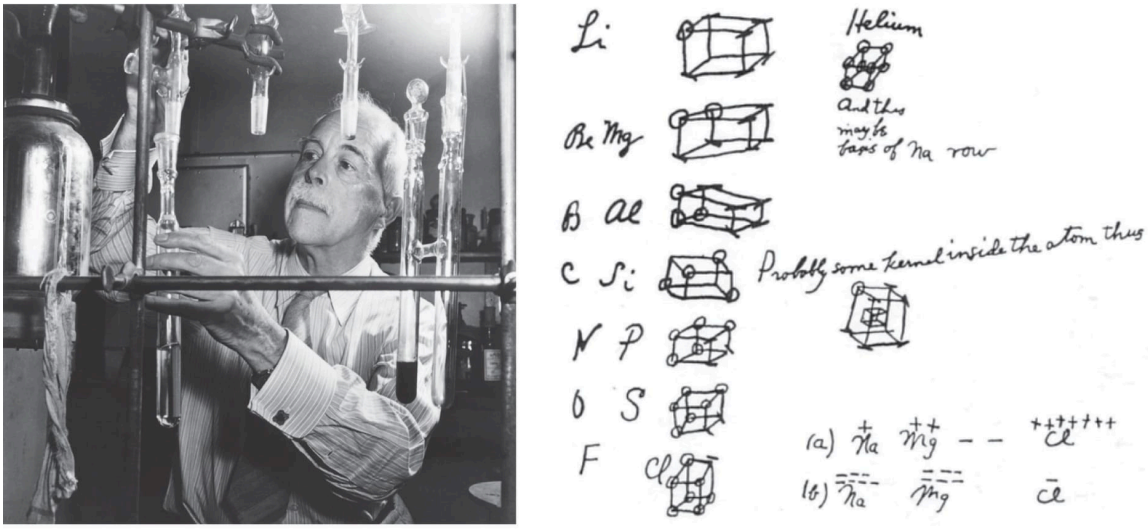


Figure 3.4.1: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Symbols

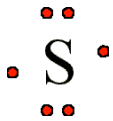
At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

Note

Lewis Dot symbols:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is $[Ne]3s^2 3p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration $[He]2s^2 2p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



Figure 3.4.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 3.4.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Element	Electron config.	Electron dot symbol
Li	$[He]2s^1$	
Be	$[He]2s^2$	
B	$[He]2s^2 2p^1$	
C	$[He]2s^2 2p^2$	
N	$[He]2s^2 2p^3$	
O	$[He]2s^2 2p^4$	
F	$[He]2s^2 2p^5$	
Ne	$[He]2s^2 2p^6$	

Figure 3.4.2: Lewis Dot Symbols for the Elements in Period 2

The Octet Rule

In 1904, Richard Abegg formulated what is now known as *Abegg's rule*, which states that the difference between the maximum positive and negative valences of an element is frequently eight. This rule was used later in 1916 when Gilbert N. Lewis formulated the "octet rule" in his cubical atom theory.

The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. Atoms will react to get in the most stable state possible. A complete octet is very stable because all orbitals will be full. Atoms with greater stability have less energy, so a reaction that increases the stability of the atoms will release energy in the form of heat or light ;reactions that decrease stability must absorb energy, getting colder.

When discussing the octet rule, we do not consider *d* or *f* electrons. Only the s and p electrons are involved in the octet rule, making it a useful rule for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6.

Octet Rule

A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

1. Normally two electrons pairs up and forms a bond, e.g., H_2
2. For most atoms there will be a maximum of eight electrons in the valence shell (octet structure), e.g., CH_4

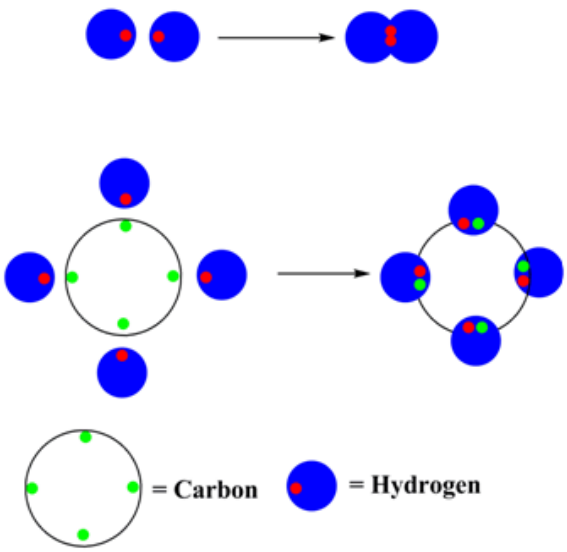


Figure 1: Bonding in H_2 and methane (CH_4)

The other tendency of atoms is to maintain a neutral charge. Only the noble gases (the elements on the right-most column of the periodic table) have zero charge with filled valence octets. All of the other elements have a charge when they have eight electrons all to themselves. The result of these two guiding principles is the explanation for much of the reactivity and bonding that is observed within atoms: atoms seek to share electrons in a way that minimizes charge while fulfilling an octet in the valence shell.

Note

The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

Example 1: Salt

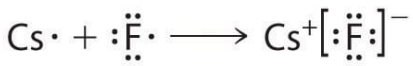
The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why?

Solution

Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium has one valence electron, so giving it up would result in the same electron configuration as neon. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon when it gains an electron.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gasses, with a full valence shell. However, their charges would be much higher. It would be Na^{7-} and Cl^{7+}, which is much less stable than Na^+ and Cl^-. Atoms are more stable when they have no charge, or a small charge.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

Note

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe elsewhere. These include molecules in which one or more atoms contain fewer or more than eight electrons.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Lewis Theory of Bonding: https://youtu.be/TZ6C5_k-SPs

Summary

- Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds.

One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

Contributors and Attributions

Mike Blaber (Florida State University)

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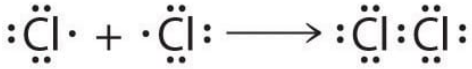
3.5: Writing Lewis Structures

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

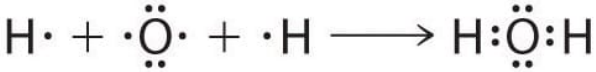
Using Lewis Dot Symbols to Describe Covalent Bonding

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:



Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond. Examples of this type of bonding are presented in Section 8.6 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the –2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double**

or triple) bonds to the central atom to achieve an octet. This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

> Note
>
> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^- Ion

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

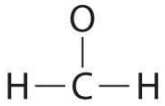
The CH_2O Molecule

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



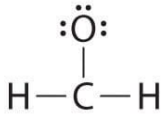
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

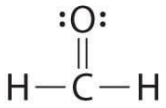
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid. An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 3.5.1

Write the Lewis electron structure for each species.

1. NCl_3
2. S_2^{2-}
3. NOCl

Given: chemical species

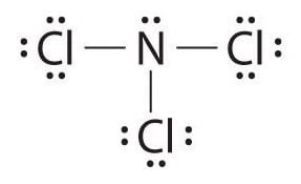
Asked for: Lewis electron structures

Strategy:

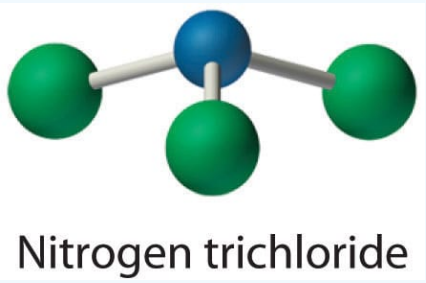
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

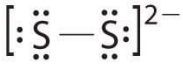
1. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:



Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



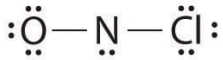
2. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the –2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



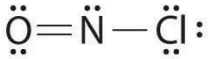
3. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



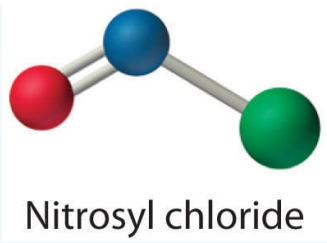
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



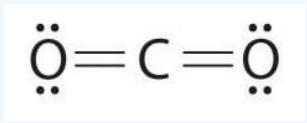
All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



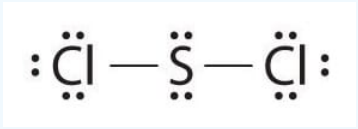
Exercise 3.5.1

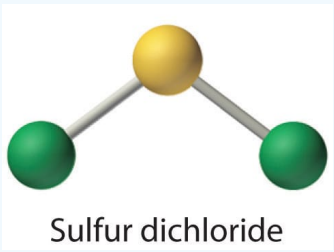
Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer

1. 



2. 



YouTube Video

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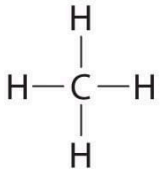
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Lewis Structure of Molecules: https://youtu.be/xWiFCqA9Ur0

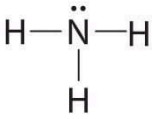
Using Lewis Electron Structures to Explain Stoichiometry

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of Group 17 (the halogens), this number is

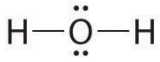
one; for the elements of Group 16 (the chalcogens), it is two; for Group 15 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Group 14



Group 15

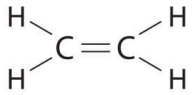


Group 16



Group 17

Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



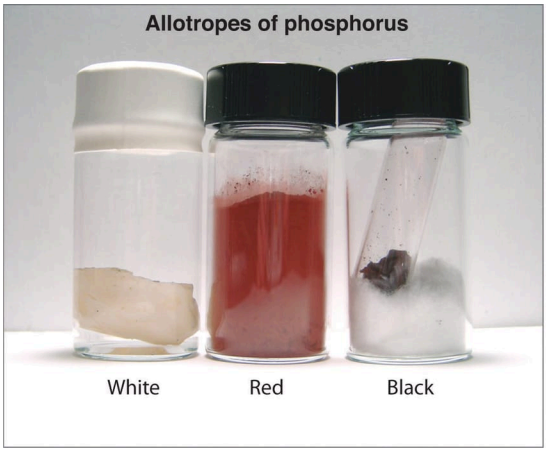
Ethylene

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

Note

Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 3.5.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

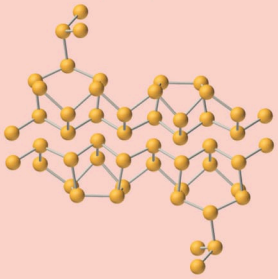


White phosphorus



Volatile waxy white solid. Dangerously reactive in air: glows with a white light and spontaneously bursts into flame.
Melting point: 44.2°C

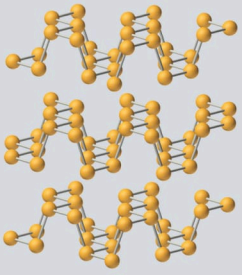
Red phosphorus



Red powder. Nonreactive with air at 25°C.

Melting point: 590°C

Black phosphorus



Black crystalline solid. Nonreactive with air at 25°C.
Melting point: 610°C

Figure 3.5.3*: The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.*

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

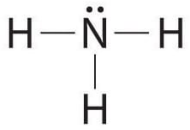
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$formal\ charge = \underset{(free\ atom)}{valence\ e^-} - \underset{(atom\ in\ Lewis\ structure)}{\left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right)} \text{ (atom in Lewis structure)}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding e^-/2)]. Substituting into Equation 8.5.2, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \tag{3.5.1}$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^-/2)]. Using Equation 8.5.2 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \tag{3.5.2}$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

Note

An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.

YouTube Video

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Lewis Structure of Charged Molecules: https://youtu.be/pTkziPtvMYU

Example 3.5.2

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

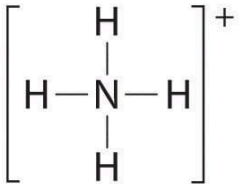
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 8.5.2 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



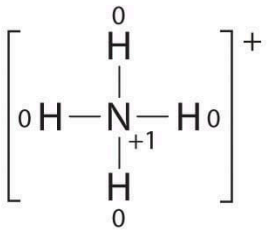
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation 8.5.1, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 1 \tag{3.5.3}$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0 \tag{3.5.4}$$

The formal charges on the atoms in the NH_4^+ ion are thus

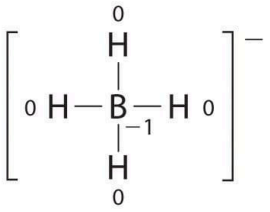


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 3.5.2

Write the formal charges on all atoms in BH_4^-.

Answer



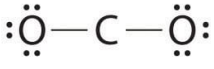
If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable Lewis Structures

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for CO_2. Both structures conform to the rules for Lewis electron structures.

CO_2

1. C is less electronegative than O, so it is the central atom.
2. C has 4 valence electrons and each O has 6 valence electrons, for a total of 16 valence electrons.
3. Placing one electron pair between the C and each O gives O–C–O, with 12 electrons left over.
4. Dividing the remaining electrons between the O atoms gives three lone pairs on each atom:



This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

5. No electrons are left for the central atom.
6. To give the carbon atom an octet of electrons, we can convert two of the lone pairs on the oxygen atoms to bonding electron

pairs. There are, however, two ways to do this. We can either take one electron pair from each oxygen to form a symmetrical structure or take both electron pairs from a single oxygen atom to give an asymmetrical structure:



Both Lewis electron structures give all three atoms an octet. How do we decide between these two possibilities? The formal charges for the two Lewis electron structures of CO_2 are as follows:



Both Lewis structures have a net formal charge of zero, but the structure on the right has a +1 charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.

Note

The Lewis structure with the set of formal charges closest to zero is usually the most stable.

Example 3.5.3: The Thiocyanate Ion

The thiocyanate ion (SCN^-), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which is the preferred arrangement of electrons.

Given: chemical species

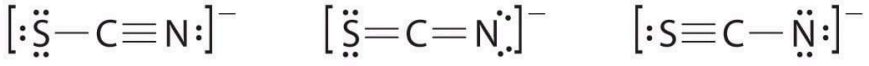
Asked for: Lewis electron structures, formal charges, and preferred arrangement

Strategy:

A. Use the step-by-step procedure to write two plausible Lewis electron structures for SCN^-.
B. Calculate the formal charge on each atom using Equation 8.5.1.
C. Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

Solution:

A Possible Lewis structures for the SCN^- ion are as follows:



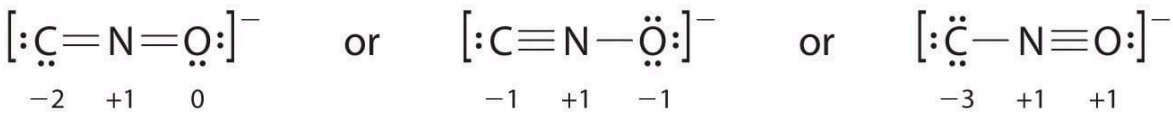
B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore $6-\left(6+\frac{2}{2}\right)=-1.5$ $-\left(4+\frac{4}{2}\right)=-1$ In (c), nitrogen has a formal charge of –2.

C Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, –1 versus +1, –2.

Exercise 3.5.3: The Fulminate Ion

Salts containing the fulminate ion (CNO^-) are used in explosive detonators. Draw three Lewis electron structures for CNO^- and use formal charges to predict which is more stable. (Note: N is the central atom.)

Answer



The second structure is predicted to be more stable.

Summary

- Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries.

A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. If both electrons in a covalent bond come from the same atom, the bond is called a **coordinate covalent bond**. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families. Neutral compounds of group 14 elements typically contain four bonds around each atom (a double bond counts as two, a triple bond as three), whereas neutral compounds of group 15 elements typically contain three bonds. In cases where it is possible to write more than one Lewis electron structure with octets around all the nonhydrogen atoms of a compound, the **formal charge** on each atom in alternative structures must be considered to decide which of the valid structures can be excluded and which is the most reasonable. The formal charge is the difference between the number of valence electrons of the free atom and the number of electrons assigned to it in the compound, where bonding electrons are divided equally between the bonded atoms. The Lewis structure with the lowest formal charges on the atoms is almost always the most stable one.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

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3.6: Resonance

Learning Objectives

- To understand the concept of resonance.

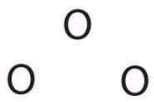
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding a single polyatomic species including fractional bonds and fractional charges. Resonance structure are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integer number of covalent bonds.

When one Lewis Structure is not enough

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. 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 contributing structures (also called resonance structures or canonical forms). 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°.

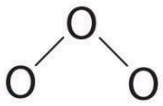
Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



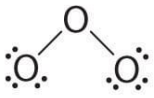
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



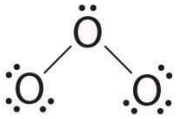
with 14 electrons left over.

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:

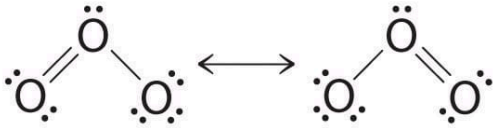


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



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.

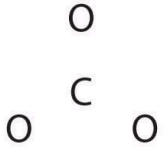
Note

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 Carbonate (CO_3^{2-}) Ion

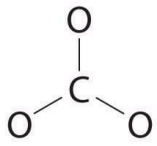
Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

1. Because carbon is the least electronegative element, we place it in the central position:

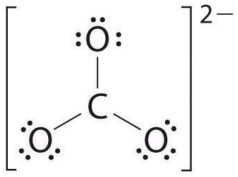


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the –2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

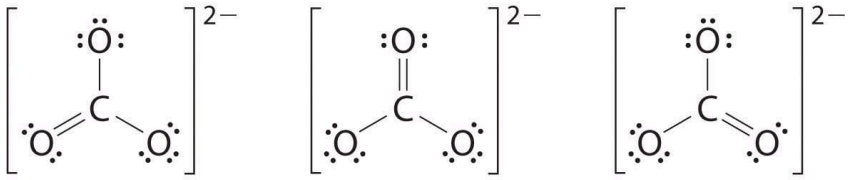


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the –2 charge:

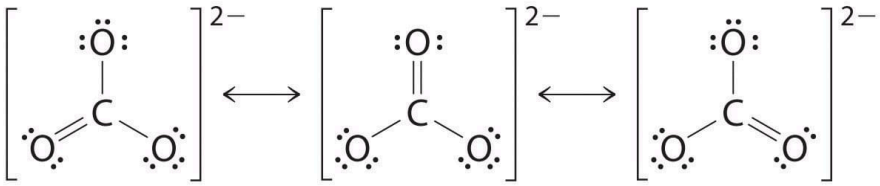


5. No electrons are left for the central atom.

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:

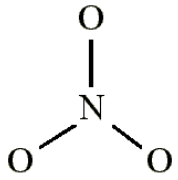


The actual structure is an average of these three resonance structures.

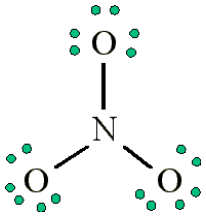
The Nitrate (NO_3^-) ion

1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

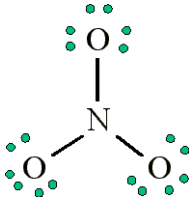
2. Draw the bond connectivities:



3. Add octet electrons to the atoms bonded to the center atom:

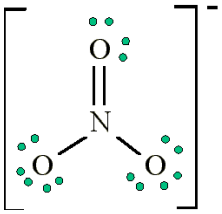


4. Place any leftover electrons (24-24 = **0**) on the center atom:



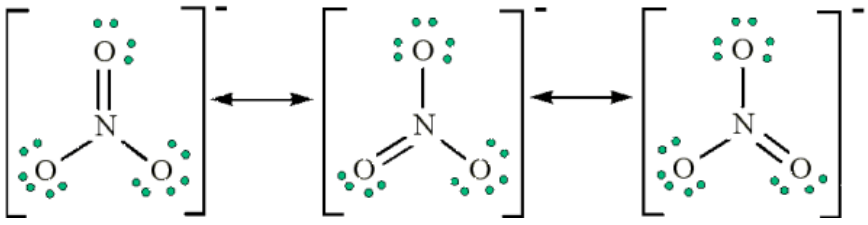
5. Does the central atom have an octet?

- **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

Example 3.6.1: 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

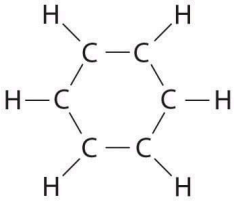
Asked for: resonance structures

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.

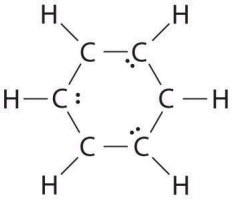
Solution:

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:



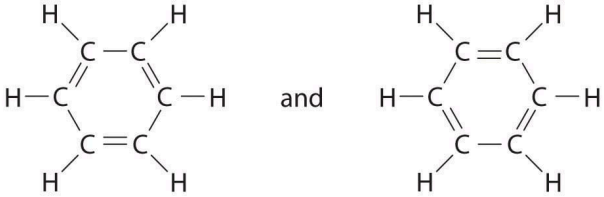
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

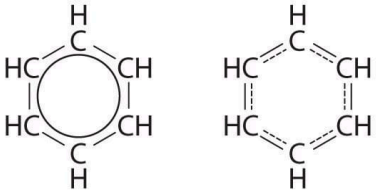


Three carbon atoms now have an octet configuration and a formal charge of –1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double 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:

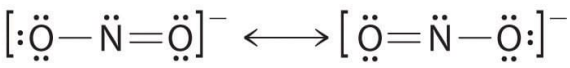


Benzene

Exercise 3.6.1: Nitrate Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Resonance Structures: https://youtu.be/aSP0D72MKe4

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

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3.7: Exceptions to the Octet Rule

Learning Objectives

- To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

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:

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

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 Nitrogen (II) Oxide (NO ,refer to figure one). Nitrogen has 5 valence electrons while Oxygen has 6. 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*.

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. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitrogen monoxide had ten valence electrons we would come up with the Lewis Structure (Figure 3.7.1):

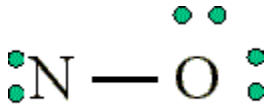


Figure 3.7.1: This is if Nitrogen monoxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure 3.7.2 based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure 3.7.1, 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 3.7.1, 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 3.7.2):

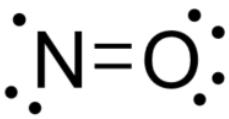


Figure 3.7.2: The proper Lewis structure for NO molecule

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. In order 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, odd Number of Valence Electrons will result in the molecule being 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 3.7.3):

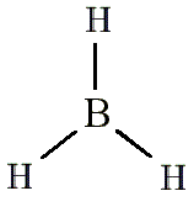


Figure 3.7.3

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 3.7.4).

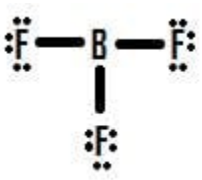


Figure 3.7.4

If you look Figure 3.7.4, 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 3.7.5):

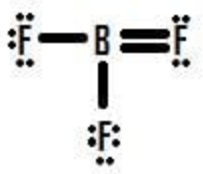


Figure 3.7.5

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 3.7.5, 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 3.7.6:

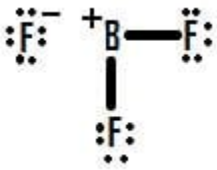


Figure 3.7.6

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 3.7.4), the one with the double bond (Figure 3.7.5), and the one with the ionic bond (Figure 3.7.6). The most contributing structure is probably the incomplete octet structure (due to Figure 3.7.5 being basically impossible and Figure 3.7.6 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 .

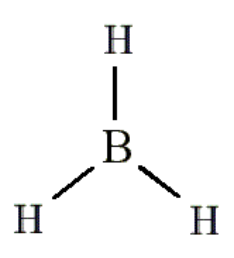
Example 3.7.1: NF_3

Draw the Lewis structure for boron trifluoride (BF_3).

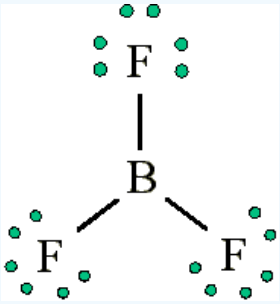
Solution

1. Add electrons (3*7) + 3 = **24**

2. Draw connectivities:



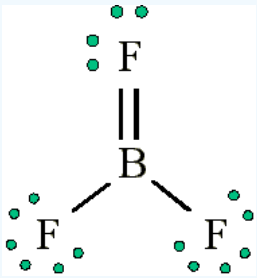
3. Add octets to outer atoms:



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:

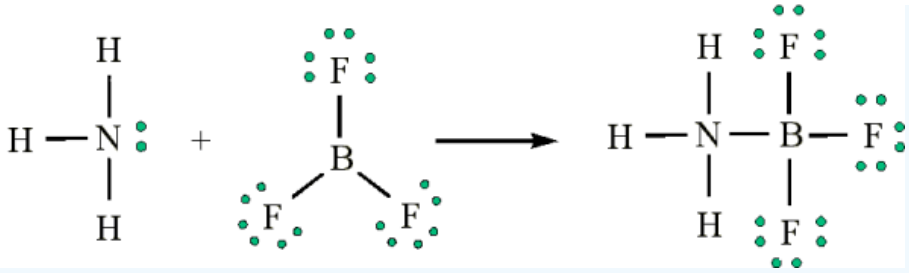


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

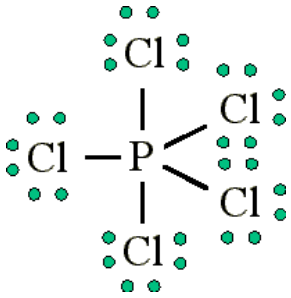
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single 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

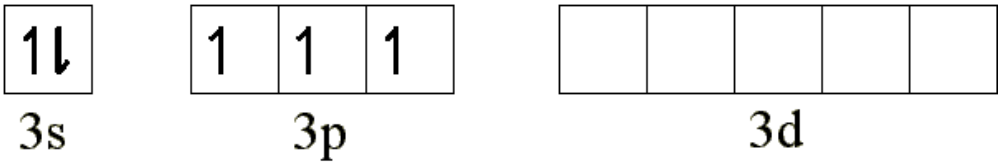
More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, 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:



Note

Expanded valence shells are observed **only** for elements in period 3 (i.e. n=3) and beyond

The 'octet' rule is based upon available ns 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.

Example 3.7.2: The SO_4^{-2} ion

Such is the case for the sulfate ion, SO_4^{-2}. A strict adherence to the octet rule forms the following Lewis structure:

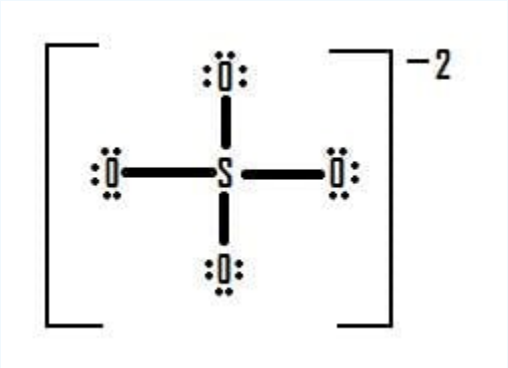


Figure 3.7.12

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 oxygens 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 more 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:

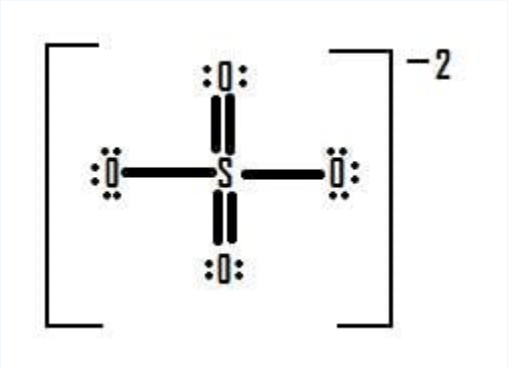


Figure 3.7.13

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 3.7.12, as opposed to +2 and -1 (difference of 3) in Figure 3.7.12) 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.

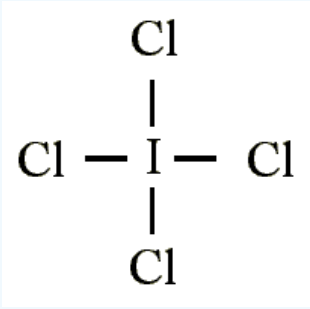
Example 3.7.3: The ICl_4^- Ion

Draw the Lewis structure for ICl_4^- ion.

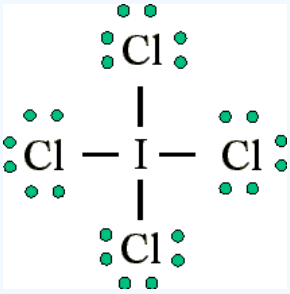
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

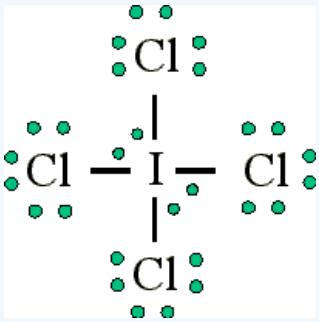
2. Draw the connectivities:



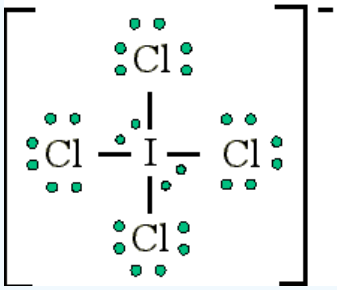
3. Add octet of electrons to outer atoms:



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.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Expanded Valence Shell Bonding: https://youtu.be/Y4fBdOJBSHI

Outside links

- http://www.saskschools.ca/curr_content/chem20/covmolec/exceptns.html
- student.ccbcmd.edu/~cyau1/121...ctetSp2006.pdf
- http://www.youtube.com/watch?v=KEQw9uQ8fUU
- www.rice.edu/~jenky/sports/antiox.html

References

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.

Contributors and Attributions

- Mike Blaber (Florida State University)

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3.8: Shapes of Molecules

Learning Objectives

- To use the VSEPR model to predict molecular geometries.
- To predict whether a molecule has a dipole moment.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion** (VSEPR) model (pronounced "vesper"), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

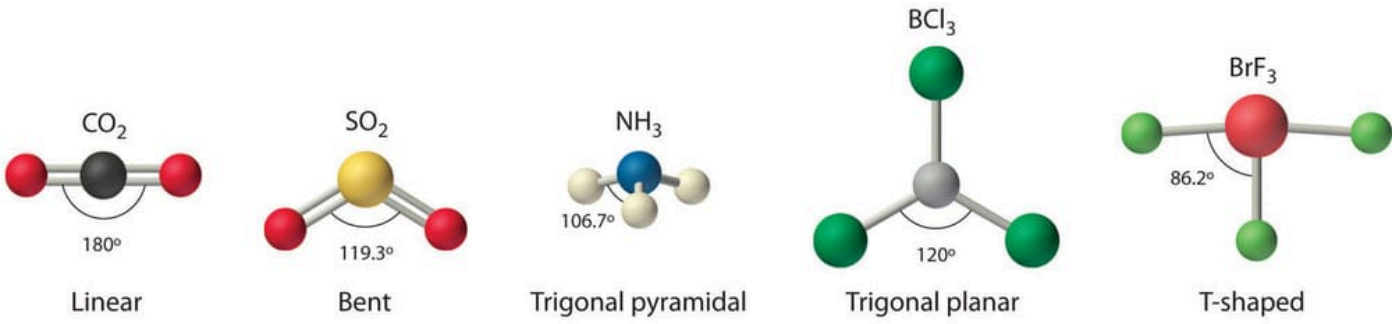


Figure 3.8.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figures 3.8.1 and 3.8.2.

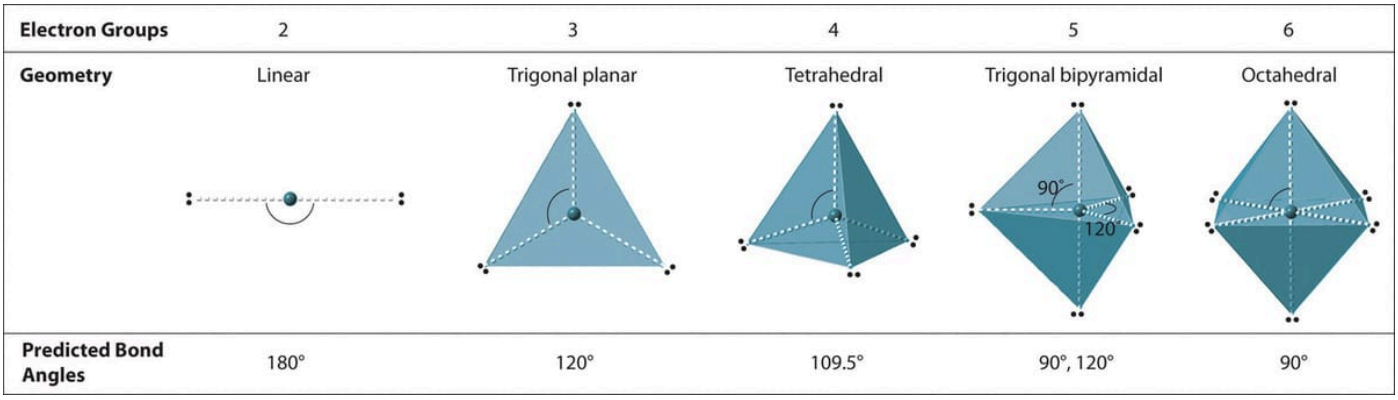


Figure 3.8.2: Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions. (CC BY-NC-SA; anonymous)

In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles. Using this information, we can describe the molecular geometry, the arrangement of the *bonded atoms* in a molecule or polyatomic ion.

VESPR Produce to predict Molecular geometry

This VESPR procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure 3.8.2 and Figure 3.8.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

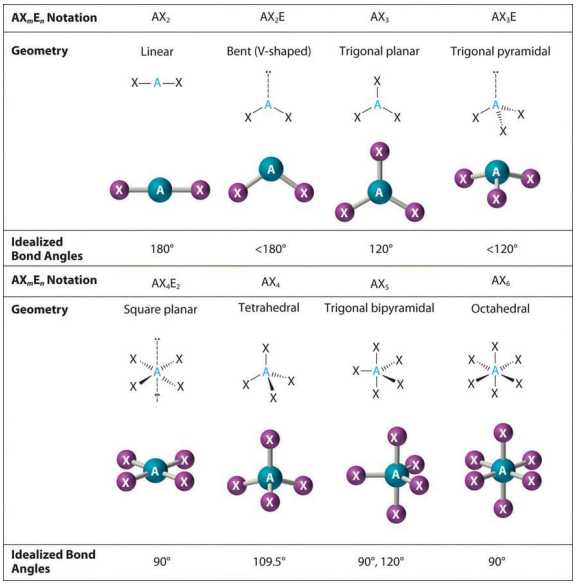


Figure 3.8.3: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line. (CC BY-NC-SA; anonymous)

Linear, bent, trigonal planar, trigonal pyramidal, square planar, tetrahedral, trigonal bipyramidal, octahedral.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2 Molecules: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

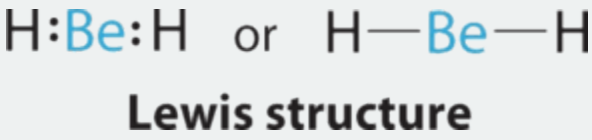


Figure 3.8.2 that the arrangement that minimizes repulsions places the groups 180° apart. (CC BY-NC-SA; anonymous)

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 3.8.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2 Molecules: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

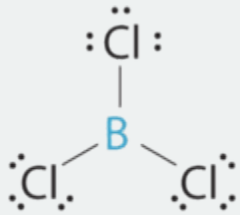
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 3.8.3). The structure of CO_2 is shown in Figure 3.8.1.

Three Electron Groups

AX_3 Molecules: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

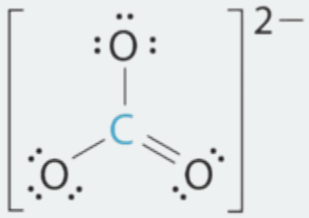
Figure 3.8.2): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 3.8.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 3.8.2.

AX_3 Molecules: CO_3^{2-}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as



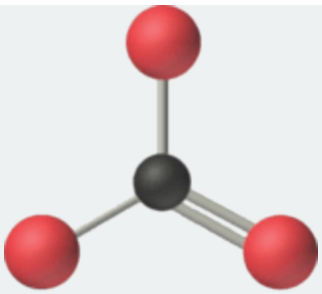
Lewis structure

Figure 3.8.2).

The three oxygens are arranged in a triangular shape with carbon at the center. Two of the oxygens have three lone pairs. One ocht oxygens has 2 lone pairs and is double bonded to the carbon. The molecule has a minus 2 charge.

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure 3.8.3 that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.



Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E Molecules: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.

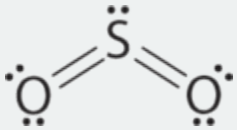


Figure 3.8.2): (CC BY-NC-SA; anonymous)

The two oxygens are double bonded to the sulfur. The oxygens have 2 lone pairs while sulfur had one lone pair.

3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 3.8.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures 3.8.2 and 3.8.3). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

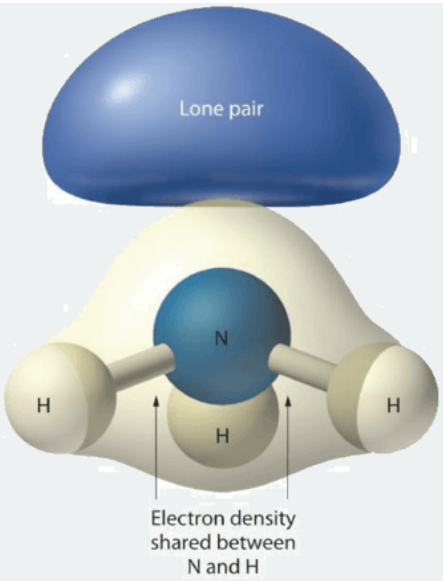
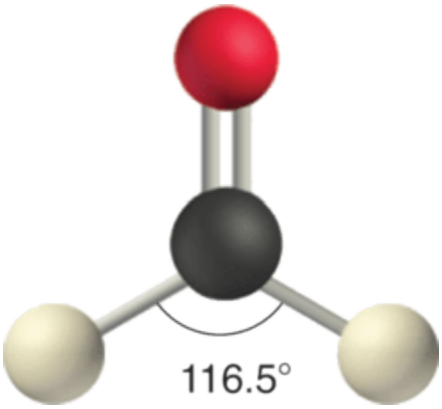


Figure 3.8.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair. (CC BY-NC-SA; anonymous)

As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

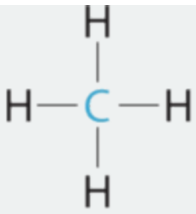


Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4 Molecules: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

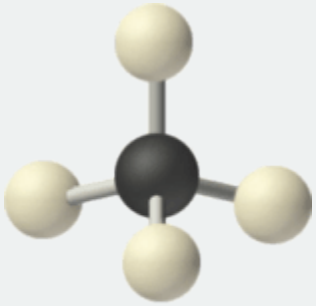


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 3.8.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

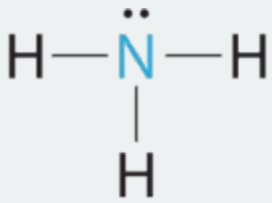
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 3.8.3).



Molecular geometry
(tetrahedral)

AX_3E Molecules: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 3.8.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 3.8.3 and Figure 3.8.4).

AX_2E_2 Molecules: H_2O

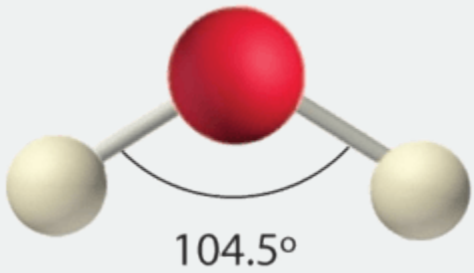
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



Figure 3.8.2: (CC BY-NC-SA; anonymous)

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.



Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5 Molecules: PCl_5

1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is

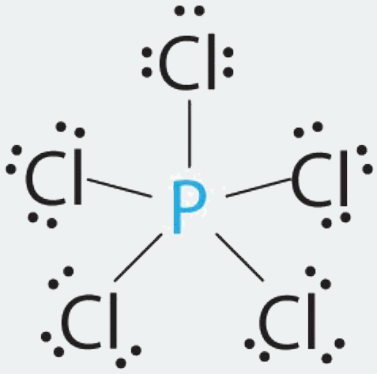
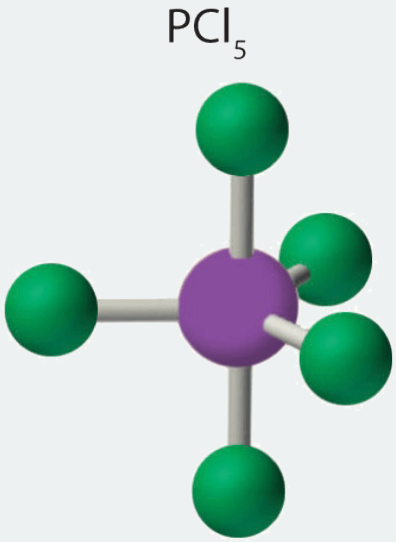


Figure 3.8.2): (CC BY-NC-SA; anonymous)

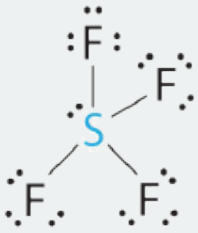
3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 3.8.3. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



AX_4E Molecules: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

Four fluorenes are bonded to a central sulfur. Each fluorine has three lone pairs. Sulfur has one lone pair.

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 3.8.2.

3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the axial position, we have three LP–BP repulsions at 90°. If we place it in the equatorial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the *equatorial position is more stable than the one with the lone pair in the axial position*. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

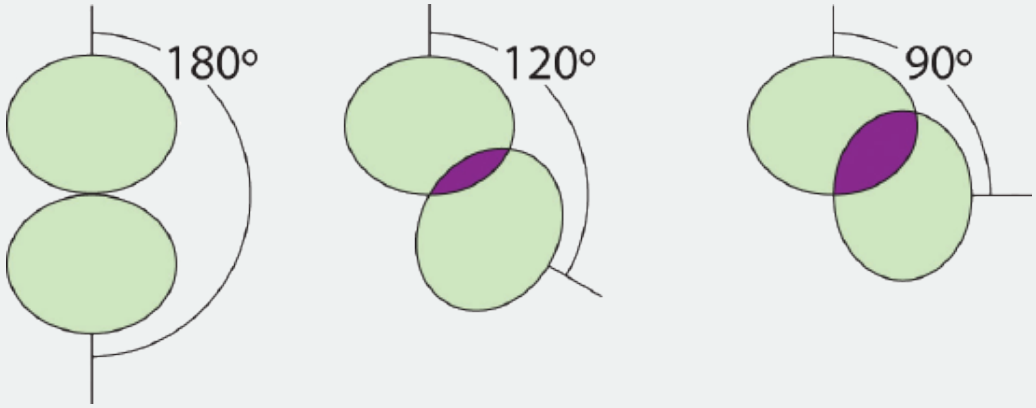
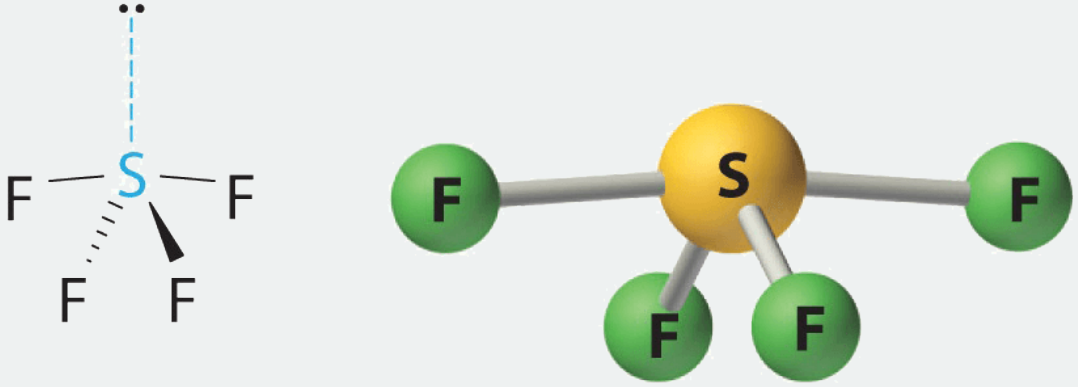


Figure 3.8.5: Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

180 degree angle has no shared space between teo electron pair, 120 degree angle has some shared area between two electron pairs. 90 degree angle has more shared space than 120.

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

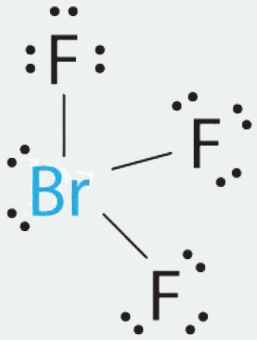
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2 Molecules: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



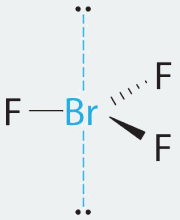
Lewis structure

Three fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has two lone pairs.

Once again, we have a compound that is an exception to the octet rule.

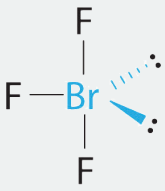
2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



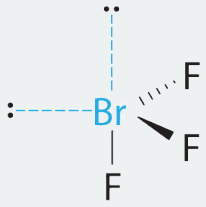
Lone pairs axial

(a)



Lone pairs equatorial

(b)



Lone pairs axial and equatorial

(c)

Interactions

90º LP–LP	0	0	1
90º LP–BP	6	4	3

If the lone pairs are axiam, the 90 degree LP-LP interactions are o and the 90 degree LP-BP interaction is zero. If the Lone pares are equatorial there are zero 90 degree LP-LP interactions and four 90 degree LP-BP intereactions. If the lone pairs are axial and equatorial there is one 90 degree LP-LP interaction and three 90 degree LP-BP interaction.

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions (Figure 3.8.2.1).

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

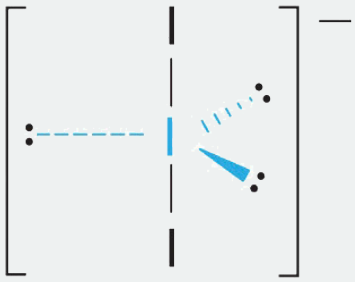
AX_2E_3 Molecules: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



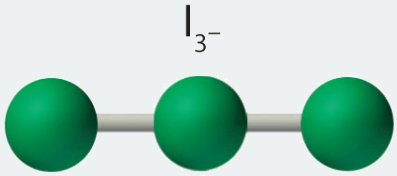
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

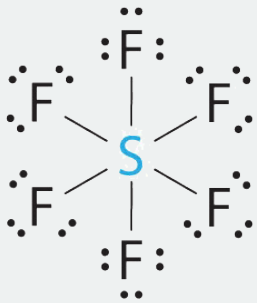


Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 3.8.2.)

AX_6 Molecules: SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



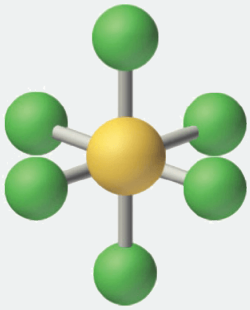
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 3.8.2 that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

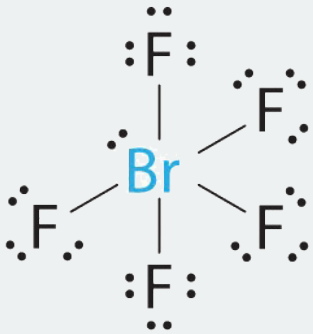
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX_5E Molecules: BrF_5

1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is

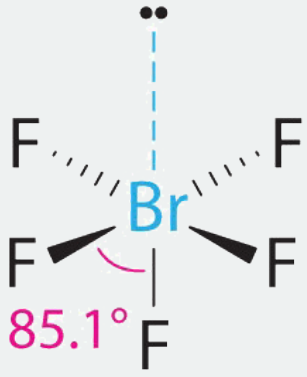


Lewis structure

Five fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has one lone pair.

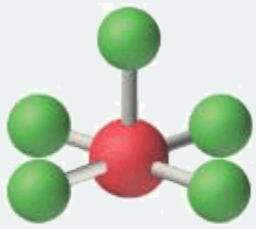
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

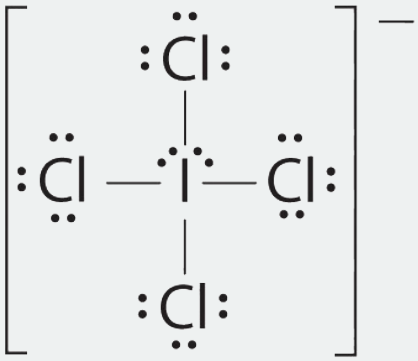
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



Molecular geometry
(square pyramidal)

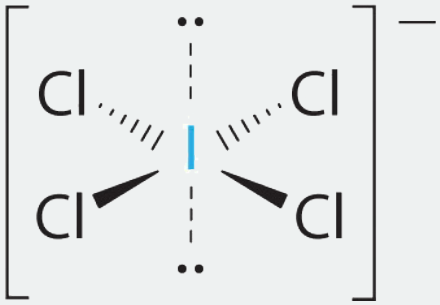
AX_4E_2 Molecules: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



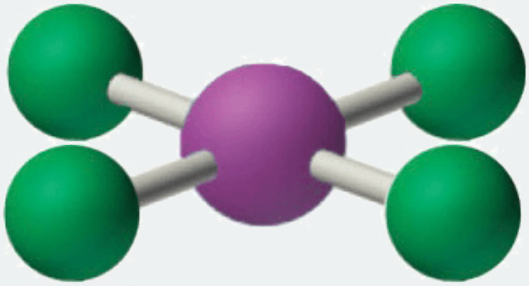
Four chlorines are bonded to a central iodine. Each chlorine has three electron pairs. The iodine has two electron pairs. The molecule is negatively charged.

2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl4– ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure 3.8.6.

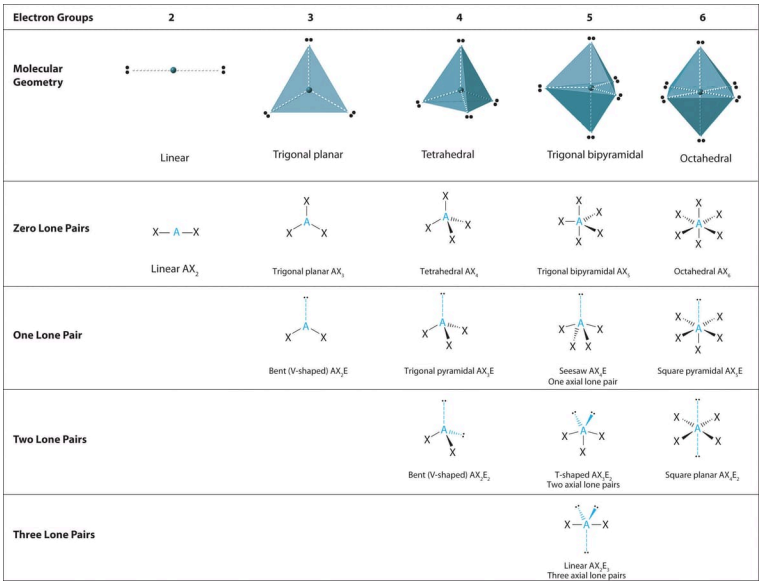


Figure 3.8.6***:*** *Overview of Molecular Geometries*

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Example 3.8.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A. Draw the Lewis electron structure of the molecule or polyatomic ion.
B. Determine the electron group arrangement around the central atom that minimizes repulsions.
C. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.
D. Describe the molecular geometry.

Solution:

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is

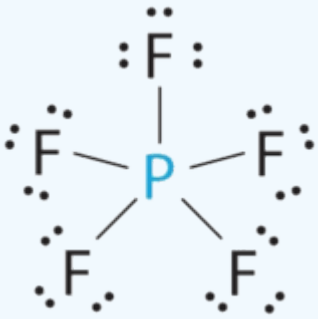


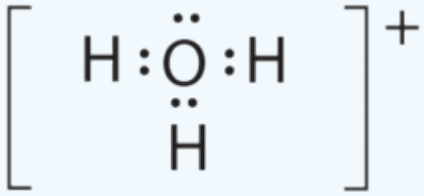
Figure 3.8.6): (CC BY-NC-SA; anonymous)

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is

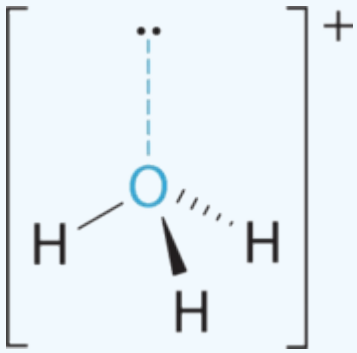


Three hydrogens are bonded to a central oxygen. The oxygen has two lone pairs. The molecule has a charge of plus one.

B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



Exercise 3.8.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer a available at the end of this section.

Example 3.8.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example3.8.1.

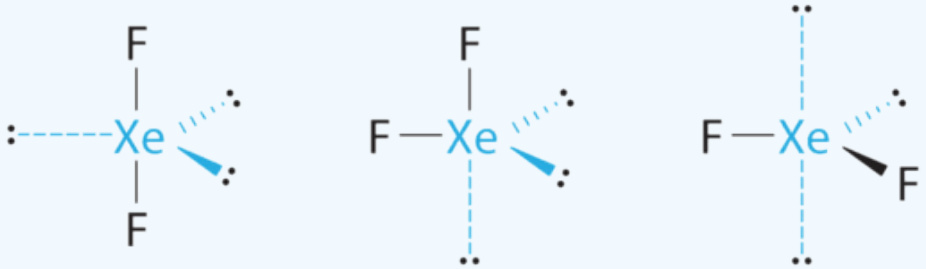
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



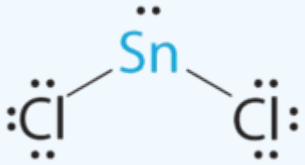
Interactions			
90 LP–LP	0	2	2

If the two F atoms are axial ther are zero 90 LP-LP interactions. If the two F atoms are axial and equatorial or just equatorial, there are 2 90 LP-LP interactions.

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



Two chlorines are bonded to a central tin. Each chlorine has three lone pairs. Tin has one lone pair.

B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise 3.8.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a available at the end of this section.

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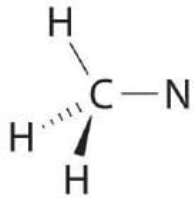
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Molecules with No Single Central Atom

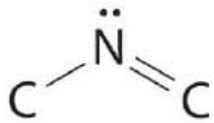
The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4. We can therefore predict the CH_3–N portion of the molecule to be roughly

tetrahedral, similar to methane:



The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



One carbon bonded to nitrogen and another carbon double bonded to the nitrogen. The nitrogen has one lone pair.

Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:

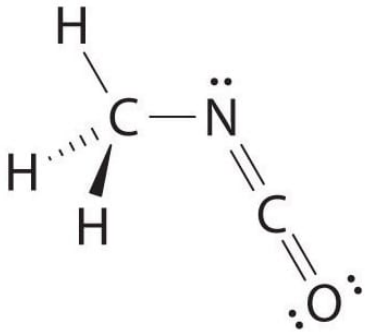


Figure 3.8.7).

Three hydrogens are bonded to a carbon. The carbon is also bonded to a nitrogen. The nitrogen is double bonded to another carbon. The second carbon is double bonded to an oxygen. The nitrogen has one lone pair. The oxygen has two lone pairs.

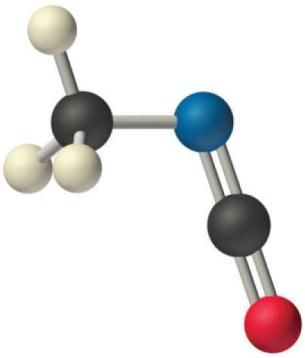


Figure 3.8.7: The Experimentally Determined Structure of Methyl Isocyanate

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules

will help you predict the molecular geometries of more complex molecules.

Example 3.8.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C≡CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 3.8.3 to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

Exercise 3.8.3

Predict the geometry of allene ($H_2C=C=CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer available at the end of this section.

Molecular Dipole Moments

You previously learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (Figure 3.8.8*a*). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (Figure 3.8.8*b*); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

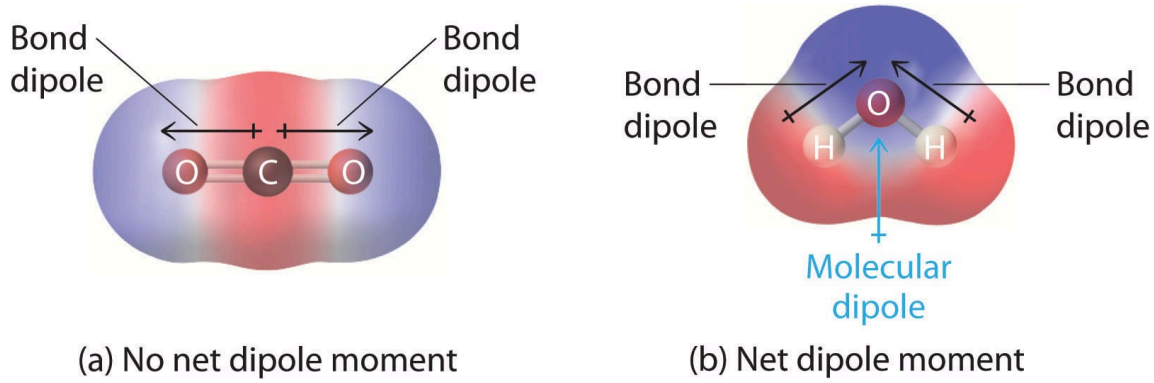


Figure 3.8.8: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.

Other examples of molecules with polar bonds are shown in Figure 3.8.9. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment. Molecules with asymmetrical charge distributions have a net dipole moment.

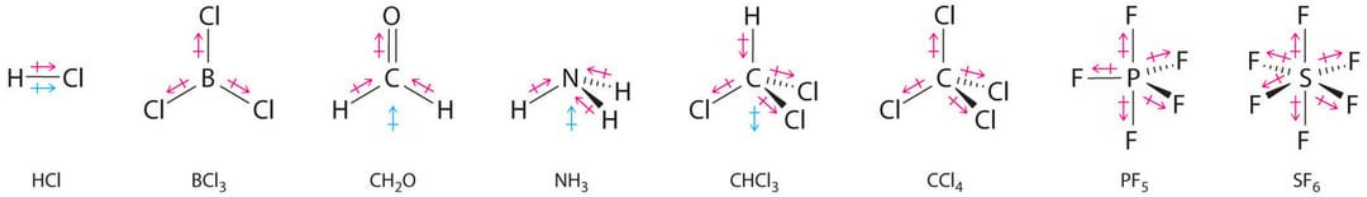


Figure 3.8.9: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

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Example 3.8.4

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

Given: three chemical compounds

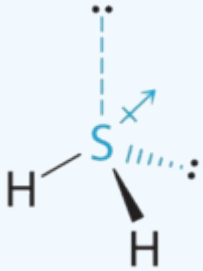
Asked for: net dipole moment

Strategy:

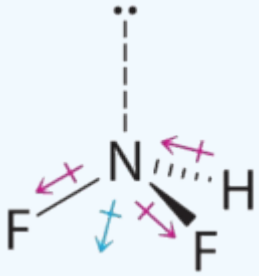
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

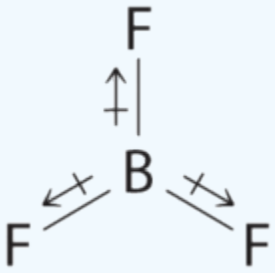
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of $\mathrm{H_2S}$ is bent (Figure $3.8.6$). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



2. Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.



3. The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:



Exercise $3.8.4$

Which molecule(s) has a net dipole moment?

- $\mathrm{CH_3Cl}$
- $\mathrm{SO_3}$
- $\mathrm{XeO_3}$

Answer available at the end of this section.

Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds. A combination of VSEPR and a bonding model, such as Lewis electron structures, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

Answers

Exercise 3.8.1

trigonal pyramidal

octahedral

linear

Exercise 3.8.2

trigonal planar

square planar

Exercise 3.8.3

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

Exercise 3.8.4

CH_3Cl and XeO_3

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4: BONDING THEORIES

4.1: Hybrid Atomic Orbitals
4.2: Multiple Covalent Bonds

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4.1: Hybrid Atomic Orbitals

Learning Objectives

- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two 2*p* orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two 2*p* orbitals with the 1s orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90°, as shown in Figure 4.1.1, because *p* orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.

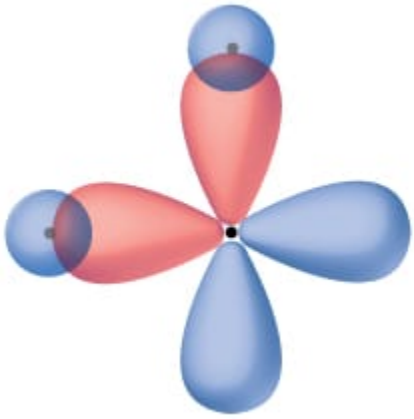


Figure 4.1.1: The hypothetical overlap of two of the 2p orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

Two peanut-shaped orbitals lie perpendicular to one another. They overlap with spherical orbitals to the left and top of the diagram.

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the 1s orbital of the hydrogen atoms with the 2*p* orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ, contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called hybridization and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later). The new orbitals that result are called hybrid orbitals. The valence orbitals in an *isolated* oxygen atom are a 2*s* orbital and three 2*p* orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure 4.1.2). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

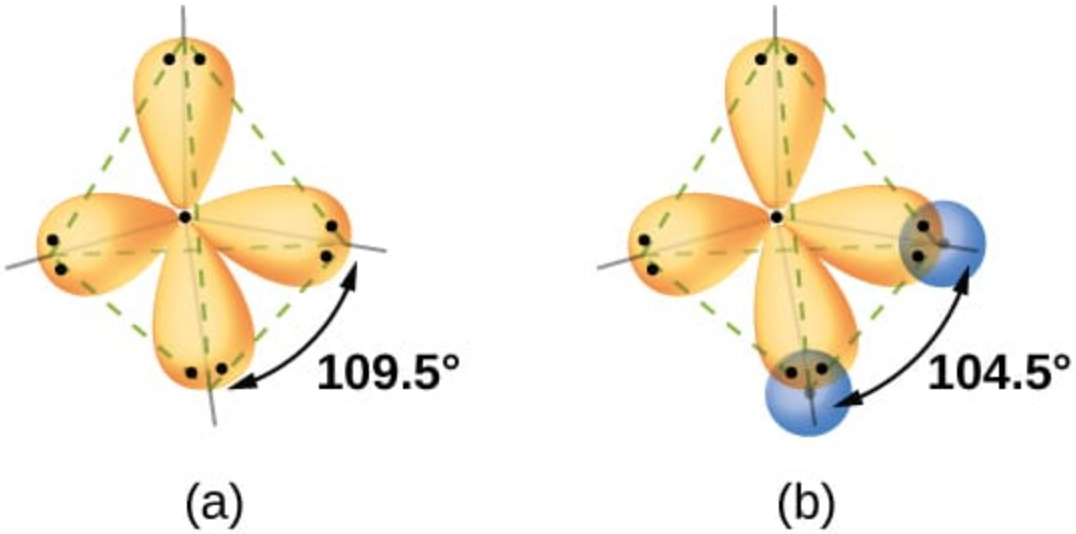


Figure 4.1.2: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

Two diagrams are shown and labeled “a” and “b.” Diagram a shows two peanut-shaped orbitals lying in a tetrahedral arrangement around the letter “O.” Diagram b shows the same two orbitals, but they now overlap to the top and to the left with two spherical orbitals, each labeled “H.” A pair of electrons occupies each lobe of the peanut-shaped orbitals.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom’s four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence *s* orbital with one of the valence *p* orbitals to yield two equivalent *sp* hybrid orbitals that are oriented in a linear geometry (Figure 4.1.3). In this figure, the set of *sp* orbitals appears similar in shape to the original *p* orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The *p* orbital is one orbital that can hold up to two electrons. The *sp* set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the *s* orbital are now distributed to the two *sp* orbitals, which are half filled. In gaseous $BeCl_2$, these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.

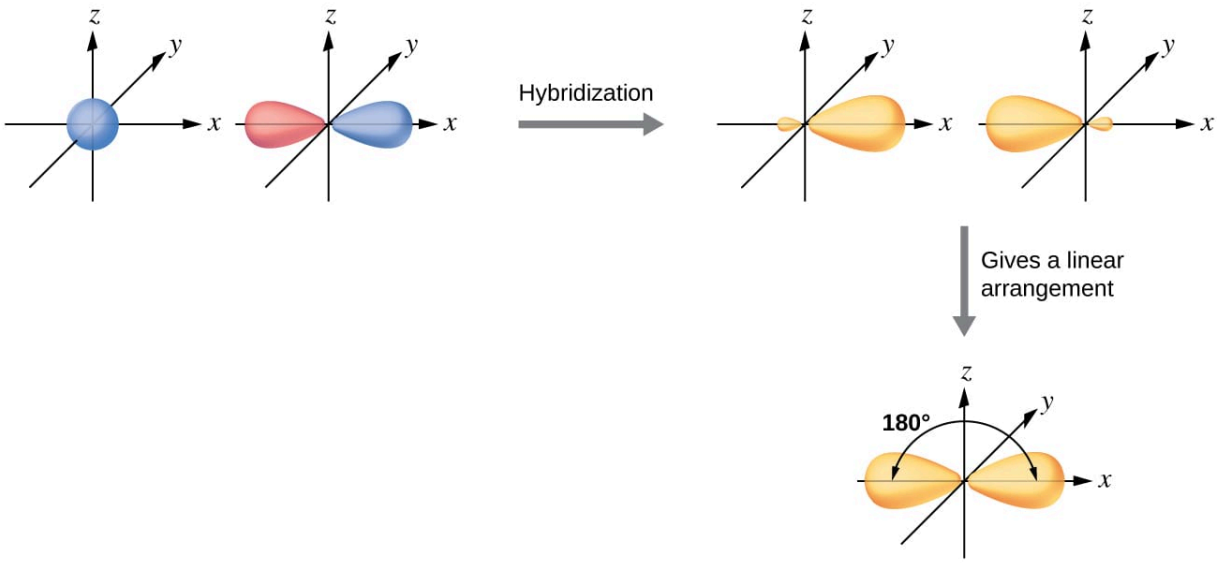


Figure 4.1.3: Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180°, which is consistent with the geometry for two domains.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a linear arrangement,” are shown. The first diagram shows a blue spherical orbital and a red, peanut-shaped orbital, each placed on an X, Y, Z axis system. The second diagram shows the same two orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies along the x-axis in the drawing. The third diagram shows the same two orbitals, but their smaller lobes now overlap along the x-axis while their larger lobes are located at and labeled as “180 degrees” from one another.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure 4.1.4. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.

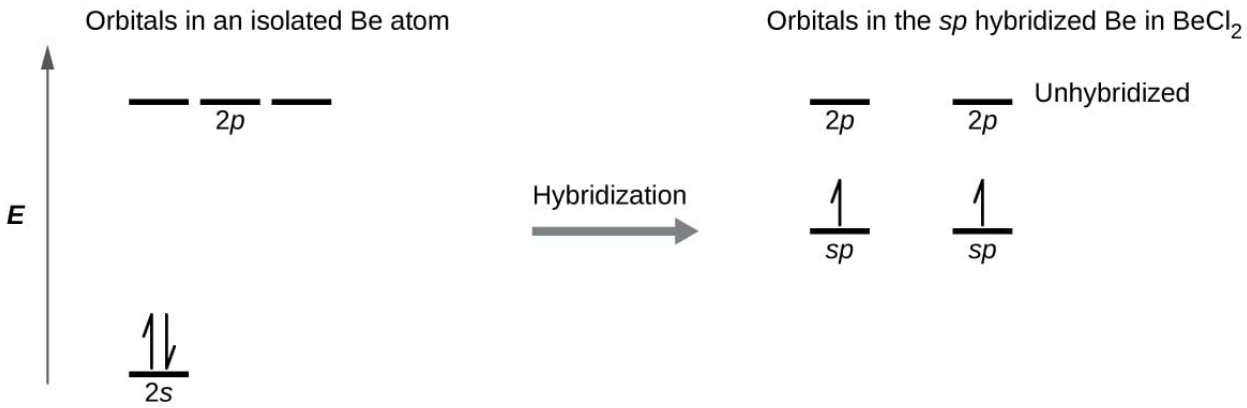


Figure 4.1.4: This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled, “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above these two sets of lines is the phrase, “Orbitals in an isolated B e atom.” The right side of the diagram shows two short, horizontal lines placed halfway up the space and each labeled, “s p.” An upward-facing half arrow is drawn vertically on each line. Above these lines are two other short, horizontal lines, each labeled, “2 p.” Above these two sets of lines is the phrase, “Orbitals in the s p hybridized B e in B e C l subscript 2.”

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds. Any central atom surrounded

by just two regions of valence electron density in a molecule will exhibit *sp* hybridization. Other examples include the mercury atom in the linear $HgCl_2$ molecule, the zinc atom in $Zn(CH_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2.

sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three sp^2 hybrid orbitals and one unhybridized *p* orbital. This arrangement results from sp^2 hybridization, the mixing of one *s* orbital and two *p* orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (Figure 4.1.5).

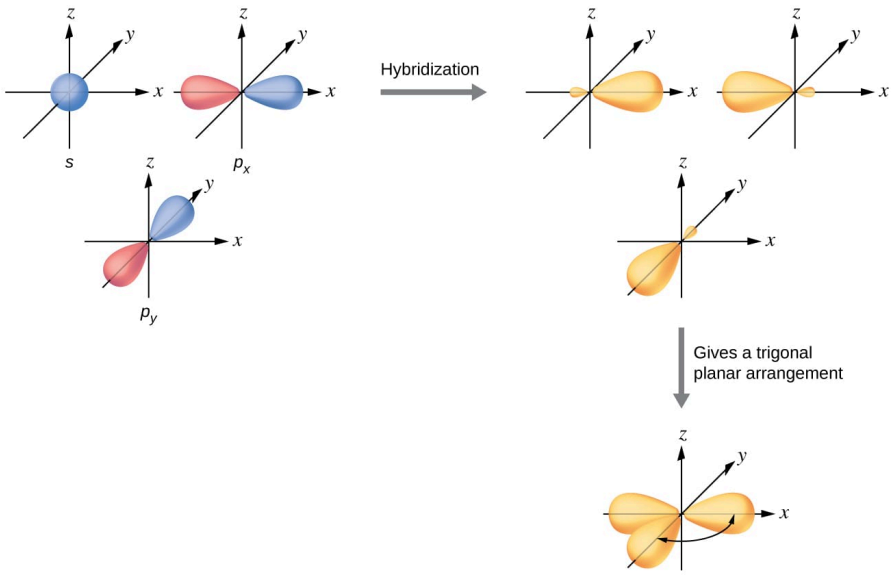


Figure 4.1.5: The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a trigonal planar arrangement,” are shown. The first diagram shows a blue spherical orbital and two red, peanut-shaped orbitals, each placed on an X, Y, Z axis system. The two red orbitals are located on the x and z axes, respectively. The second diagram shows the same three orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies in a different axis in the drawing. The third diagram shows the same three orbitals, but their smaller lobes now overlap while their larger lobes are located at and labeled as “120 degrees” from one another.

Although quantum mechanics yields the “plump” orbital lobes as depicted in Figure 4.1.5, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure 4.1.6, to avoid obscuring other features of a given illustration. We will use these “thinner” representations whenever the true view is too crowded to easily visualize.

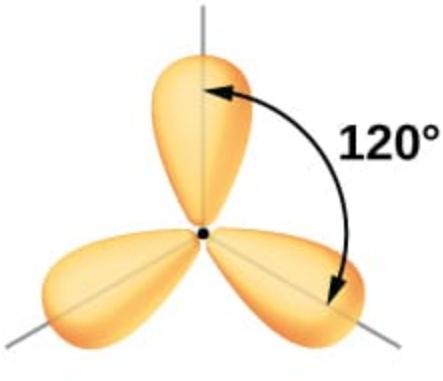


Figure 4.1.6: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures. Three balloon-like orbitals are shown, and connect together near their narrower ends in one plane. The angle between a pair of lobes is labeled, “120 degrees.”

The observed structure of the borane molecule, BH_3, suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure 4.1.7).

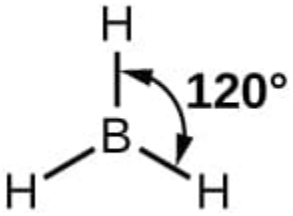


Figure 4.1.7: BH_3 is an electron-deficient molecule with a trigonal planar structure. A boron atom is shown connected to three hydrogen atoms, which are arranged around it like a pyramid. The angle from one line connecting the boron atom to a hydrogen atom to another line connecting the boron atom to a hydrogen atom is labeled, “120 degrees.”

We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH_3 as shown in the orbital energy level diagram in Figure 4.1.8. We redistribute the three valence electrons of the boron atom in the three sp^2 hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.

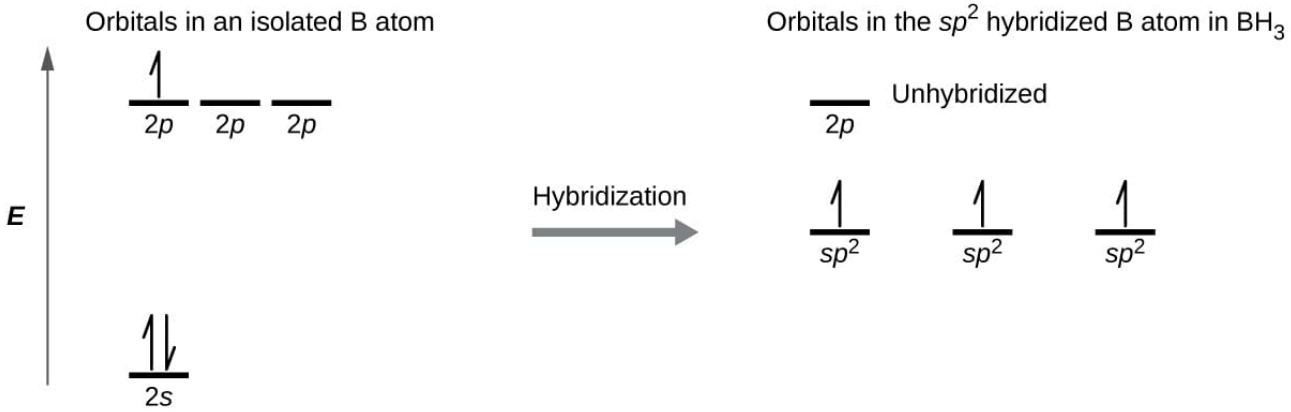


Figure 4.1.8: In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above both sets of these lines is the phrase, “Orbitals in an isolated B atom.” One of the lines has a vertical, up-facing arrow drawn on it. The right side of the diagram shows three short, horizontal lines placed halfway up the space and each labeled, “s p superscript 2.” An upward-facing half arrow is drawn vertically on each line. Above these lines is one other short, horizontal line, labeled, “2 p.” Above both sets of lines is the phrase, “Orbitals in the s p superscript 2 hybridized B atom in B H subscript 3.”

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as ClNO (Figure 4.1.9), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O, and ethene, H_2CCH_2.

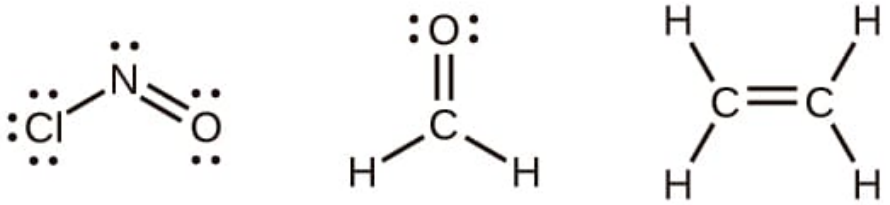


Figure 4.1.9: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

Three Lewis structures are shown. The left-hand structure shows a chlorine atom surrounded by three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons and double bonded to an oxygen atom with two lone pairs of electrons. The middle structure shows a carbon atom single bonded to two hydrogen atoms and double bonded to an oxygen atom that has two lone pairs of electrons. The right-hand structure shows two carbon atoms, double bonded to one another and each single bonded to two hydrogen atoms.

sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four sp^3 hybrid orbitals. The hybrids result from the mixing of one s orbital and all three *p* orbitals that produces four identical sp^3 hybrid orbitals (Figure 4.1.10). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

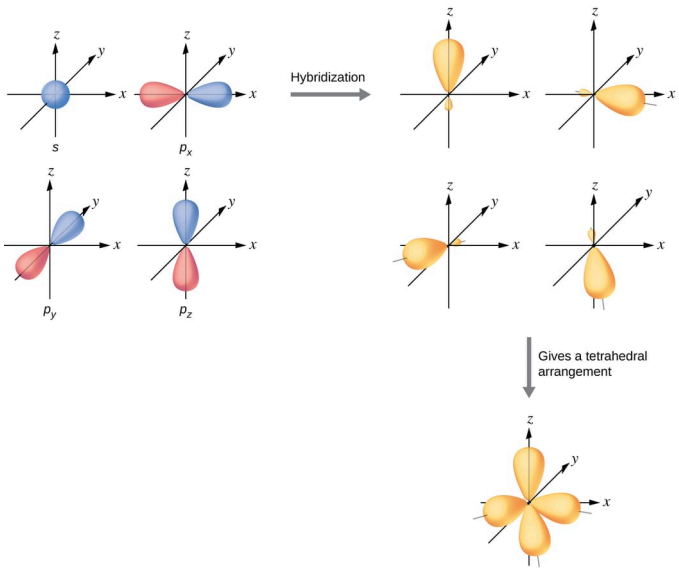


Figure 4.1.10: The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a tetrahedral arrangement,” are shown. The first diagram shows a blue spherical orbital and three red, peanut-shaped orbitals, each placed on an x, y, z axis system. The three red orbitals are located on the x , y and z axes, respectively. The second diagram shows the same four orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies in a different axis in the drawing. The third diagram shows the same four orbitals, but their smaller lobes now overlap to form a tetrahedral structure.

A molecule of methane, CH_4, consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in Figure 4.1.11. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.

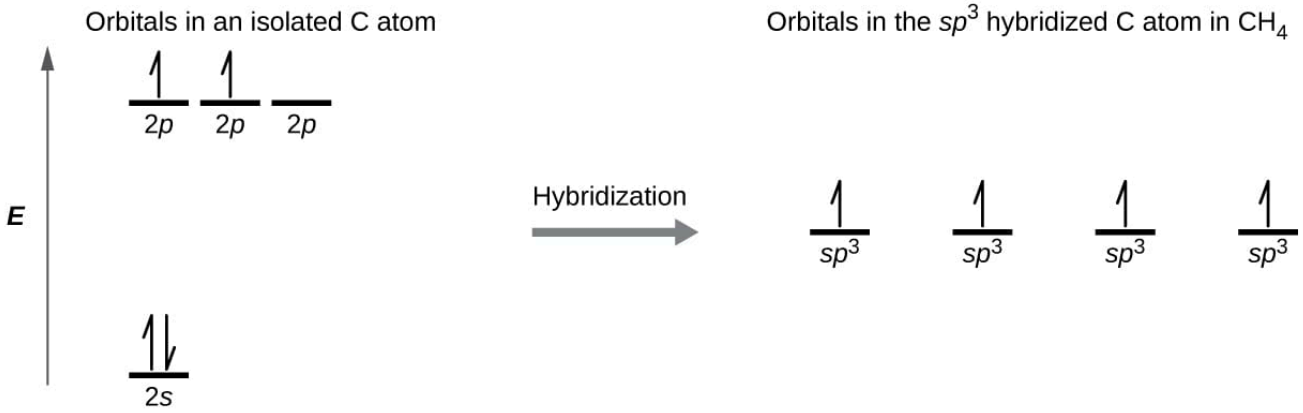


Figure 4.1.11: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Two of the lines have a vertical, up-facing arrow drawn on them. Above both sets of lines is the phrase, “Orbitals in an isolated C atom.” The right side of the diagram shows four short, horizontal lines placed halfway up the space and each labeled, “s p superscript 3.” An upward-facing half arrow is drawn vertically on each line. Above these lines is the phrase, “Orbitals in the s p superscript 3 hybridized C atom in C H subscript 4.”

In a methane molecule, the 1s orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom

and each of the hydrogen atoms to produce the methane molecule, CH_4.

The structure of ethane, C_2H_6, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure 4.1.10). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp^3 hybrid orbitals overlaps with an s orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure 4.1.12. The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

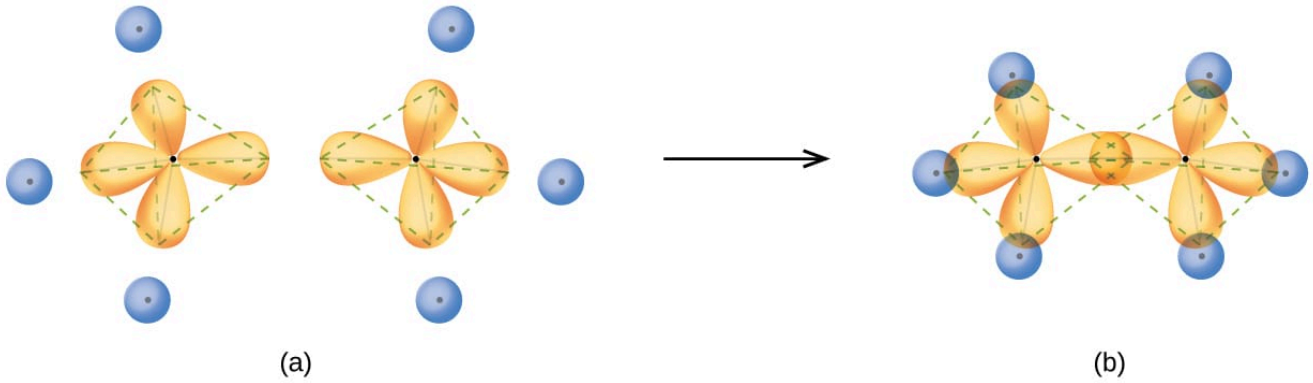


Figure 4.1.12: (a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

Two diagrams are shown and labeled “a” and “b.” Diagram a shows two carbon atoms, each surrounded by their four s p subscript three hybridized orbitals in a three dimensional arrangement. Each of the orbitals is shown overlapping with a spherical hydrogen atom. Diagram b shows the same general arrangement, but the hydrogen atoms are just represented by an, “H” and their spherical orbitals are not shown.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl_4, PCl_3, and NCl_3.

sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the *s* orbital, the three *p* orbitals, and one of the *d* orbitals), which gives five sp^3d hybrid orbitals. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the *s* orbital, the three *p* orbitals, and two of the *d* orbitals in its valence shell), which gives six sp^3d^2 hybrid orbitals. These hybridizations are only possible for atoms that have *d* orbitals in their valence subshells (that is, not those in the first or second period).

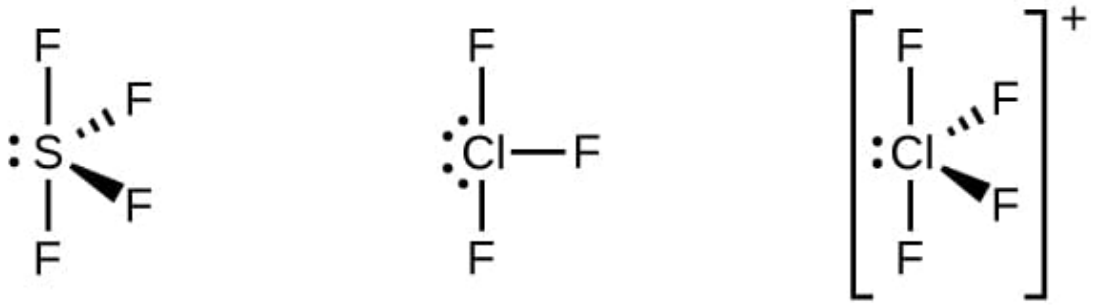


Figure 4.1.13: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and ClF_4^+ *have one lone pair of electrons on the central atom, and* ClF_3 *has two lone pairs giving it the T-shape shown.*

Three Lewis structures are shown along with designations of molecular shape. The left image shows a sulfur atom singly bonded to four fluorine atoms. The sulfur atom has one lone pair of electrons while each fluorine has three. Two fluorine atoms are drawn vertically up and down from the sulfur while the other two are shown going into and out of the page. The second structure shows one chlorine atom singly bonded to three fluorine atoms. The chlorine has two lone pairs of electrons while each fluorine has three. Two fluorine atoms are drawn vertically up and down from the sulfur while the other is shown horizontally. The right structure shows a chlorine atom singly bonded to four fluorine atoms. The chlorine atom has one lone pair of electrons and a superscript plus sign, while each fluorine has three lone pairs of electrons. Two fluorine atoms are drawn vertically up and down from the sulfur while the other two are shown going into and out of the page.

In a molecule of phosphorus pentachloride, PCl_5, there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the 3*s* orbital, the three 3*p* orbitals, and one of the 3*d* orbitals to form the set of five sp^3d hybrid orbitals (Figure 4.1.13) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in ClF_4^+. (The electrons on fluorine atoms are omitted for clarity.)

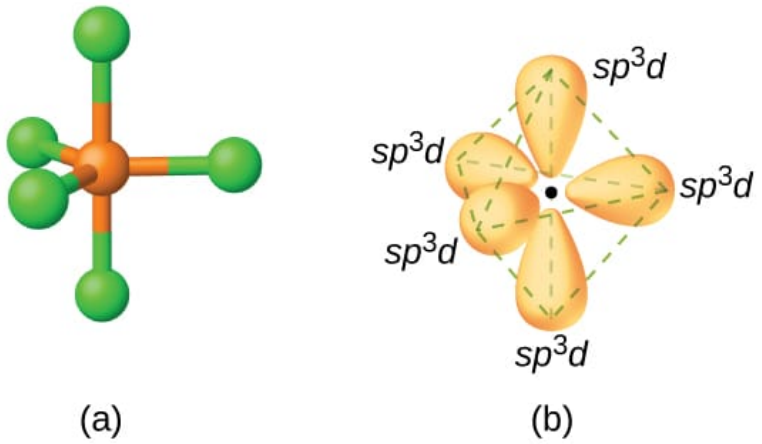


Figure 4.1.14: (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

Two images are shown and labeled “a” and “b.” Image a depicts a ball-and-stick model in a trigonal bipyramidal arrangement. Image b depicts the hybrid orbitals in the same arrangement and each is labeled, “s p superscript three d.”

The sulfur atom in sulfur hexafluoride, SF_6, exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the 3*s* orbital, the three 3*p* orbitals, and two of the 3*d* orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in PCl_6^-, the iodine atom in the interhalogens IF_6^+, IF_5, ICl_4^-, IF_4^- and the xenon atom in XeF_4.

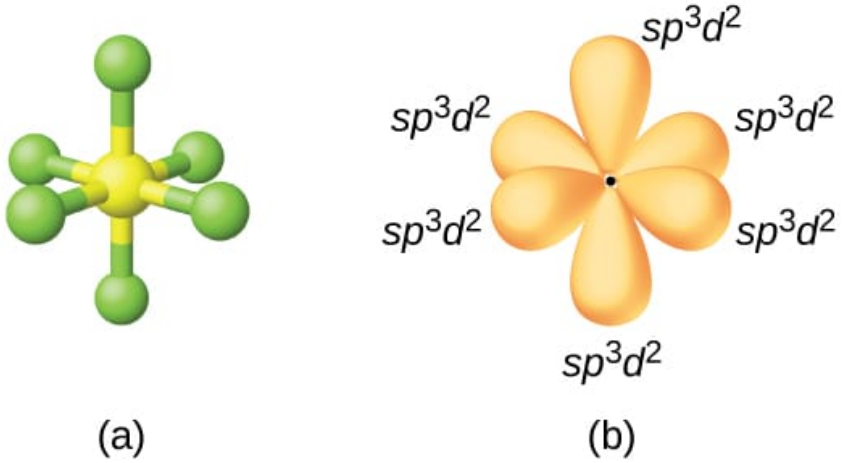


Figure 4.1.15: (a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

Two images are shown and labeled “a” and “b.” Image a depicts a ball-and-stick model in an octahedral arrangement. Image b depicts the hybrid orbitals in the same arrangement and each is labeled, “s p superscript three d superscript two.”

Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in Figure 4.1.16. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

1. Determine the Lewis structure of the molecule.
2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure 4.1.16 that corresponds to this geometry.

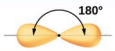
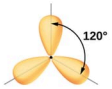
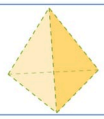
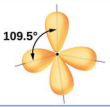
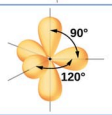
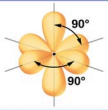
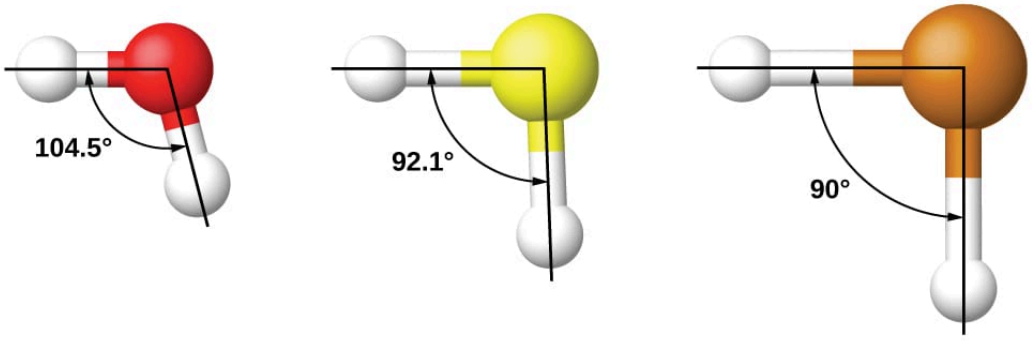
Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

Figure 4.1.16: The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion.

A table is shown that is composed of five columns and six rows. The header row contains the phrases, “Regions of electron density,” “Arrangement,” (which has two columns below it), and “Hybridization,” (which has two columns below it). The first column contains the numbers “2,” “3,” “4,” “5,” and “6.” The second column contains images of a line, a triangle, a three sided pyramid, a trigonal bipyramid, and an eight-faced ocatahedron. The third column contains the terms, “Linear,” “Trigonal planar,” “Tetrahedral,” “Trigonal bipyramidal,” and “Octahedral.” The fourth column contains the terms “s p,” “s p superscript 2,” “s p superscript 3,” “s p superscript 3 d,” and “s p superscript 3 d superscript 2.” The last column contains drawings of the molecules beginning with a peanut-shaped structure marked with an angle of “180 degrees.” The second structure is made up of three equal-sized, rounded structures connected at one point with an angle of “120 degrees,” while the third structure is a three-dimensional arrangement of four equal-sized, rounded structures labeled as “109.5 degrees.” The fourth structure is made up of five equal-sized, rounded structures connected at “120 and 90 degrees,” while the fifth structure has six equal-sized, rounded structures connected at “90 degrees.”

> It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries, not the other way around.

The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data.



Three Lewis structures are shown. The left structure shows an oxygen atom with two lone pairs of electrons single bonded to two hydrogen atoms. The middle structure is made up of a sulfur atom with two lone pairs of electrons single bonded to two hydrogen atoms. The right structure is made up of a tellurium atom with two lone pairs of electrons single bonded to two hydrogen atoms. From left to right, the bond angles of each molecule decrease.

For example, we have discussed the H–O–H bond angle in H_2O, 104.5°, which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with 2*p* orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure.

However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te, the observed bond angle (90°) is consistent with overlap of the 5*p* orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.

Example 4.1.1: Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion, SO_4^{2-}?

Solution

The Lewis structure of sulfate shows there are four regions of electron density.

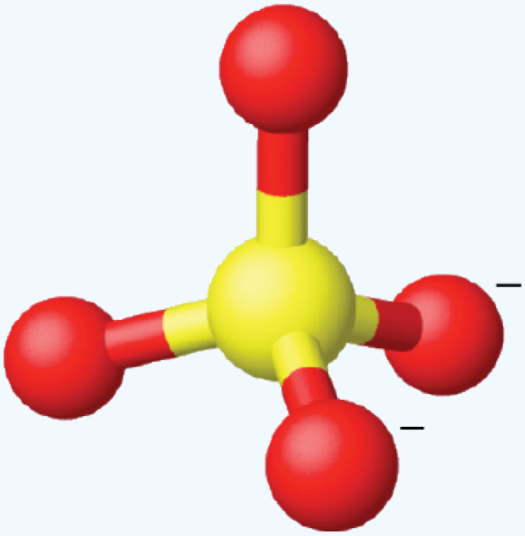
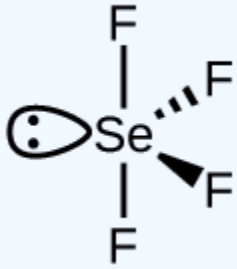


Figure 4.1.16).

A structure is shown in which a sulfur atom is bonded to four oxygen atoms in a tetrahedral arrangement. Two of the oxygen atoms have a negative charge.

Exercise 4.1.1

What is the hybridization of the selenium atom in SeF_4?



A Lewis structure is shown in which four fluorine atoms are each attached to one sulfur atom. Two of the attached fluorine atoms are vertically attached up and down, while two are attached into and out of the page to the right. The sulfur also has one lone pair of electrons attached to the left of the structure.

Answer available at the end of this section.

Example 4.1.2: Assigning Hybridization

Urea, $NH_2C(O)NH_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of each nitrogen and carbon atom in urea?

Solution

The Lewis structure of urea is

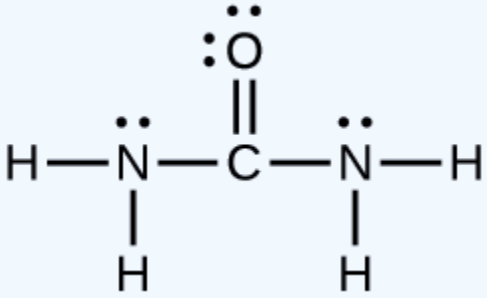


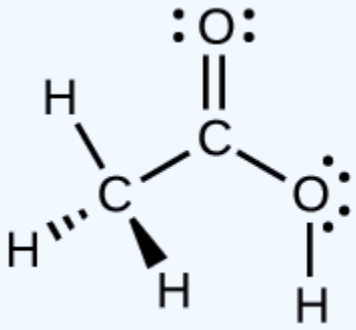
Figure 4.1.16). This is the hybridization of the nitrogen atoms in urea.

A Lewis structure is shown in which a carbon atom is double bonded to an oxygen atom that has two lone pairs of electrons. The carbon atom forms single bonds to two nitrogen atoms. Each nitrogen is single bonded to two hydrogen atoms, and each nitrogen atoms has one lone pair of electrons.

The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (Figure 4.1.16), which is the hybridization of the carbon atom in urea.

Exercise 4.1.1

Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?



A Lewis structure is shown in which a carbon atom is double bonded to an oxygen atom that has two lone pairs of electrons and single bonded to another oxygen atom that is single boned to a hydrogen atom. This second oxygen atom has two lone pairs of electrons. The carbon is also single bonded to a carbon atom that is single bonded to three hydrogen atoms.

Answer available at the end of this section.

Summary

We can use hybrid orbitals, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the electron density around covalently bonded atoms. These hybrid orbitals either form sigma (σ) bonds directed toward other atoms

of the molecule or contain lone pairs of electrons. We can determine the type of hybridization around a central atom from the geometry of the regions of electron density about it. Two such regions imply *sp* hybridization; three, sp^2 hybridization; four, sp^3 hybridization; five, sp^3d hybridization; and six, sp^3d^2 hybridization. Pi (π) bonds are formed from unhybridized atomic orbitals (*p* or *d* orbitals).

Footnotes

1. Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.

Glossary

hybrid orbital
: orbital created by combining atomic orbitals on a central atom

hybridization
: model that describes the changes in the atomic orbitals of an atom when it forms a covalent compound

***sp* hybrid orbital**
: one of a set of two orbitals with a linear arrangement that results from combining one *s* and one *p* orbital

***sp*^{2} hybrid orbital**
: one of a set of three orbitals with a trigonal planar arrangement that results from combining one *s* and two *p* orbitals

***sp*^{3} hybrid orbital**
: one of a set of four orbitals with a tetrahedral arrangement that results from combining one *s* and three *p* orbitals

***sp*^{3}*d* hybrid orbital**
: one of a set of five orbitals with a trigonal bipyramidal arrangement that results from combining one s, three *p*, and one *d* orbital

***sp*^{3}*d*^{2} hybrid orbital**
: one of a set of six orbitals with an octahedral arrangement that results from combining one s, three *p*, and two *d* orbitals

Answers

Exercise 4.1.1

The selenium atom is sp^3d hybridized.

Exercise 4.1.1

$H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

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4.2: Multiple Covalent Bonds

Learning Objectives

- To explain resonance structures using molecular orbitals.

So far in our molecular orbital descriptions we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using molecular orbitals formed by unhybridized *np* atomic orbitals.

Non-singular Bonding

We begin our discussion by considering the bonding in ethylene (C_2H_4). Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied s orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + s) and one C–C (sp^2 + sp^2) (part (a) in Figure 4.2.1). The sp^2 hybridization can be represented as follows:

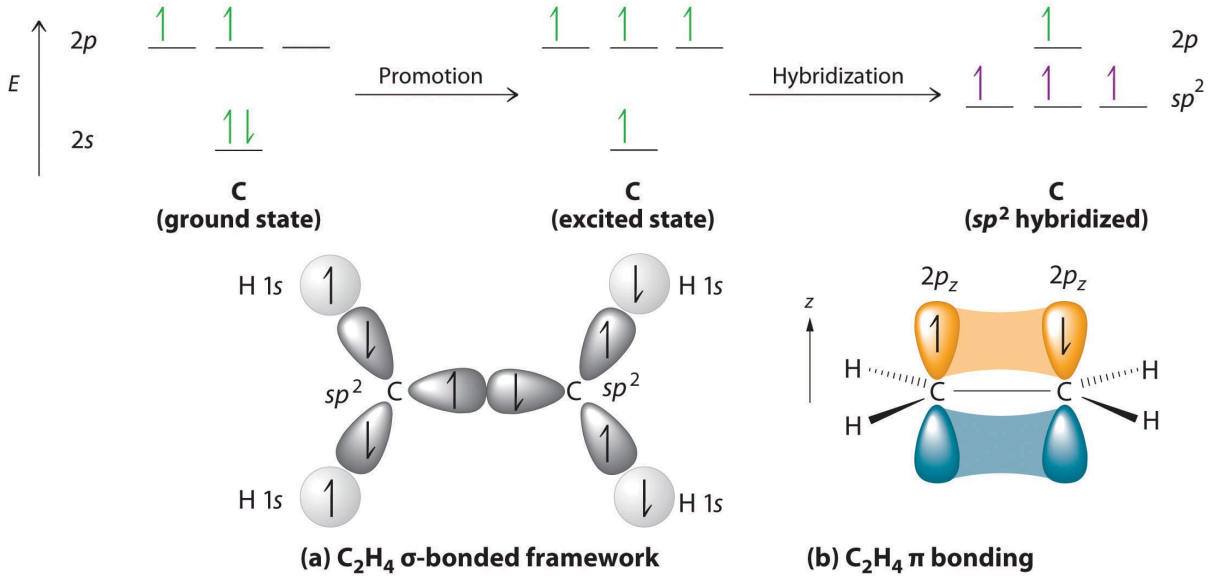


Figure 4.2.1: Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.)

After hybridization, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure 4.2.1). The two singly occupied $2p_z$ orbitals can overlap to form a π bonding orbital and a π * antibonding orbital, which produces the energy-level diagram shown in Figure 4.2.2. With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. The π* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis. Because each $2p_z$ orbital has a single electron, there are only two electrons, enough to fill only the bonding (π) level, leaving the π* orbital empty. Consequently, the C–C bond in ethylene consists of a σ bond and a π bond, which together give a C=C double bond. Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two CH_2 fragments are coplanar, which maximizes the overlap of the two singly occupied $2p_z$ orbitals.

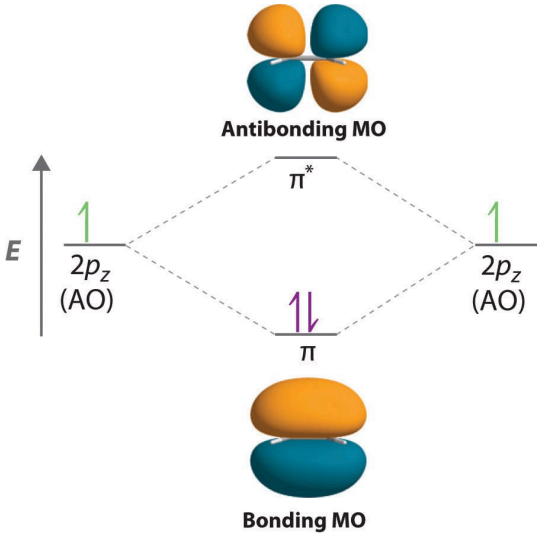


Figure 4.2.2: Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene. As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.

YouTube Video

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View this YouTube Video online

sp2 Hybridization: https://youtu.be/EepTvePnfBA

Triple bonds, as in acetylene (C_2H_2), can also be explained using a combination of hybrid atomic orbitals and molecular orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is *sp* hybridized. If one *sp* lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized 2*p* orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure 4.2.3).

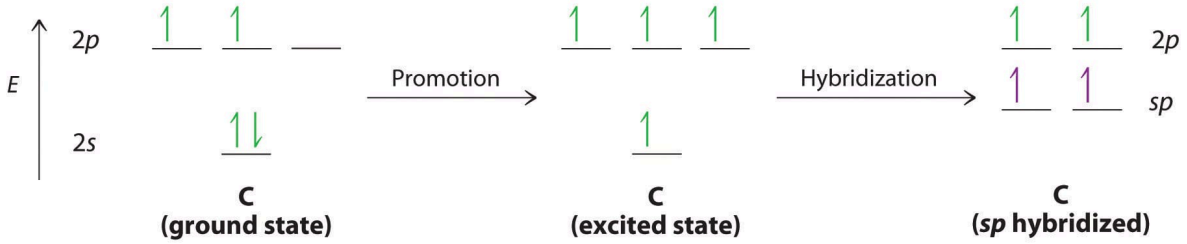
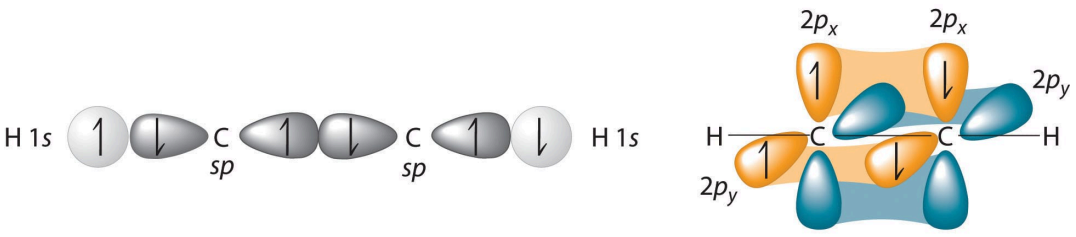


Figure 4.2.3). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.



(a) C_2H_2 σ-bonded framework **(b) C_2H_2 π bonding**

Figure 4.2.3***:*** *Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon sp hybrid orbitals and two singly occupied hydrogen 1s orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.*

Note

In complex molecules, *hybrid orbitals* and *valence bond theory* can be used to describe σ bonding, and unhybridized π orbitals and *molecular orbital theory* can be used to describe π bonding.

Example 4.2.1

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

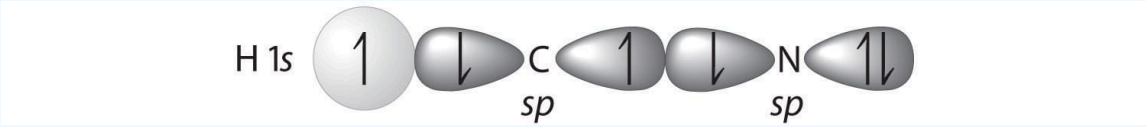
Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

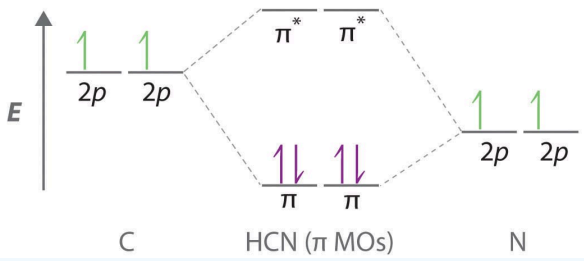
A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.
B. Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals to form π and π* orbitals.
C. Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.

Solution:

A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of *sp* hybridization at carbon. Because the nitrogen atom can also be described as *sp* hybridized, we can use one *sp* hybrid on each atom to form a C–N σ bond. This leaves one *sp* hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:



B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized 2*p* atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four 2*p* atomic orbitals can be combined to give four molecular orbitals: two π (bonding) orbitals and two π* (antibonding) orbitals. **C** With 4 electrons available, only the π orbitals are filled. The overall result is a triple bond (1 σ and 2 π) between C and N.



Exercise

Describe the bonding in formaldehyde ($H_2C{=}O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer

- σ-bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C–H bonds, and one sp^2 hybrid orbital on C and O forms a C–O σ bond.
- π bonding: Unhybridized, singly occupied 2*p* atomic orbitals on carbon and oxygen interact to form π (bonding) and π^* (antibonding) molecular orbitals. With two electrons, only the π (bonding) orbital is occupied.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

sp Hybridization: https://youtu.be/epQXzG9WDRw

Summary

- Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding.

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized *np* orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as O_2 and N_2.

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5: FUNCTIONAL GROUPS AND IR SPECTROSCOPY

5.1: Organic Structural Representations- Bond-Line Notation
5.2: Functional Groups and Classes of Organic Compounds
5.3: IR Spectroscopy Background
5.4: Interpreting Infrared Spectra
5.5: Identifying the Presence of Particular Groups
5.6: The Fingerprint Region

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5.1: Organic Structural Representations- Bond-Line Notation

Learning Objectives

- Define bond-line notation.
- Represent an organic molecule using bond-line notation.
- Identify the compositional characteristics of a molecule that can be determined by analyzing a structure that is represented using bond-line notation.

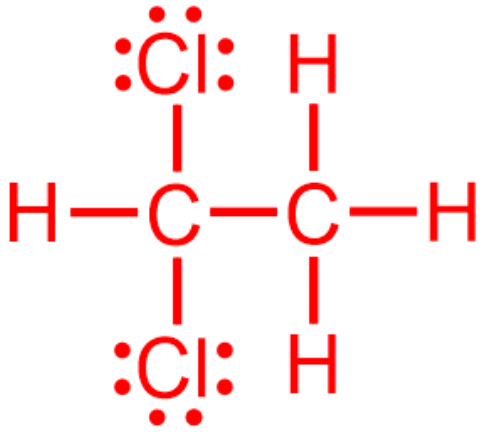
As stated previously, organic chemists use several different notations to represent organic molecules. While a molecular formula only indicates the types and quantities of elements that are present in a molecule, nearly all of the compositional characteristics of an organic substance can be determined by analyzing a structure that is symbolized using expanded structural notation. The types of elements that are present are indicated by the elemental symbols that are shown in the corresponding structural representation. The quantity of each element, as well as the total number of bonds and lone pairs that are present in a molecule, can be established by counting the number of times that each symbol is written in a molecular image. Furthermore, the connectivity, or relative bonding arrangement, of each atom, bond, and lone pair can be explained by describing the placement of each of these components, relative to one another, in an organic structural representation. The types of bonds that are found in a molecule can be determined by counting the number of lines that are drawn between any two atoms in the corresponding image. Structures that are drawn using Valence Shell Electron Pair Repulsion notation also reflect the three-dimensional spatial orientations of organic molecules and their constituent atoms, in addition to all of the compositional characteristics that are listed above above. However, since organic molecules can contain thousands of individual carbon atoms, the expanded and VSEPR images of these substances can become prohibitively-large in size. Furthermore, representing large molecules using these notations is incredibly time-consuming, due to the amount of detail that must be incorporated into the pictures that are generated. Therefore, in order to visually-represent organic molecules using smaller images, organic chemists have symbolized these substances using condensed structural notation, which eliminates specific structural components from a provided expanded structure or VSEPR picture and, instead, uses a "formula-style" format to indicate the number of hydrogens that are bonded to a particular non-metal. A second, more minimalistic, drawing convention, which is known as bond-line notation, will be discussed in the following paragraphs.

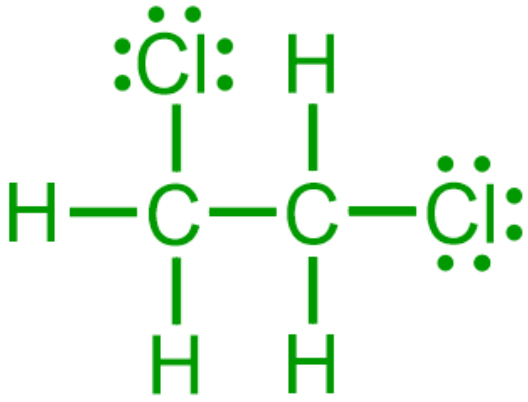
Images that are symbolized using **bond-line notation**, which uses "zig-zag" lines to represent the bonds that exist between consecutive carbon atoms, are generated by eliminating specific structural components from a provided expanded, VSEPR, or condensed picture. Therefore, bond-line structures are substantially smaller in scale, compared to the structures from which they are derived. In particular,

- all lone pairs,
- all non-metal/hydrogen bonds,
- all elemental symbols that represent carbon, C, and
- any hydrogen, H, elemental symbols that are *associated with carbon atoms*

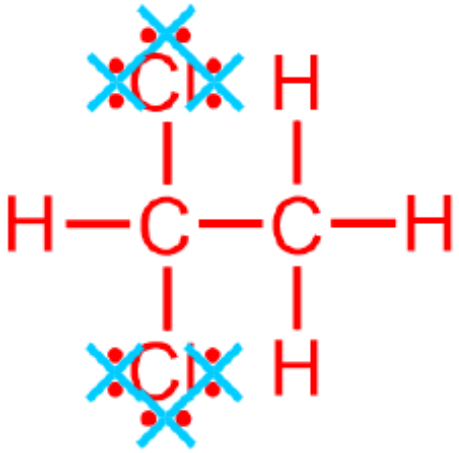
should be removed when generating a bond-line structure from an image that is drawn using a more detailed notation. All remaining single bonds should be represented using "zig-zag" lines that are analogous to those that are used in VSEPR notation. This "zig-zag" pattern can be initiated using either an upward or a downward angle, because, as stated previously, the second atom in any organic structure can be bonded to any "side" of the first elemental symbol that is written. Any *double* or *triple* bonds that are present in a molecule should be symbolized by writing an extra "floating" line in the corresponding position in the "zig-zag" pattern that has been drawn. Furthermore, any hydrogen atoms that are *bonded to heteroatoms* should be *retained* and represented using the condensed "JH_Q" format that was introduced in the previous section of this chapter. Recall that the generic placeholder letter "J" should be replaced with the elemental symbol of a non-metal and that the "Q" subscript corresponds to the number of hydrogens that are bonded to that atom. If only a single hydrogen is associated with a particular atom, no subscript should be written, since values of "1" are usually implicitly-understood in chemistry.

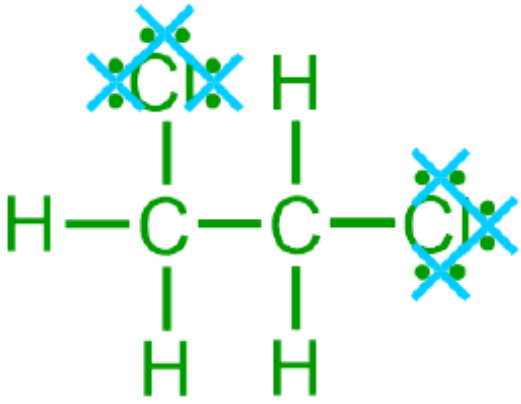
For example, represent each of the following organic molecular structures using bond-line notation.



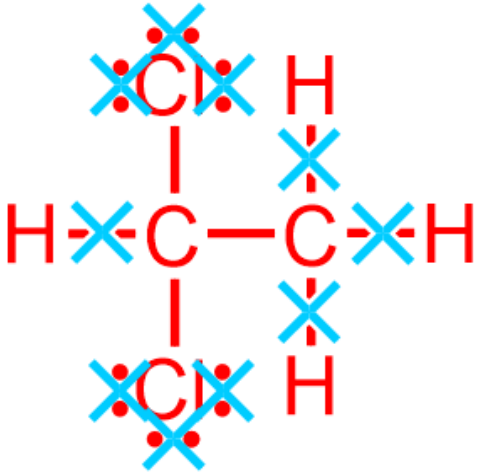


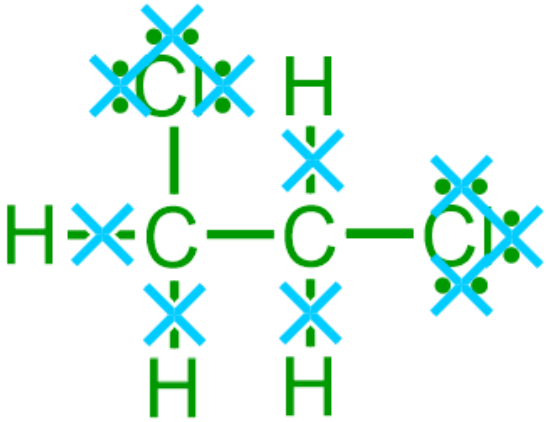
A bond-line structure is generated by eliminating specific structural components from a provided expanded, VSEPR, or condensed picture. In particular, when generating a bond-line structure from an image that is represented in a more detailed notation, all lone pairs,



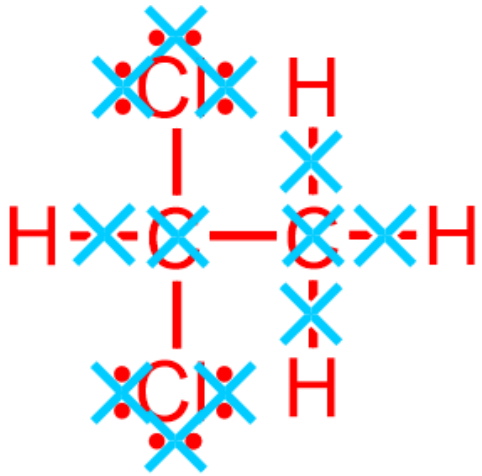


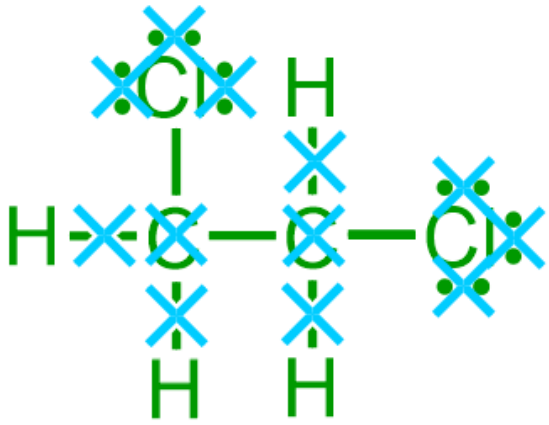
all non-metal/hydrogen bonds,



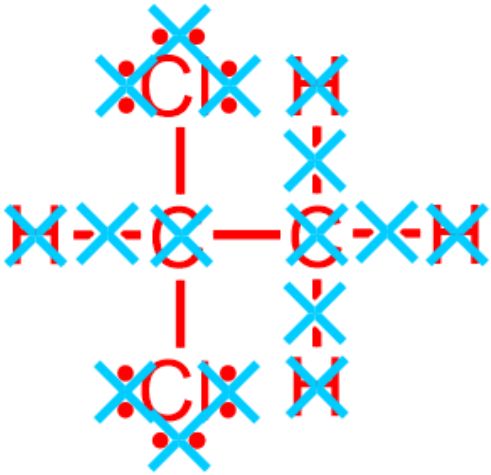


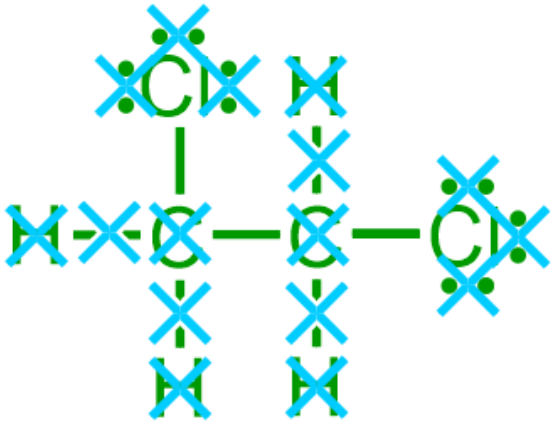
all elemental symbols that represent carbon, C,



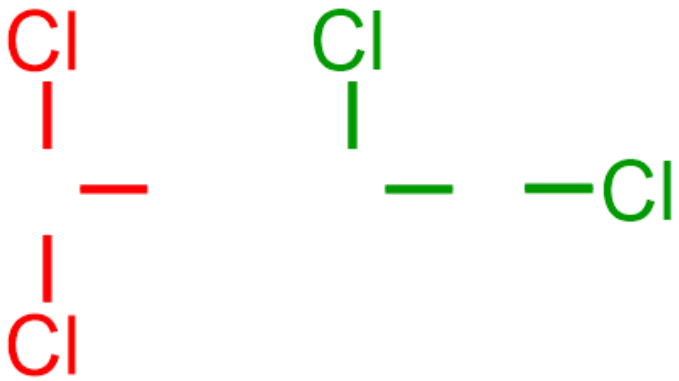


and any hydrogen, H, elemental symbols that are *associated with carbon atoms*

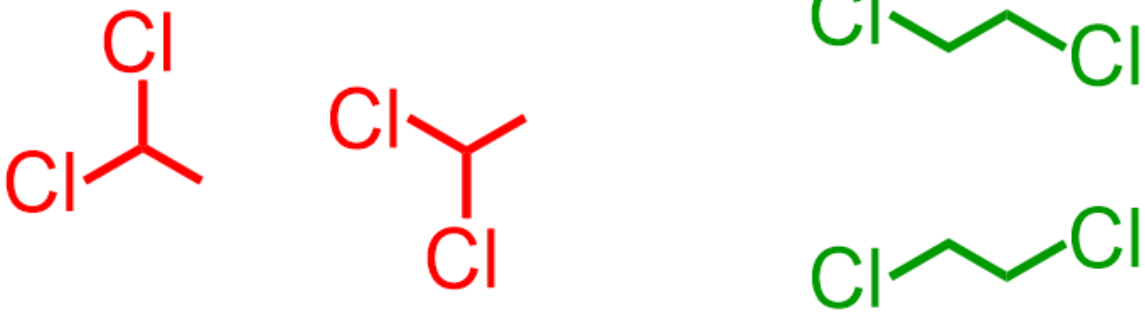




are removed, as indicated by the light blue "X" symbols in the images that are shown above. After eliminating all of these structural characteristics from the given molecule, the following elemental symbols and bonds remain.



In a bond-line structure, these remaining single bonds are represented using "zig-zag" lines that are analogous to those that are used in VSEPR notation. This "zig-zag" pattern can be initiated using either an upward or a downward angle, because, as stated previously, the second atom in any organic structure can be bonded to any "side" of the first elemental symbol that is written. Therefore, both red structures that are shown below are equivalent to one another, as are both green images. These pictures, which are substantially smaller in scale, relative to the expanded structures from which they were derived, are both chemically-correct bond-line representations of the given images.



Although bond-line structures are significantly more challenging to interpret, relative to expanded, VSEPR, and condensed representations, nearly all of the compositional characteristics of a molecule can still be determined by analyzing a structure that is symbolized using bond-line notation. The types and quantities of heteroatoms that are present in a molecule can be determined by counting the number of times that each elemental symbol is written in a molecular image. In bond-line notation, a carbon atom is understood to be located at every point at which two or more bonds meet and on the end of every line that is not explicitly-associated with a heteroatom. Furthermore, each carbon atom is assumed to be bonded to enough hydrogens to achieve its preferred four-bond configuration. The total number of bonds and lone pairs that are present in a molecule, as well as the connectivity of each atom, bond, and lone pair, can be inferred by applying an understanding of standard non-metal bonding configurations. Finally, the types of bonds that are found in a molecule can be determined by counting the number of lines that are drawn between any two atoms in the corresponding bond-line image. However, the bond-line images that are drawn above are two-dimensional drawing conventions and, therefore, do not correctly depict the spatial orientations of organic molecules or their constituent atoms.

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5.2: Functional Groups and Classes of Organic Compounds

Learning Objectives

- To know the major classes of organic compounds and identify important functional groups.

You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). The major families of organic compounds are characterized by their functional groups. Figure 5.2.1 summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

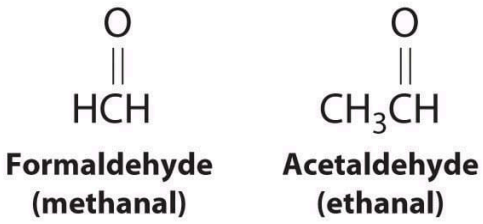
Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	$RC{\equiv}CR'$	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH^a		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX^a		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH^a	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	$ArOH^a$		phenol	-ol
Ethers	ROR'	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	RCHO		acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	$RR'C{=}O$		acetone (2-propanone)	-one
Carboxylic acids	RCO_2H		acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO_2R'		methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	$RCONHR'$		*N*-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH_2, $RNHR'$, $RNR'R''$	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC{\equiv}N$	$H_3CC{\equiv}N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2^a$		nitrobenzene	nitro-

[a]R indicates an alkyl group; Ar indicates an *aryl* group.

Figure 5.2.1: Major Classes of Organic Compounds

The first family listed in Figure 5.2.1 is the hydrocarbons. These include alkanes, with the general molecular formula C_nH_{2n+2} where n is an integer; alkenes, represented by C_nH_{2n}; alkynes, represented by C_nH_{2n-2}; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the $–CO_2H$ functional group is replaced by either an alkoxy (–OR) group, producing an ester, or by an amido (–NRR′, where R and R′ can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a C≡N bond; and nitro compounds, which contain the $–NO_2$ group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2C{=}O$]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.



Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first CH_3 group in dimethyl benzene is indicated with a 1, but the second CH_3 group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure 5.2.2). In common nomenclature, in contrast, the prefixes ortho-, meta-, and para- are used to describe the relative positions of groups attached to an aromatic ring. If the CH_3 groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called ortho-xylene, abbreviated o-xylene. If they are across from each other on the ring, the compound is commonly called para-xylene or p-xylene. When the arrangement is intermediate between those of ortho- and para-compounds, the name is meta-xylene or m-xylene.

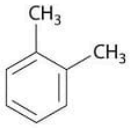
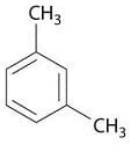
Prefix	Positions of Methyl Groups	Example	Common Name (Systematic Name)
ortho-	1,2		*o*-xylene (1,2-dimethylbenzene)
meta-	1,3		*m*-xylene (1,3-dimethylbenzene)
para-	1,4		*p*-xylene (1,4-dimethylbenzene)

Figure 5.2.2: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

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5.3: IR Spectroscopy Background

This page describes what an infra-red spectrum is and how it arises from bond vibrations within organic molecules.

How an infra-red spectrum is produced

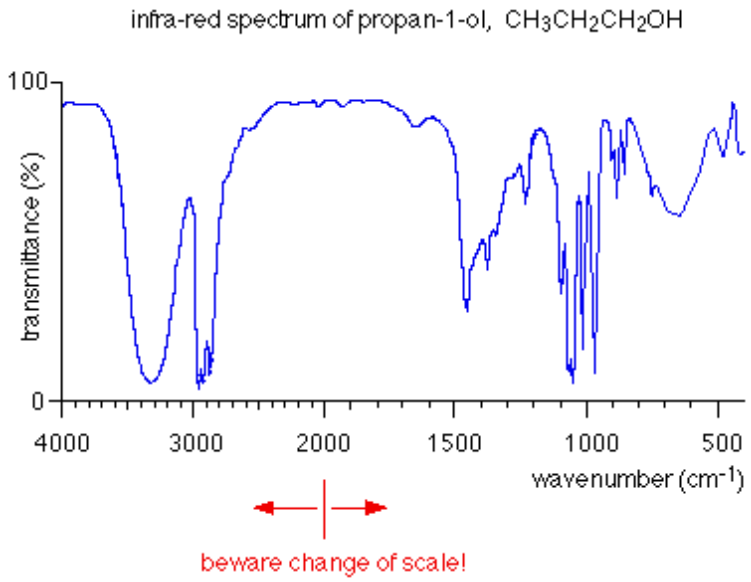
You probably know that visible light is made up of a continuous range of different electromagnetic frequencies - each frequency can be seen as a different color. Infra-red radiation also consists of a continuous range of frequencies - it so happens that our eyes can't detect them.

If you shine a range of infra-red frequencies one at a time through a sample of an organic compound, you find that some frequencies get absorbed by the compound. A detector on the other side of the compound would show that some frequencies pass through the compound with almost no loss, but other frequencies are strongly absorbed.

How much of a particular frequency gets through the compound is measured as percentage transmittance. A percentage transmittance of 100 would mean that all of that frequency passed straight through the compound without any being absorbed. In practice, that never happens - there is always some small loss, giving a transmittance of perhaps 95% as the best you can achieve. A transmittance of only 5% would mean that nearly all of that particular frequency is absorbed by the compound. A very high absorption of this sort tells you important things about the bonds in the compound.

What an infra-red spectrum looks like

A graph is produced showing how the percentage transmittance varies with the frequency of the infra-red radiation.



Notice that an unusual measure of frequency is used on the horizontal axis. Wavenumber is defined like this:

$$\text{wavenumber} = \frac{1}{\text{wavelength in cm}} \quad cm^{-1}$$

Similarly, don't worry about the change of scale half-way across the horizontal axis. You will find infra-red spectra where the scale is consistent all the way across, infra-red spectra where the scale changes at around 2000 cm^{-1}, and very occasionally where the scale changes again at around 1000 cm^{-1}. As you will see when we look at how to interpret infra-red spectra, this does not cause any problems - you simply need to be careful reading the horizontal scale.

What causes some frequencies to be absorbed?

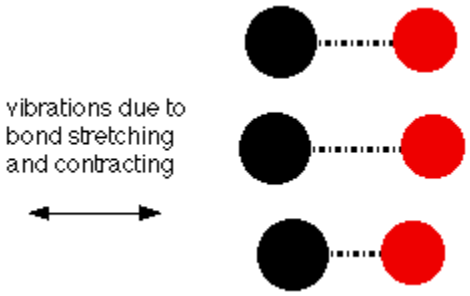
Each frequency of light (including infra-red) has a certain energy. If a particular frequency is being absorbed as it passes through the compound being investigated, it must mean that its energy is being transferred to the compound.

Energies in infra-red radiation correspond to the energies involved in bond vibrations.

Bond stretching

In covalent bonds, atoms aren't joined by rigid links - the two atoms are held together because both nuclei are attracted to the same pair of electrons. The two nuclei can vibrate backwards and forwards - towards and away from each other - around an average position.

The diagram shows the stretching that happens in a carbon-oxygen single bond. There will, of course, be other atoms attached to both the carbon and the oxygen. For example, it could be the carbon-oxygen bond in methanol, CH_3OH.

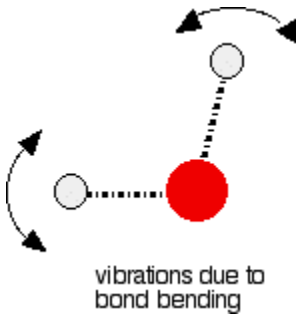


The energy involved in this vibration depends on things like the length of the bond and the mass of the atoms at either end. That means that each different bond will vibrate in a different way, involving different amounts of energy.

Bonds are vibrating all the time, but if you shine exactly the right amount of energy on a bond, you can kick it into a higher state of vibration. The amount of energy it needs to do this will vary from bond to bond, and so each different bond will absorb a different frequency (and hence energy) of infra-red radiation.

Bond bending

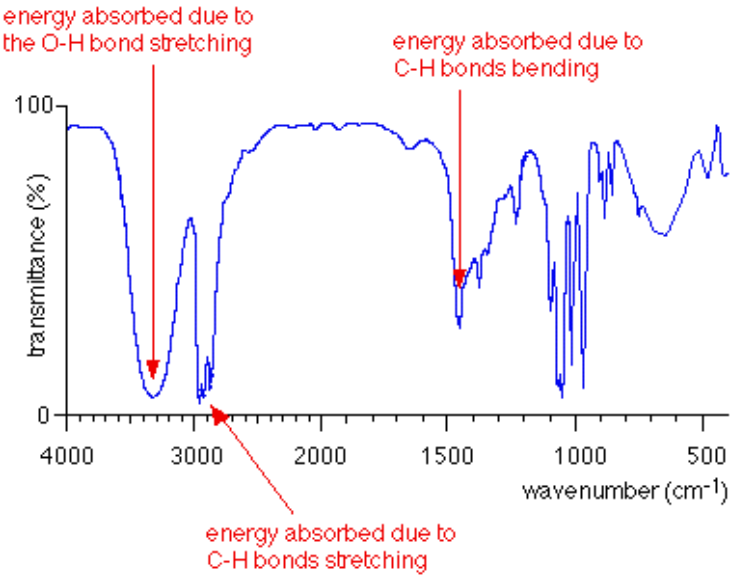
As well as stretching, bonds can also bend. The diagram shows the bending of the bonds in a water molecule. The effect of this, of course, is that the bond angle between the two hydrogen-oxygen bonds fluctuates slightly around its average value. Imagine a lab model of a water molecule where the atoms are joined together with springs. These bending vibrations are what you would see if you shook the model gently.



Again, bonds will be vibrating like this all the time and, again, if you shine exactly the right amount of energy on the bond, you can kick it into a higher state of vibration. Since the energies involved with the bending will be different for each kind of bond, each different bond will absorb a different frequency of infra-red radiation in order to make this jump from one state to a higher one.

Tying all this together

Look again at the infra-red spectrum of propan-1-ol, $CH_3CH_2CH_2OH$:



In the diagram, three sample absorptions are picked out to show you the bond vibrations which produced them. Notice that bond stretching and bending produce different troughs in the spectrum.

Contributor

Jim Clark (Chemguide.co.uk)

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5.4: Interpreting Infrared Spectra

Objectives

After completing this section, you should be able to

1. describe how the so-called “fingerprint region” of an infrared spectrum can assist in the identification of an unknown compound.
2. identify the functional group or groups present in a compound, given a list of the most prominent absorptions in the infrared spectrum and a table of characteristic absorption frequencies.
3. identify the broad regions of the infrared spectrum in which occur absorptions caused by
   a. N — H, C — H, and O — H
   b. You can't use 'macro parameter character #' in math mode and You can't use 'macro parameter character #' in math mode
   c. C = O, C = N$, and$C = C

Key Terms

Make certain that you can define, and use in context, the key term below.

- fingerprint region

Study Notes

When answering assignment questions, you may use this IR table to find the characteristic infrared absorptions of the various functional groups. However, you should be able to indicate in broad terms where certain characteristic absorptions occur. You can achieve this objective by memorizing the following table.

Region of Spectrum (cm^{-1})	**Absorption**
2500-4000	$\ce{\sf{N–H}}$, $\ce{\sf{O–H}}$, $\ce{\sf{C–H}}$
2000-2500	$\ce{\sf{C#C}}$, $\ce{\sf{C#N}}$
1500-2000	$\ce{\sf{C=O}}$, $\ce{\sf{C=N}}$, $\ce{\sf{C=C}}$
below 1500	Fingerprint region

The Origin of Group Frequencies

An important observation made by early researchers is that many functional group absorb infrared radiation at about the same wavenumber, regardless of the structure of the rest of the molecule. For example, C-H stretching vibrations usually appear between 3200 and 2800cm^{-1} and carbonyl(C=O) stretching vibrations usually appear between 1800 and 1600cm^{-1}. This makes these bands diagnostic markers for the presence of a functional group in a sample. These types of infrared bands are called group frequencies because they tell us about the presence or absence of specific functional groups in a sample.

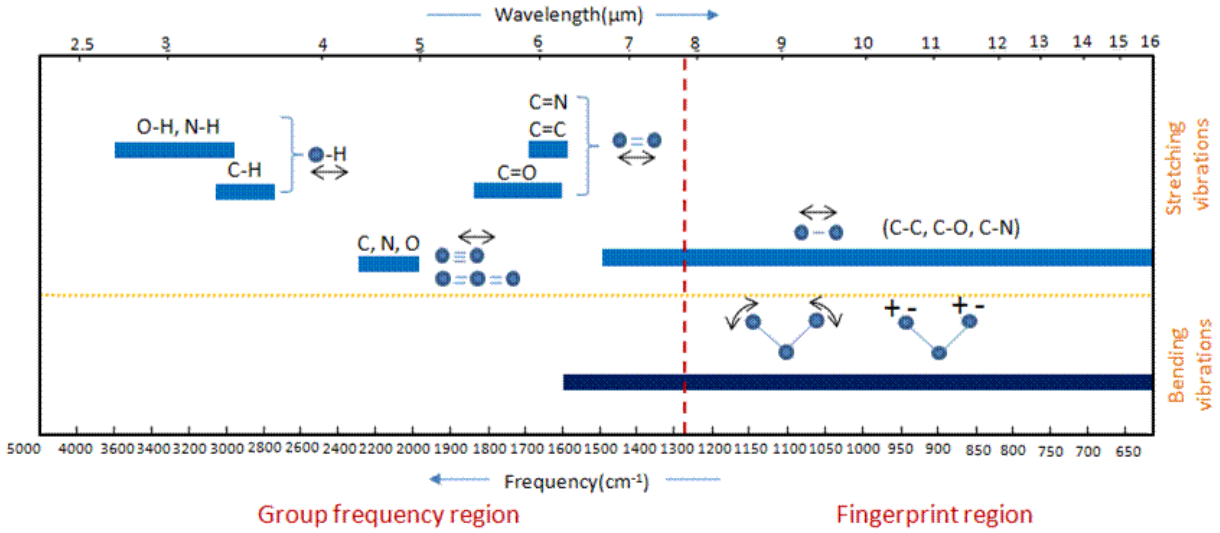
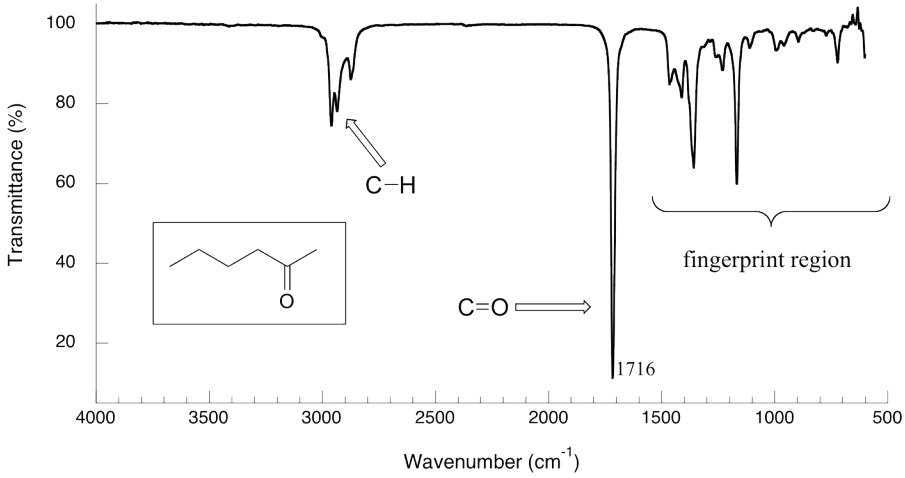


Figure 2. Group frequency and fingerprint regions of the mid-infrared spectrum

The region of the infrared spectrum from 1200 to 700 cm^{-1} is called the fingerprint region. This region is notable for the large number of infrared bands that are found there. Many different vibrations, including C-O, C-C and C-N single bond stretches, C-H bending vibrations, and some bands due to benzene rings are found in this region. The fingerprint region is often the most complex and confusing region to interpret, and is usually the last section of a spectrum to be interpreted. However, the utility of the fingerprint region is that the many bands there provide a fingerprint for a molecule.

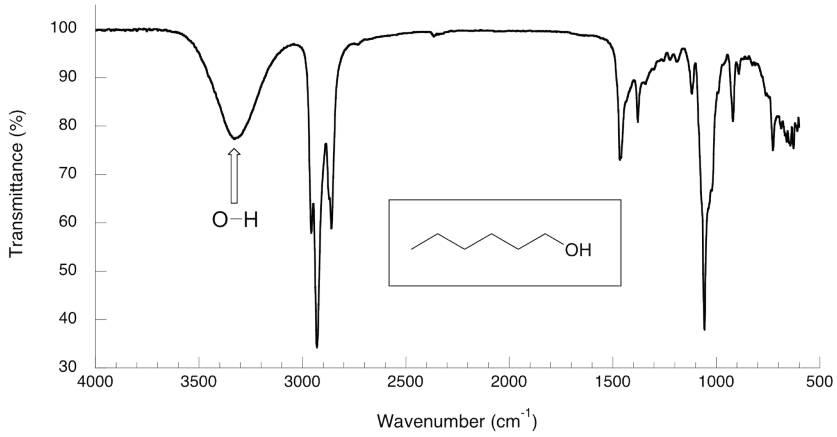


The key absorption peak in this spectrum is that from the carbonyl double bond, at 1716 cm^{-1} (corresponding to a wavelength of 5.86 mm, a frequency of 5.15 x 10^{13} Hz, and a ΔE value of 4.91 kcal/mol). Notice how strong this peak is, relative to the others on the spectrum: *a strong peak in the 1650-1750 cm^{-1} region is a dead giveaway for the presence of a carbonyl group*. Within that range, carboxylic acids, esters, ketones, and aldehydes tend to absorb in the shorter wavelength end (1700-1750 cm-1), while conjugated unsaturated ketones and amides tend to absorb on the longer wavelength end (1650-1700 cm^{-1}).

The jagged peak at approximately 2900-3000 cm^{-1} is characteristic of tetrahedral carbon-hydrogen bonds. This peak is not terribly useful, as just about every organic molecule that you will have occasion to analyze has these bonds. Nevertheless, it can serve as a familiar reference point to orient yourself in a spectrum.

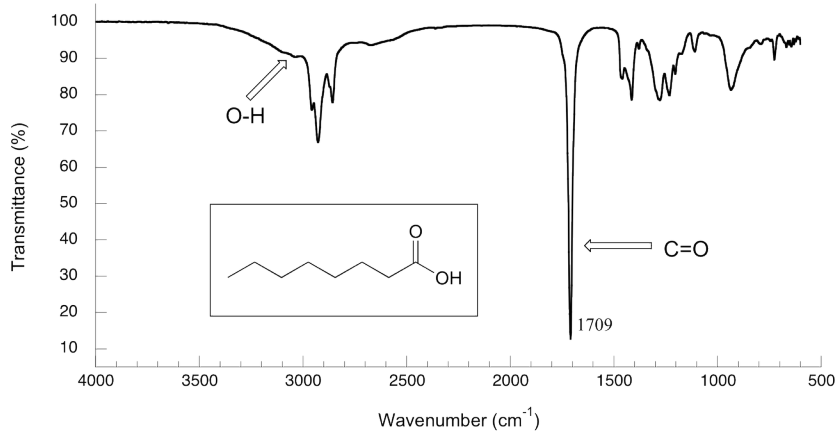
You will notice that there are many additional peaks in this spectrum in the longer-wavelength 400 -1400 cm^{-1} region. This part of the spectrum is called the **fingerprint region**. While it is usually very difficult to pick out any specific functional group identifications from this region, it does, nevertheless, contain valuable information. The reason for this is suggested by the name: just like a human fingerprint, the pattern of absorbance peaks in the fingerprint region is unique to every molecule, meaning that the data from an unknown sample can be compared to the IR spectra of known standards in order to make a positive identification. In the mid-1990's, for example, several paintings were identified as forgeries because scientists were able to identify the IR footprint region of red and yellow pigment compounds that would not have been available to the artist who supposedly created the painting (for more details see Chemical and Engineering News, Sept 10, 2007, p. 28).

Now, let's take a look at the IR spectrum for 1-hexanol.



As you can see, the carbonyl peak is gone, and in its place is a very broad 'mountain' centered at about 3400 cm^{-1}. This signal is characteristic of the O-H stretching mode of alcohols, and is a dead giveaway for the presence of an alcohol group. The breadth of this signal is a consequence of hydrogen bonding between molecules.

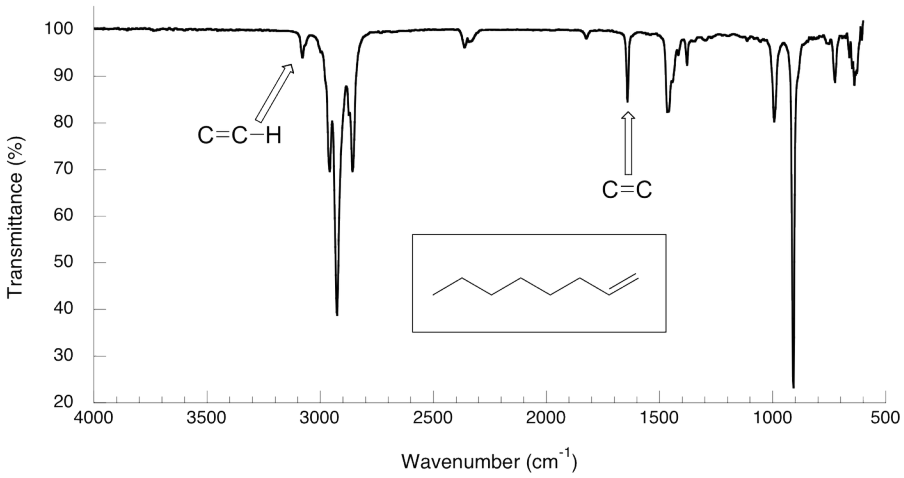
In the spectrum of octanoic acid we see, as expected, the characteristic carbonyl peak, this time at 1709 cm^{-1}.



We also see a low, broad absorbance band that looks like an alcohol, except that it is displaced slightly to the right (long-

wavelength) side of the spectrum, causing it to overlap to some degree with the C-H region. This is the characteristic carboxylic acid O-H single bond stretching absorbance.

The spectrum for 1-octene shows two peaks that are characteristic of alkenes: the one at 1642 cm^{-1} is due to stretching of the carbon-carbon double bond, and the one at 3079 cm-1 is due to stretching of the s bond between the alkene carbons and their attached hydrogens.



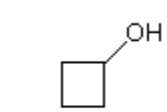
Alkynes have characteristic IR absorbance peaks in the range of 2100-2250 cm^{-1} due to stretching of the carbon-carbon triple bond, and terminal alkenes can be identified by their absorbance at about 3300 cm-1, due to stretching of the bond between the sp-hybridized carbon and the terminal hydrogen.

It is possible to identify other functional groups such as amines and ethers, but the characteristic peaks for these groups are considerably more subtle and/or variable, and often are overlapped with peaks from the fingerprint region. For this reason, we will limit our discussion here to the most easily recognized functional groups, which are summarized in this table.

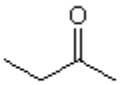
As you can imagine, obtaining an IR spectrum for a compound will not allow us to figure out the complete structure of even a simple molecule, unless we happen to have a reference spectrum for comparison. In conjunction with other analytical methods, however, IR spectroscopy can prove to be a very valuable tool, given the information it provides about the presence or absence of key functional groups. IR can also be a quick and convenient way for a chemist to check to see if a reaction has proceeded as planned. If we were to run a reaction in which we wished to convert cyclohexanone to cyclohexanol, for example, a quick comparison of the IR spectra of starting compound and product would tell us if we had successfully converted the ketone group to an alcohol.

More examples of IR spectra

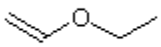
To illustrate the usefulness of infrared absorption spectra, examples for five C_4H_8O isomers are presented below their corresponding structural formulas. Try to associate each spectrum with one of the isomers in the row above it.



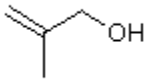
cyclobutanol



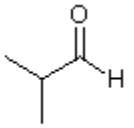
2-butanone



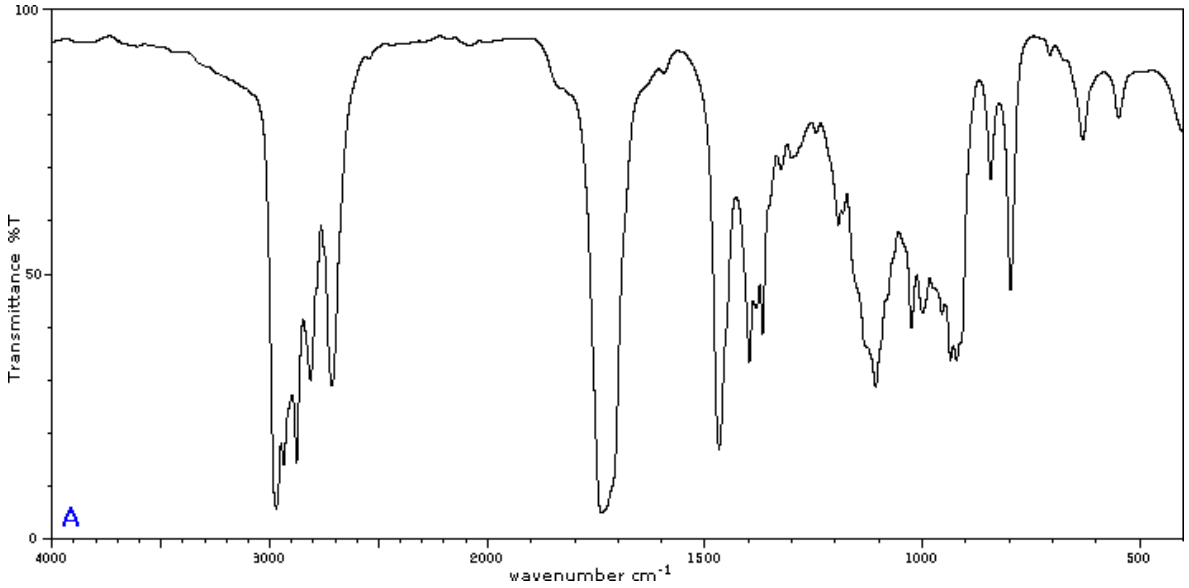
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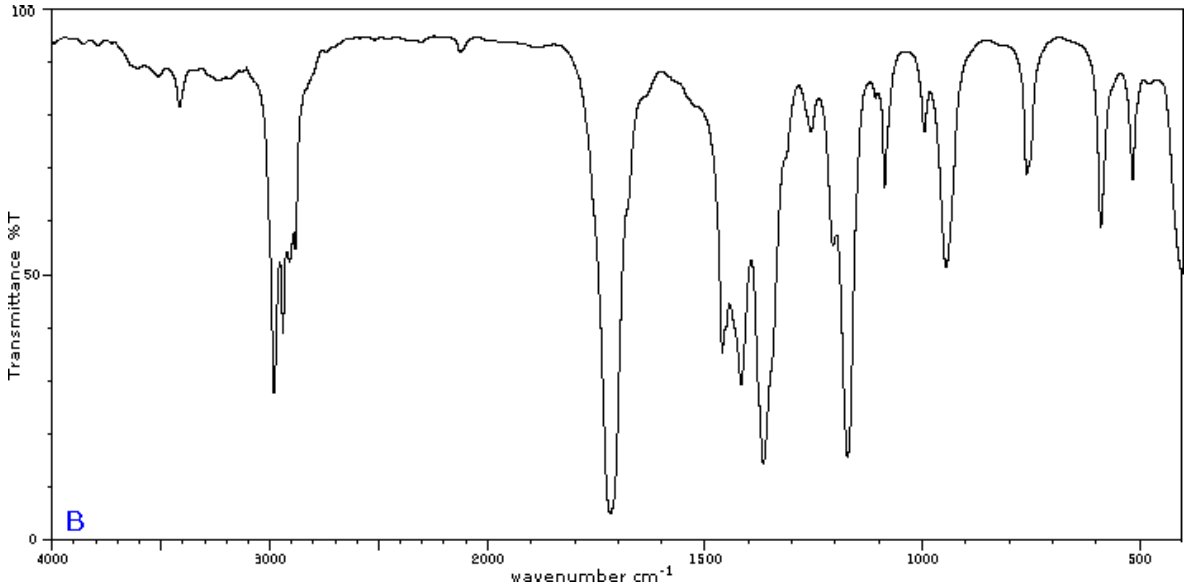


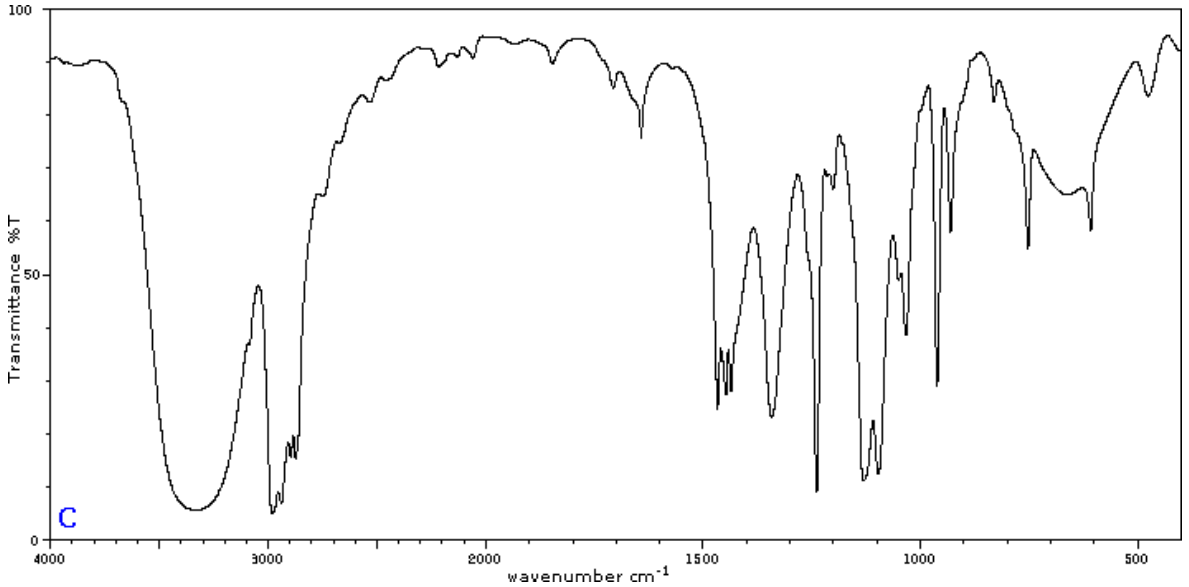
2-methyl-2-propen-1-ol

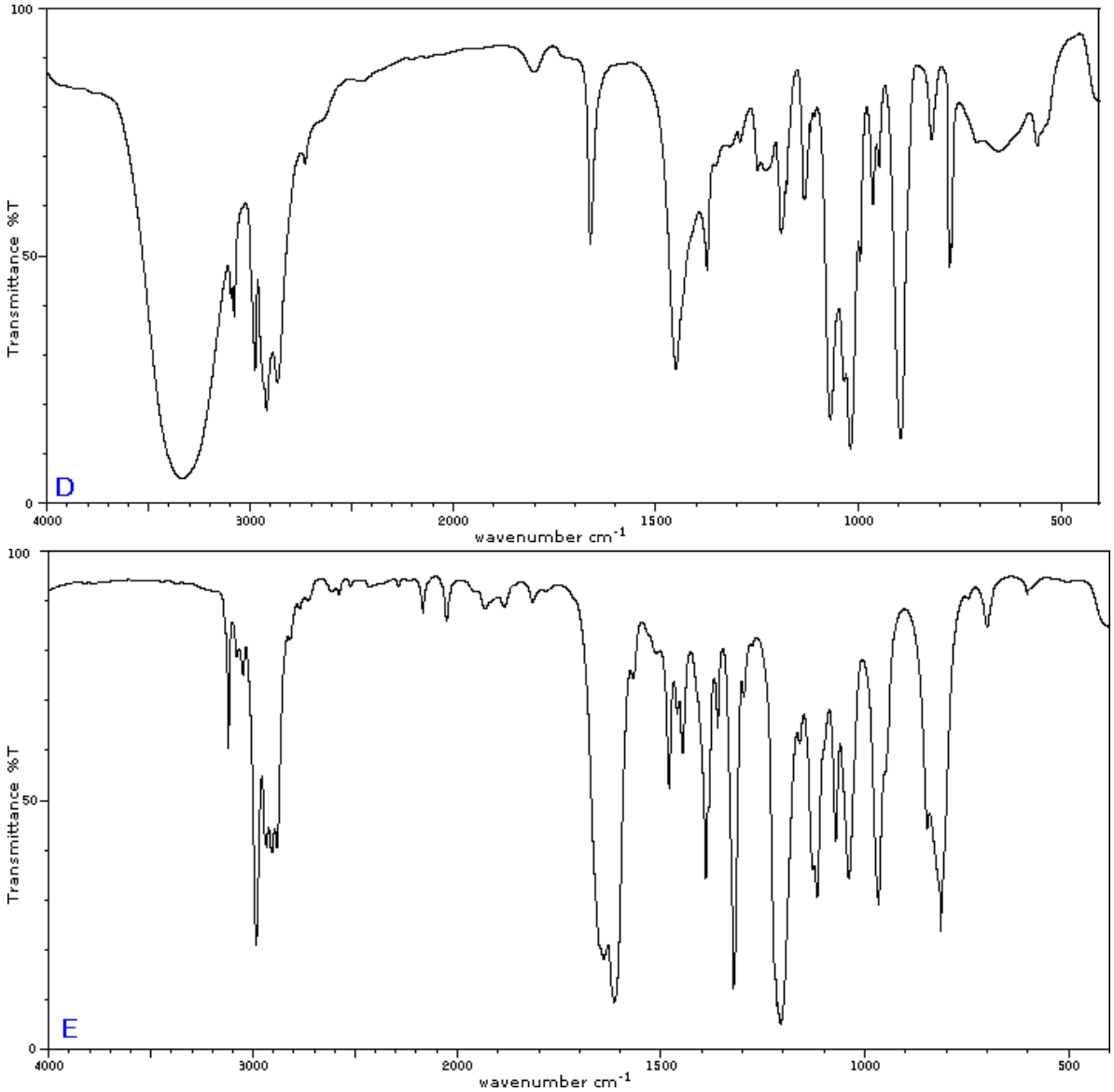


2-methylpropanal


100
50
0
Transmittance %T
A
4000
3000
2000
1500
1000
500
wavenumber cm-1


100
50
0
Transmittance %T
B
4000
3000
2000
1500
1000
500
wavenumber cm-1


100
50
0
Transmittance %T
C
4000
3000
2000
1500
1000
500
wavenumber cm-1



Exercises

Questions

Q12.7.1

What functional groups give the following signals in an IR spectrum?

A) 1700 cm^{-1}

B) 1550 cm^{-1}

C) 1700 cm^{-1} and 2510-3000 cm^{-1}

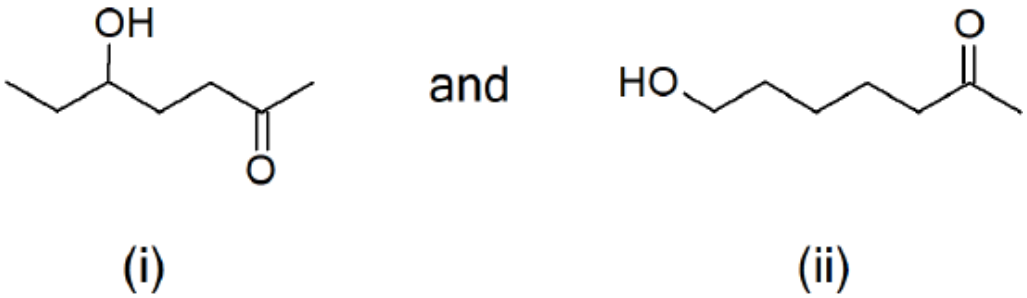
Q12.7.2

How can you distinguish the following pairs of compounds through IR analysis?

A) CH_3OH (Methanol) and $CH_3CH_2OCH_2CH_3$ (Diethylether)

B) Cyclopentane and 1-pentene.

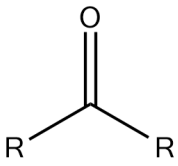
C)



(i) (ii)

Solutions

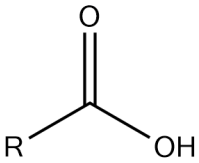
S12.7.1

A) 

Carbonyl

B)

Nitro

C) 

Carboxylic Acid

S12.7.2

A) A OH peak will be present around 3300 cm^{-1} for methanol and will be absent in the ether.

B) 1-pentene will have a alkene peak around 1650 cm^{-1} for the C=C and there will be another peak around 3100 cm^{-1} for the sp^2 C-H group on the alkene

C) Cannot distinguish these two isomers. They both have the same functional groups and therefore would have the same peaks on an IR spectra.

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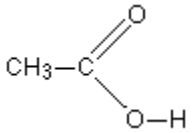
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5.5: Identifying the Presence of Particular Groups

This page explains how to use an infra-red spectrum to identify the presence of a few simple bonds in organic compounds.

The infrared spectrum for a simple carboxylic acid: Ethanoic acid

Ethanoic acid has the structure:



You will see that it contains the following bonds:

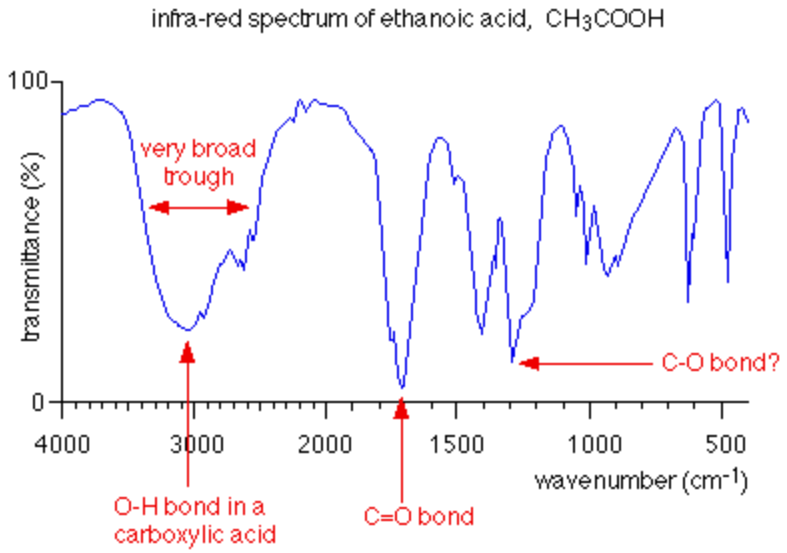
- carbon-oxygen double, C=O
- carbon-oxygen single, C-O
- oxygen-hydrogen, O-H
- carbon-hydrogen, C-H
- carbon-carbon single, C-C

The carbon-carbon bond has absorptions which occur over a wide range of wavenumbers in the fingerprint region - that makes it very difficult to pick out on an infra-red spectrum. The carbon-oxygen single bond also has an absorbtion in the fingerprint region, varying between 1000 and 1300 cm^{-1} depending on the molecule it is in. You have to be very wary about picking out a particular trough as being due to a C-O bond.

The other bonds in ethanoic acid have easily recognized absorptions outside the fingerprint region.

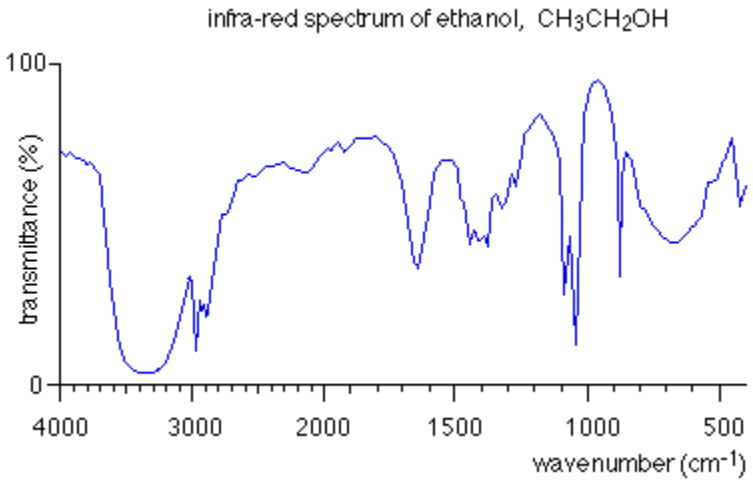
- The C-H bond (where the hydrogen is attached to a carbon which is singly-bonded to everything else) absorbs somewhere in the range from 2853 - 2962 cm^{-1}. Because that bond is present in most organic compounds, that's not terribly useful! What it means is that you can ignore a trough just under 3000 cm^{-1}, because that is probably just due to C-H bonds.
- The carbon-oxygen double bond, C=O, is one of the really useful absorptions, found in the range 1680 - 1750 cm^{-1}. Its position varies slightly depending on what sort of compound it is in.
- The other really useful bond is the O-H bond. This absorbs differently depending on its environment. It is easily recognised in an acid because it produces a very broad trough in the range 2500 - 3300 cm^{-1}.

The infrared spectrum for ethanoic acid looks like this:



The possible absorption due to the C-O single bond is queried because it lies in the fingerprint region. You couldn't be sure that this trough wasn't caused by something else.

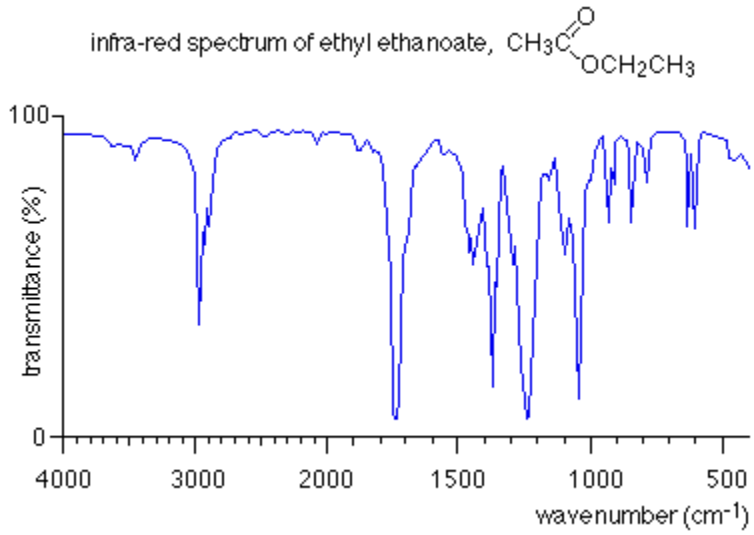
The infrared spectrum for an alcohol: Ethanol



The O-H bond in an alcohol absorbs at a higher wavenumber than it does in an acid - somewhere between 3230 - 3550 cm^{-1}. In fact this absorption would be at a higher number still if the alcohol isn't hydrogen bonded - for example, in the gas state. All the infra-red spectra on this page are from liquids - so that possibility will never apply.

> Notice the absorption due to the C-H bonds just under 3000 cm^{-1}, and also the troughs between 1000 and 1100 cm^{-1} - one of which will be due to the C-O bond.

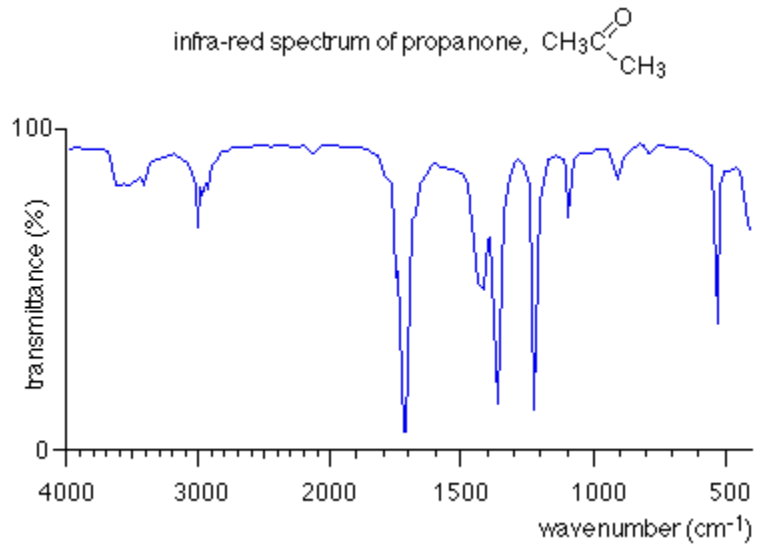
The infrared spectrum for an ester: Ethyl ethanoate



This time the O-H absorption is missing completely. Don't confuse it with the C-H trough fractionally less than 3000 cm^{-1}. The presence of the C=O double bond is seen at about 1740 cm^{-1}.

The C-O single bond is the absorption at about 1240 cm^{-1}. Whether or not you could pick that out would depend on the detail given by the table of data which you get in your exam, because C-O single bonds vary anywhere between 1000 and 1300 cm^{-1} depending on what sort of compound they are in. Some tables of data fine it down, so that they will tell you that an absorption from 1230 - 1250 is the C-O bond in an ethanoate.

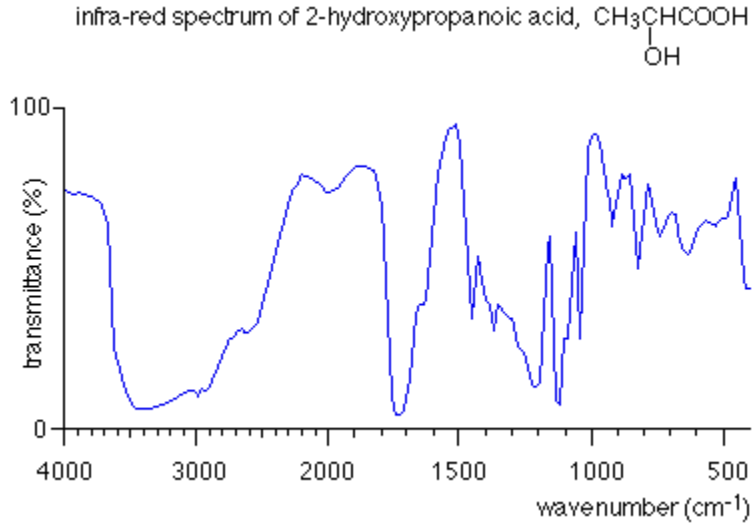
The infrared spectrum for a ketone: Propanone



You will find that this is very similar to the infra-red spectrum for ethyl ethanoate, an ester. Again, there is no trough due to the O-H bond, and again there is a marked absorption at about 1700 cm^{-1} due to the C=O.

Confusingly, there are also absorptions which look as if they might be due to C-O single bonds - which, of course, aren't present in propanone. This reinforces the care you have to take in trying to identify any absorptions in the fingerprint region. Aldehydes will have similar infra-red spectra to ketones.

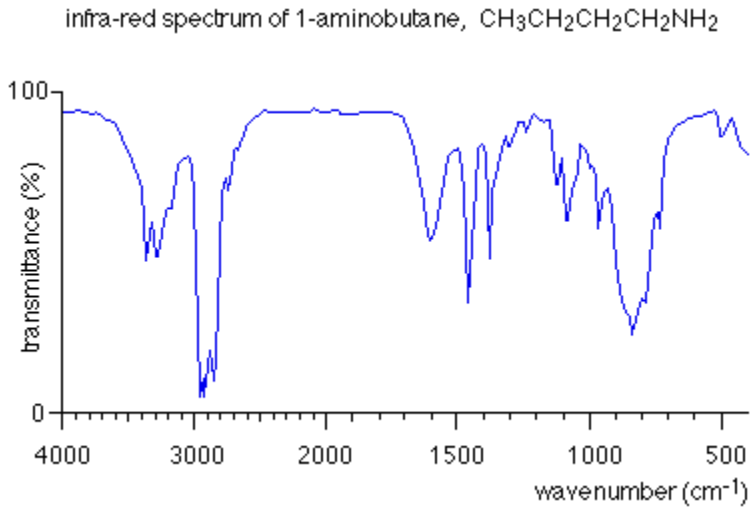
The infrared spectrum for a hydroxy-acid: 2-hydroxypropanoic acid (lactic acid)



This is interesting because it contains two different sorts of O-H bond - the one in the acid and the simple "alcohol" type in the chain attached to the -COOH group.

The O-H bond in the acid group absorbs between 2500 and 3300, the one in the chain between 3230 and 3550 cm^{-1}. Taken together, that gives this immense trough covering the whole range from 2500 to 3550 cm^{-1}. Lost in that trough as well will be absorptions due to the C-H bonds. Notice also the presence of the strong C=O absorption at about 1730 cm^{-1}.

The infrared spectrum for a primary amine: 1-aminobutane



Primary amines contain the $-NH_2$ group, and so have N-H bonds. These absorb somewhere between 3100 and 3500 cm^{-1}. That double trough (typical of primary amines) can be seen clearly on the spectrum to the left of the C-H absorptions.

Contributors and Attributions

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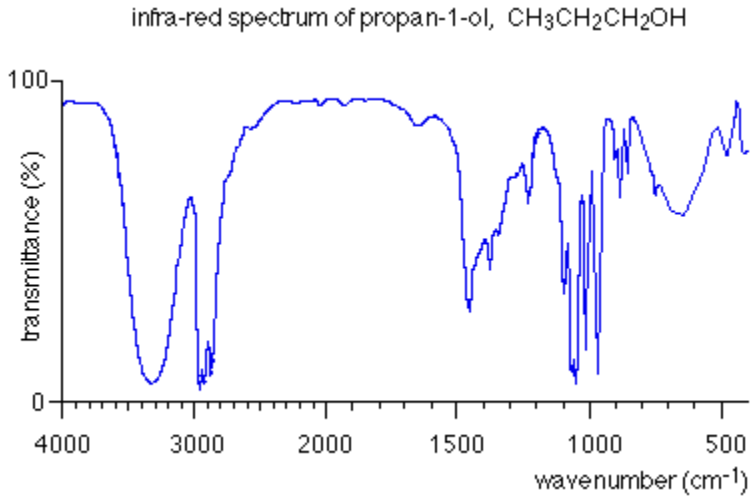
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5.6: The Fingerprint Region

This page explains what the fingerprint region of an infra-red spectrum is, and how it can be used to identify an organic molecule.

What is the fingerprint region

This is a typical infra-red spectrum:



Each trough is caused because energy is being absorbed from that particular frequency of infra-red radiation to excite bonds in the molecule to a higher state of vibration - either stretching or bending. Some of the troughs are easily used to identify particular bonds in a molecule. For example, the big trough at the left-hand side of the spectrum is used to identify the presence of an oxygen-hydrogen bond in an -OH group.

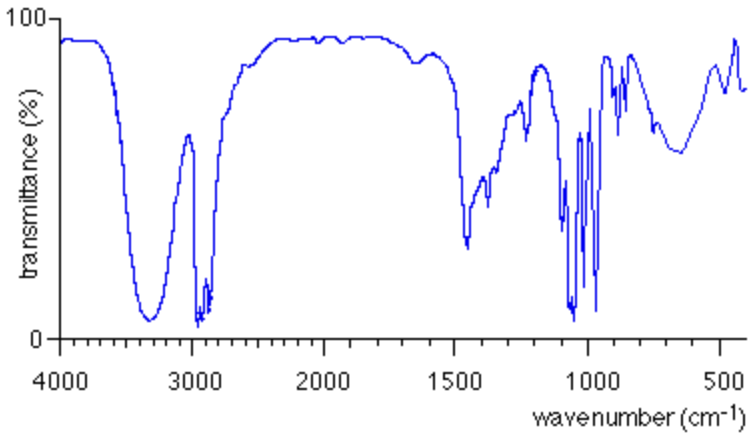
The region to the right-hand side of the diagram (from about 1500 to 500 cm-1) usually contains a very complicated series of absorptions. These are mainly due to all manner of bending vibrations within the molecule. This is called the **fingerprint region**.

It is much more difficult to pick out individual bonds in this region than it is in the "cleaner" region at higher wavenumbers. The importance of the fingerprint region is that each different compound produces a different pattern of troughs in this part of the spectrum.

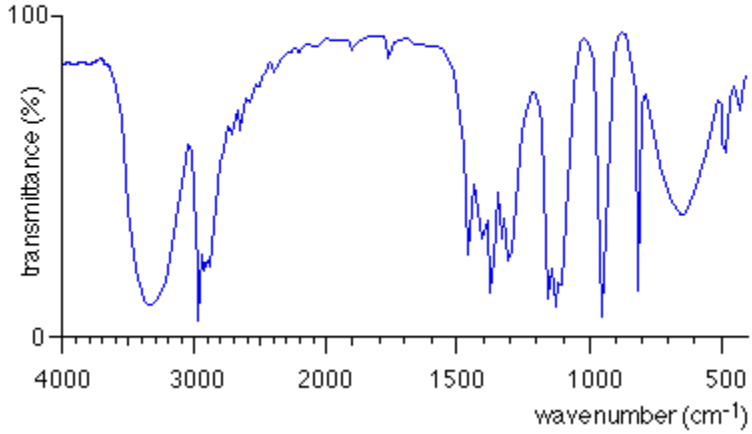
Using the fingerprint region

Compare the infra-red spectra of propan-1-ol and propan-2-ol. Both compounds contain exactly the same bonds. Both compounds have very similar troughs in the area around 3000 cm-1 - but compare them in the fingerprint region between 1500 and 500 cm-1.

infra-red spectrum of propan-1-ol, $CH_3CH_2CH_2OH$



infra-red spectrum of propan-2-ol, CH_3CHCH_3 (OH)



The pattern in the fingerprint region is completely different and could therefore be used to identify the compound. To positively identify an unknown compound, use its infra-red spectrum to identify what sort of compound it is by looking for specific bond absorptions. That might tell you, for example, that you had an alcohol because it contained an -OH group. You would then compare the fingerprint region of its infra-red spectrum with known spectra measured under exactly the same conditions to find out which alcohol (or whatever) you had.

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6: STATES OF MATTER AND INTERMOLECULAR FORCES

6.1: Overview of States of Matter

6.2: Intermolecular forces

6.3: Vapor Pressure

6.4: Solubility

6.5: Unique Properties of Liquids

6.6: Crystalline and Amorphous Solids

6.7: The Solid State of Matter

6.8: Gaseous Elements and Compounds

6.9: Gas Pressure

6.10: The Ideal Gas Law

6.11: Gas Mixtures

6.12: Kinetic Theory of Gases

6.13: Real Gases

6.14: Overview of Chromatography

6.15: General Separation Theory

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6.1: Overview of States of Matter

Learning Objectives

- Define *phase*.
- Identify the types of interactions between molecules.

A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the ***solid*** *phase*, in which individual particles can be thought of as in contact and held in place; the ***liquid*** *phase*, in which individual particles are in contact but moving with respect to each other; and the ***gas*** *phase*, in which individual particles are separated from each other by relatively large distances (see Figure 3.1.1). Not all substances will readily exhibit all phases. For example, carbon dioxide does not exhibit a liquid phase unless the pressure is greater than about six times normal atmospheric pressure. Other substances, especially complex organic molecules, may decompose at higher temperatures, rather than becoming a liquid or a gas.

> For many substances, there are different arrangements the particles can take in the solid phase, depending on temperature and pressure.

Which phase a substance adopts depends on the pressure and the temperature it experiences. Of these two conditions, temperature variations are more obviously related to the phase of a substance. When it is very cold, H_2O exists in the solid form as ice. When it is warmer, the liquid phase of H_2O is present. At even higher temperatures, H_2O boils and becomes steam.

Pressure changes can also affect the presence of a particular phase (as we indicated for carbon dioxide), but its effects are less obvious most of the time. We will mostly focus on the temperature effects on phases, mentioning pressure effects only when they are important. Most chemical substances follow the same pattern of phases when going from a low temperature to a high temperature: the solid phase, then the liquid phase, and then the gas phase. However, the temperatures at which these phases are present differ for all substances and can be rather extreme. Table 6.1.1 shows the temperature ranges for solid, liquid, and gas phases for three substances. As you can see, there is extreme variability in the temperature ranges.

Table 6.1.1: Temperature Ranges for the Three Phases of Various Substances

Substance	Solid Phase Below	Liquid Phase Above	Gas Phase Above
hydrogen (H_2)	−259°C	−259°C	−253°C
water (H_2O)	0°C	0°C	100°C
sodium chloride (NaCl)	801°C	801°C	1413°C
The *melting point* of a substance is the temperature that separates a solid and a liquid. The *boiling point* of a substance is the temperature that separates a liquid and a gas.			

What accounts for this variability? Why do some substances become liquids at very low temperatures, while others require very high temperatures before they become liquids? It all depends on the strength of the **intermolecular forces (IMF)** between the **particles** of substances and the **kinetic energies** (KE) of its molecules. (Although ionic compounds are not composed of discrete molecules, we will still use the term *intermolecular* to include interactions between the ions in such compounds.) Substances that experience **strong intermolecular interactions** require **higher temperatures to become liquids and, finally, gases.** Substances that experience **weak intermolecular interactions** do not need much energy (as measured by temperature) to become liquids and gases and will exhibit these phases at **lower temperatures.**

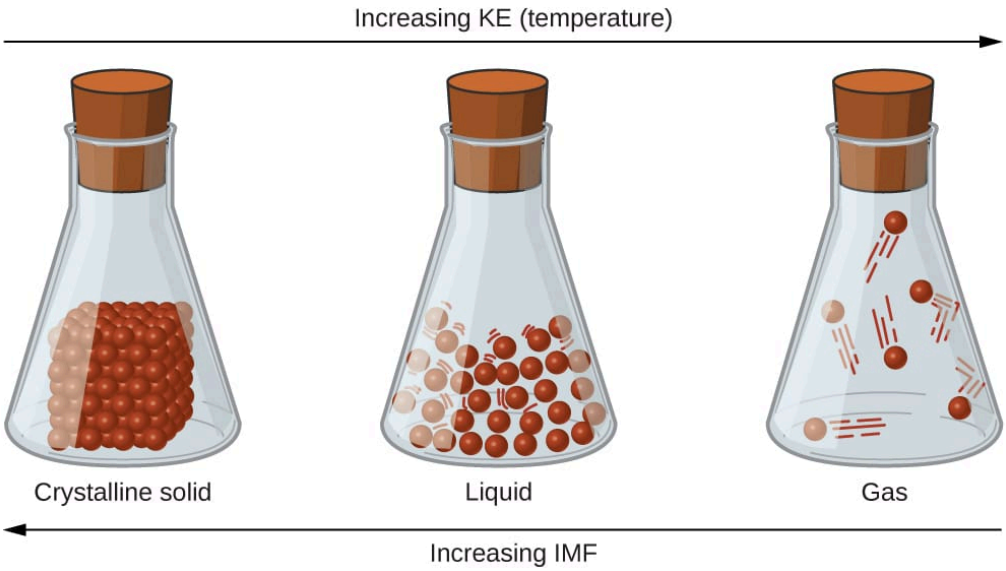


Figure 6.1.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

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6.2: Intermolecular forces

Learning Objectives

- To describe intermolecular forces.

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*.

Note the Pattern

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 three intermolecular interactions that will be studied here are *dipole–dipole interactions*, *London dispersion forces*, and *hydrogen bonds*. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Recall that 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 part (a) in Figure 11.2.1 . These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (part (c) in Figure 11.2.1). Hence dipole–dipole interactions. A kind of intermolecular interaction (force) that results between molecules with net dipole moments., such as those in part (b) in Figure 11.2.1 , are *attractive intermolecular interactions*, whereas those in part (d) in Figure 11.2.1 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 11.2.2 . On average, however, the attractive interactions dominate.

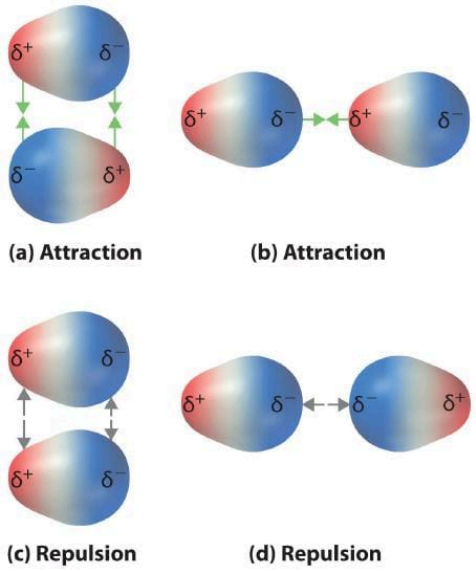


Figure 11.2.1 Attractive and Repulsive Dipole–Dipole Interactions (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

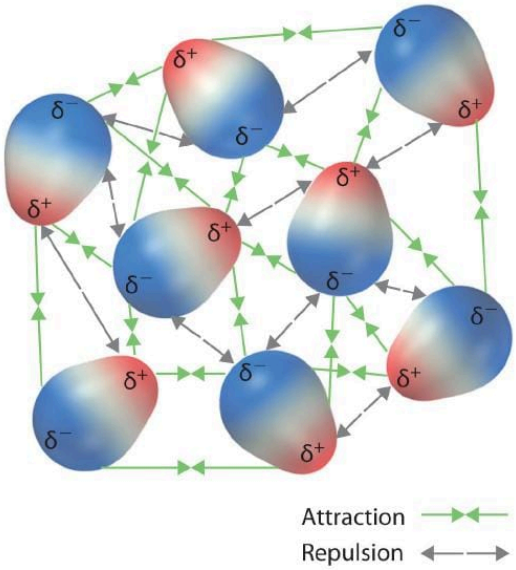


Figure 11.2.2 Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

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 we considered in Chapter 4 . 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 $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6, or 64-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, whereas 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 11.2.1 . Using what we learned in Chapter 5 about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

Table 11.2.1 Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

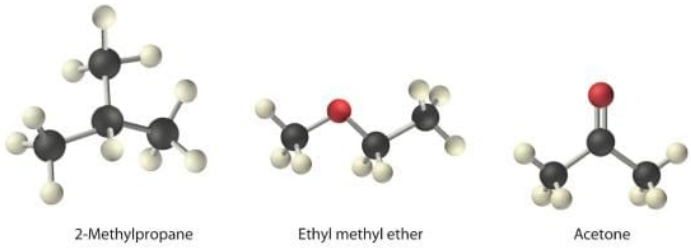
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

Note the Pattern

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

Example 11.2.1

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:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the polarities of the compounds. Compounds with greater dipole moments have the highest boiling points.

Solution:

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

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, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and 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 11.2.2)

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. The short-lived dipole moment in atoms and nonpolar molecules caused by the constant motion of their electrons, which results in an asymmetrical distribution of charge at any given instant and thus produces attractive forces called London dispersion forces. London dispersion forces are a kind of intermolecular interaction (force) that results from temporary fluctuations in the electron distribution within atoms and nonpolar molecules, and even occur between otherwise nonpolar substances.

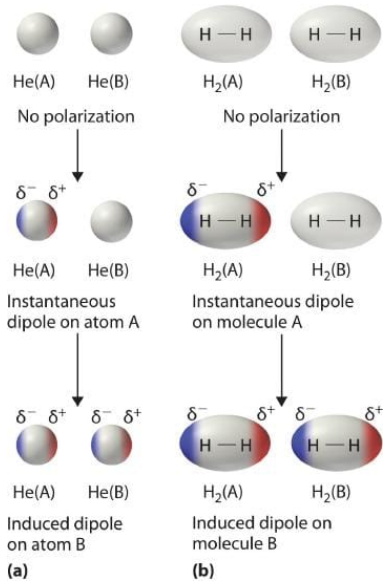


Figure 11.2.3 Instantaneous Dipole Moments The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Table 11.2.2 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 11.2.3, 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. A short-lived dipole moment that is created in atoms and nonpolar molecules adjacent to atoms or molecules with an instantaneous dipole moment., 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.

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 11.2.3 tends to become more pronounced as atomic and molecular masses increase (Table 11.2.2). 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 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 (the ease of deformation of the electron distribution in an atom or molecule). 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.

Note the Pattern

For similar substances, London dispersion forces get stronger with increasing molecular size.

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 11.2.4). 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 11.2.4 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).

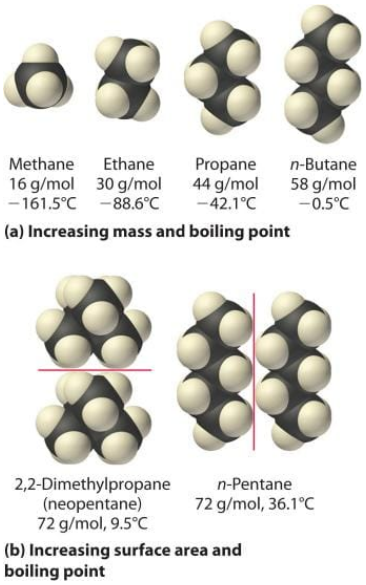


Figure 11.2.4 Mass and Surface Area Affect the Strength of London Dispersion Forces (a) In this series of four simple

alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently 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.

Example 11.2.2

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

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 11.2.5 . 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.

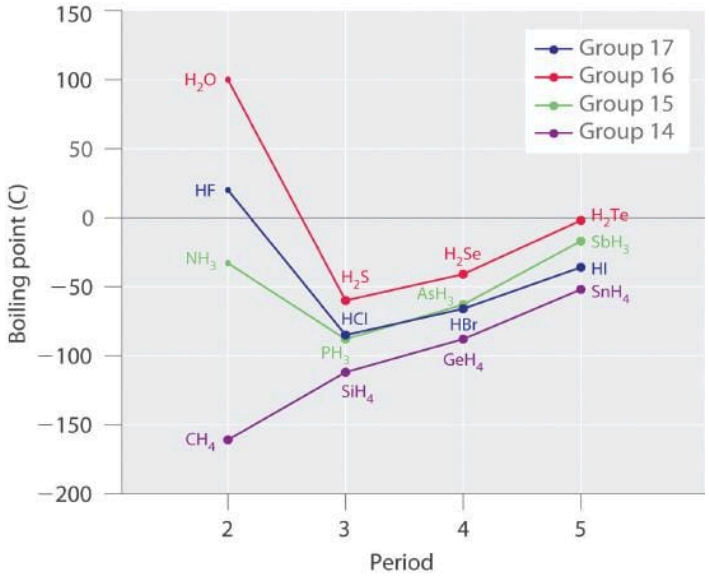


Figure 11.2.5 The Effects of Hydrogen Bonding on Boiling Points These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

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. An unusually strong dipole-dipole interaction (intermolecular force) that results when hydrogen is bonded to very electronegative elements, such as O, N, and F., as shown for ice in Figure 11.2.6 . 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.

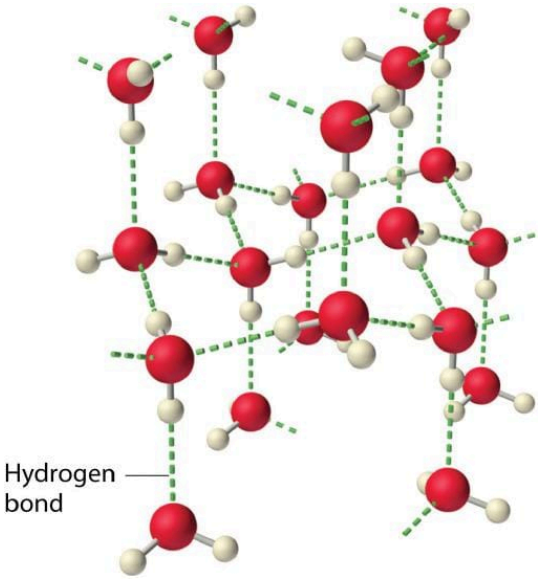


Figure 11.2.6 The Hydrogen-Bonded Structure of Ice Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

Note the Pattern

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" (we will discuss how antifreeze works in Chapter 13) and why unprotected pipes in houses break if they are allowed to freeze.

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 11.2.3

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:

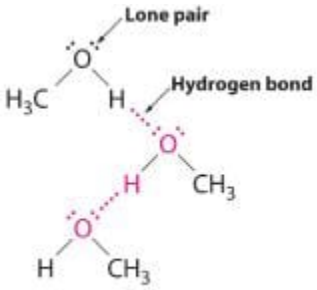
A Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

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:

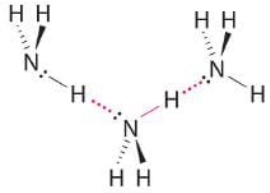


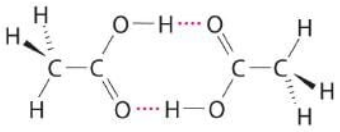
Hydrogen bonding in methanol

Exercise

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

Example 11.2.4

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: He (−269°C) < Ar (−185.7°C) < N_2O (−88.5°C) < C_{60} (>280°C) < NaCl (1465°C).

Exercise

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)

Summary

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 $1/r^6$, 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. Like dipole–dipole interactions, 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, cagelike structure that is less dense than liquid water.

Key Takeaways

- Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds.

Contributors and Attributions

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

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6.3: Vapor Pressure

Learning Objectives

- To know how and why the vapor pressure of a liquid varies with temperature.

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 pressureThe pressure created over a liquid by the molecules of a liquid substance that have enough kinetic energy to escape to the vapor phase. 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 11.4.1), 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)The physical process by which atoms or molecules in the liquid phase enter the gas or vapor phase., where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

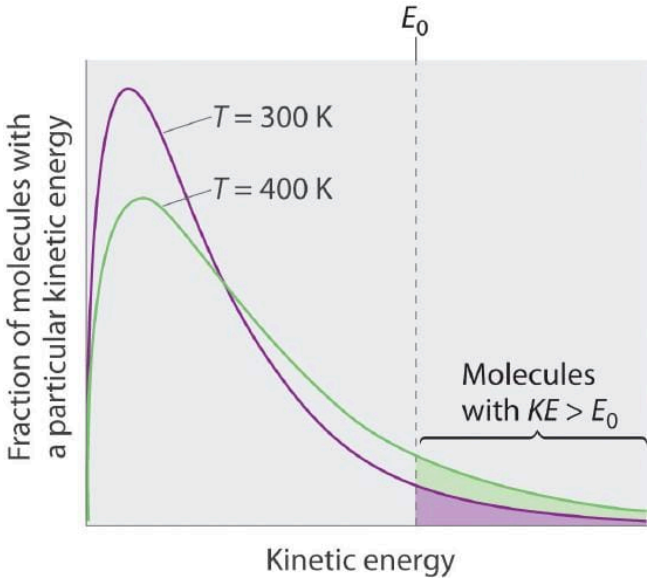


Figure 11.4.1 The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 11.4.2 . When a liquid is introduced into an evacuated chamber (part (a) in Figure 11.4.2), 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.

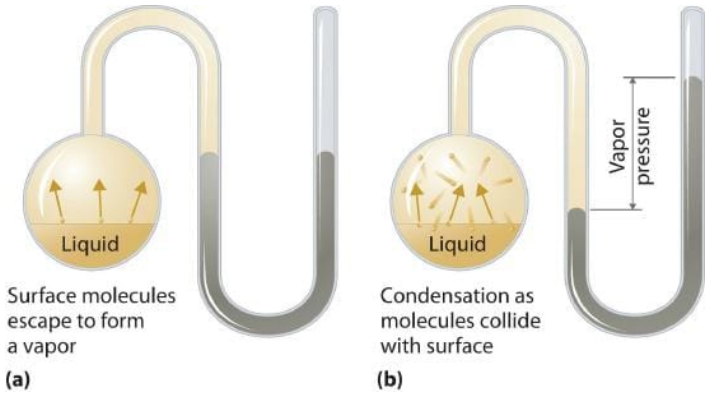


Figure 11.4.2 Vapor Pressure (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant.

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 condensationThe physical process by which atoms or molecules in the vapor phase enter the liquid phase. (part (b) in Figure 11.4.2). 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 11.4.3 .

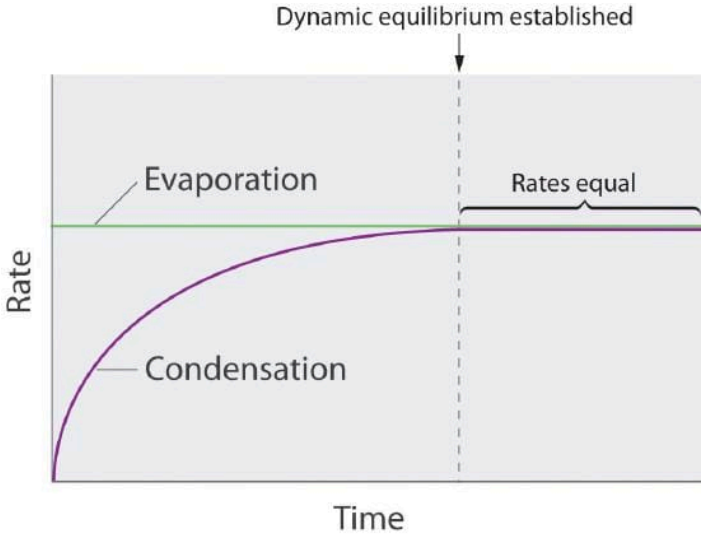


Figure 11.4.3 The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation.

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 equilibriumA state in which two opposing processes occur at the same rate, thus producing no net change in the system.. 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 pressureThe pressure exerted by a vapor in dynamic equilibrium with its liquid. 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 liquidsA liquid with a relatively high vapor pressure. have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquidsA liquid with a relatively low vapor pressure. 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 (Table 11.3.1) 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.

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 (Table 11.3.1). 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 10.4.4 . 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.

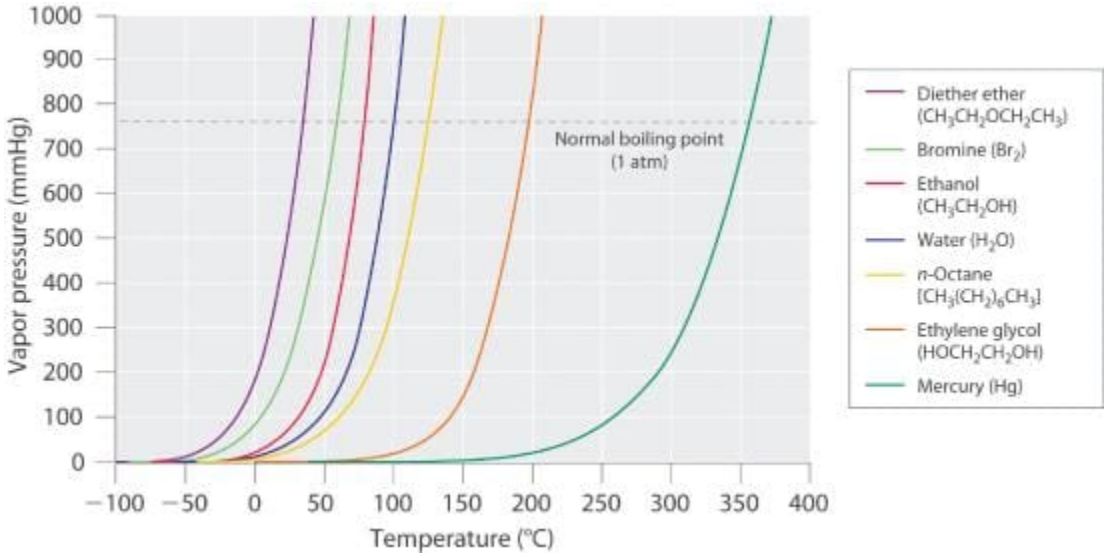


Figure 11.4.4 The Vapor Pressures of Several Liquids as a Function of Temperature The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid.

Note the Pattern

Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.

The exponential rise in vapor pressure with increasing temperature in Figure 11.4.4 allows us to use natural logarithms to express the nonlinear relationship as a linear one.For a review of natural logarithms, refer to Essential Skills 6 in Section 11.9 .

$$ln\,(P) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \tag{11.4.1}$$

where ln *P* is the natural logarithm of the vapor pressure, **Δ*H*vap** is the **enthalpy of vaporization**, *R* is the universal gas constant [8.314 J/(mol·K)], *T* is the temperature in Kelvin, and *C* is the *y*-intercept, which is a constant for any given liquid. A plot of ln *P* versus the inverse of the absolute temperature (1/*T*) is a straight line with a slope of −Δ*H*vap/*R*. Equation 11.4.1, called the Clausius–Clapeyron equationA linear relationship that expresses the nonlinear relationship between the vapor pressure of a liquid and temperature: P is the pressure, **Δ*H*vap,** R is the gas constant, T is the absolute temperature, and C is a constant. The Clausius–Clapeyron equation can be used to calculate the heat of vaporization of a liquid from its measured vapor pressure at two or more temperatures., can be used to calculate the Δ*H*vap of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine Δ*H*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 11.4.2, which is derived from the Clausius–Clapeyron equation:

$$ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{11.4.2}$$

Conversely, if we know Δ*H*vap and the vapor pressure P_1 at any temperature T_1, we can use Equation 10.4.2 to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example 6.

Example 11.4.1

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

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 (Δ*H*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: Δ*H*vap of mercury and vapor pressure at 160°C

Strategy:

A. Use Equation 11.4.2 to obtain Δ*H*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 Δ*H*vap into Equation 11.4.2 to 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 11.4.1 and find the value of Δ*H*vap from the slope of the line, an alternative approach is to use Equation 11.4.2 to obtain Δ*H*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 kelvins because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 11.4.2 gives

$$ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot K}\left(\frac{1}{(120+273)\ K} - \frac{1}{(80.0+273)\ K}\right) \tag{6.3.1}$$

$$ln\,(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot \cancel{K}}\left(-2.88 \times 10^{-4}\ \cancel{K^{-1}}\right) \tag{6.3.2}$$

$$2.13 = -\Delta H_{vap}\left(-3.46 \times 10^{-4}\right) J^{-1} \cdot mol \tag{6.3.3}$$

$$\Delta H_{vap} = 61,400\ J/mol = 61.4\ kJ/mol \tag{6.3.4}$$

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):

$$ln\left(\frac{P_2}{0.0888\ torr}\right) = \frac{-61,400\ \cancel{J/mol}}{8.314\ \cancel{J/mol}\ K^{-1}}\left(\frac{1}{(160+273)\ K} - \frac{1}{(80.0+273)\ K}\right) \tag{6.3.5}$$

Using the relationship $e^{\ln x} = x$, we have

$$ln\left(\frac{P_2}{0.0888\ Torr}\right) = 3.86 \tag{6.3.6}$$

$$\frac{P_2}{0.0888\ Torr} = e^{3.86} = 47.5 \tag{6.3.7}$$

$$P_2 = 4.21 Torr \tag{6.3.8}$$

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

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. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure 11.4.4 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.

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 11.4.1 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.

Note the Pattern

As pressure increases, the boiling point of a liquid increases and vice versa.

Table 11.4.1 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

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	–1312	799	101.4

Example 11.4.2

Use Figure 11.4.4 to estimate the following.

1. the boiling point of water in a pressure cooker operating at 1000 mmHg
2. the pressure required for mercury to boil at 250°C

Given: data in Figure 11.4.4 , 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 10.4.4 and 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:

1. **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.
2. **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

Use the data in Figure 10.4.4 to estimate the following.

1. the normal boiling point of ethylene glycol
2. the pressure required for diethyl ether to boil at 20°C.

Answer

1. 200°C
2. 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**.

Key Takeaways

- The equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- The relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Key Equations

Clausius–Clapeyron equation

$$ln\,(P) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \tag{11.4.1}$$

Using vapor pressure at two temperatures to calculate ΔH_{vap}

$$ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{11.4.2}$$

Contributors and Attributions

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6.4: Solubility

Learning Objectives

- Describe the effects of temperature and pressure on solubility
- State Henry's law and use it in calculations involving the solubility of a gas in a liquid
- Explain the degrees of solubility possible for liquid-liquid solutions

Imagine adding a small amount of salt to a glass of water, stirring until all the salt has dissolved, and then adding a bit more. You can repeat this process until the salt concentration of the solution reaches its natural limit, a limit determined primarily by the relative strengths of the solute-solute, solute-solvent, and solvent-solvent attractive forces discussed in the previous two modules of this chapter. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved salt remains. The concentration of salt in the solution at this point is known as its solubility.

The solubility of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is at equilibrium. Referring to the example of salt in water:

$$\mathrm{NaCl}(s) \rightleftharpoons \mathrm{Na}^{+}(aq) + \mathrm{Cl}^{-}(aq) \tag{6.4.1}$$

When a solute's concentration is equal to its solubility, the solution is said to be saturated with that solute. If the solute's concentration is less than its solubility, the solution is said to be unsaturated. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.

If we add more salt to a saturated solution of salt, we see it fall to the bottom and no more seems to dissolve. In fact, the added salt does dissolve, as represented by the forward direction of the dissolution equation. Accompanying this process, dissolved salt will precipitate, as depicted by the reverse direction of the equation. The system is said to be at equilibrium when these two reciprocal processes are occurring at equal rates, and so the amount of undissolved and dissolved salt remains constant. Support for the simultaneous occurrence of the dissolution and precipitation processes is provided by noting that the number and sizes of the undissolved salt crystals will change over time, though their combined mass will remain the same.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 6.4.1: Watch this impressive video showing the precipitation of sodium acetate from a supersaturated solution.

Solutions may be prepared in which a solute concentration exceeds its solubility. Such solutions are said to be supersaturated, and they are interesting examples of nonequilibrium states. For example, the carbonated beverage in an open container that has not yet "gone flat" is supersaturated with carbon dioxide gas; given time, the CO_2 concentration will decrease until it reaches its equilibrium value.

Solutions of Gases in Liquids

In an earlier module of this chapter, the effect of intermolecular attractive forces on solution formation was discussed. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical

structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14}, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure 6.4.1). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

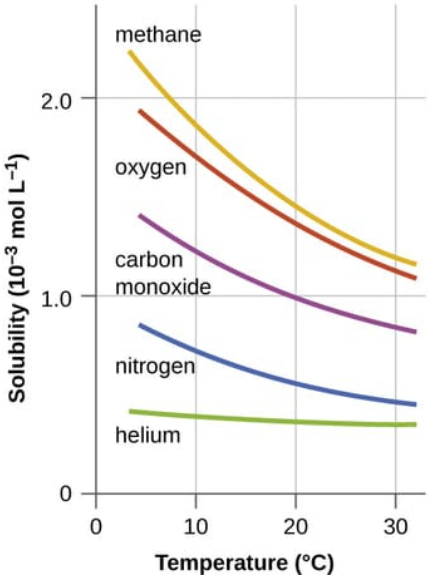


Figure 6.4.1: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure 6.4.2).



Figure 6.4.2: (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure 6.4.3). At this point, the beverage is supersaturated with carbon dioxide and, with

time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become “flat.”

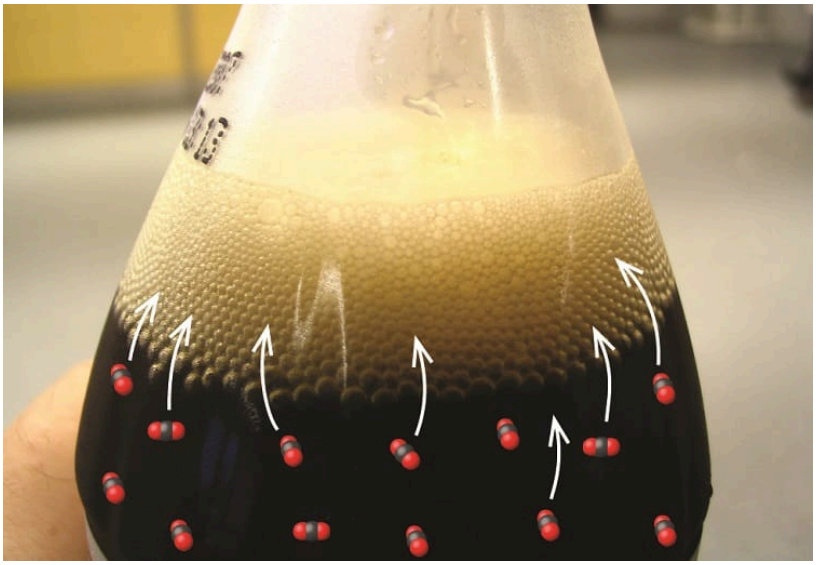


Figure 6.4.3: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

A dark brown liquid is shown in a clear, colorless container. A thick layer of beige bubbles appear at the surface of the liquid. In the liquid, thirteen small clusters of single black spheres with two red spheres attached to the left and right are shown. Red spheres represent oxygen atoms and black represent carbon atoms. Seven white arrows point upward in the container from these clusters to the bubble layer at the top of the liquid.

For many gaseous solutes, the relation between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_{\mathrm{g}} = kP_{\mathrm{g}}$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry’s law: The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.

Example 6.4.1: Application of Henry’s Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is 1.38×10^{-3} mol L^{-1}. Use Henry’s law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth’s atmosphere.

Solution

According to Henry’s law, for an ideal solution the solubility, C_g, of a gas (1.38×10^{-3} mol L^{-1}, in this case) is directly proportional to the pressure, P_g, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both C_g and P_g, we can rearrange this expression to solve for k.

$$\begin{aligned} C_{\mathrm{g}} &= kP_{\mathrm{g}} \\ k &= \frac{C_{\mathrm{g}}}{P_{\mathrm{g}}} \\ &= \frac{1.38 \times 10^{-3}\ \mathrm{mol\ L^{-1}}}{101.3\ \mathrm{kPa}} \\ &= 1.36 \times 10^{-5}\ \mathrm{mol\ L^{-1}\ kPa^{-1}} \\ &\quad (1.82 \times 10^{-6}\ \mathrm{mol\ L^{-1}\ torr^{-1}}) \end{aligned}$$

Now we can use k to find the solubility at the lower pressure.

$$C_g = kP_g$$

$$1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa}$$
$$(\text{or } 1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1} \times 155\ \text{torr})$$
$$= 2.82 \times 10^{-4}\ \text{mol L}^{-1}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Exercise 6.4.1

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Answer available at the end of this section.

Case Study: Decompression Sickness ("The Bends")

Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.



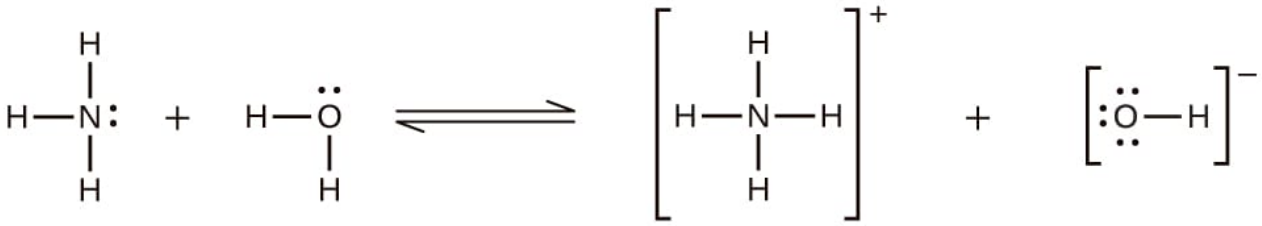
Figure 6.4.4: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

Two photos are shown. The first shows two people seated in a steel chamber on benches that run length of the chamber on each side. The chamber has a couple of small circular windows and an open hatch-type door. One of the two people is giving a thumbs up gesture. The second image provides a view through a small, circular window. Inside the two people can be seen with masks over their mouths and noses. The people appear to be reading.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at

relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 6.4.4).

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form **supersaturated solutions**. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos (Figure 6.4.5), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO_2 were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.



(a) (b)

Figure 6.4.5: (a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)

Two photos are shown. The first is an aerial view of a lake surrounded by green hills. The second shows a large body of water with a fountain sending liquid up into the air several yards or meters above the surface of the water.

Solutions of Liquids in Liquids

We know that some liquids mix with each other in all proportions; in other words, they have infinite mutual solubility and are said to be miscible. Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in Figure 6.4.6) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline.



Figure 6.4.6: Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: “dno1967”/Wikimedia commons)

Liquids that mix with water in all proportions are usually polar substances or substances that form hydrogen bonds. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom “like dissolves like.”

Two liquids that do not mix to an appreciable extent are called immiscible. Layers are formed when we pour immiscible liquids into the same container. Gasoline, oil (Figure 6.4.7), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. The attraction between the molecules of such nonpolar liquids and polar water molecules is ineffectively weak. The only strong attractions in such a mixture are between the water molecules, so they effectively squeeze out the molecules of the nonpolar liquid. The distinction between immiscibility and miscibility is really one of degrees, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.



Figure 6.4.7: Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: “Yortw”/Flickr)

This is a photo of a clear, colorless martini glass containing a golden colored liquid layer resting on top of a clear, colorless liquid.

Two liquids, such as bromine and water, that are of moderate mutual solubility are said to be partially miscible. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer (Figure 6.4.8).



Figure 6.4.8: Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers)

This figure shows three test tubes. The first test tube holds a dark orange-brown substance. The second test tube holds a clear substance. The amount of substance in both test tubes is the same. The third test tube holds a dark orange-brown substance on the bottom with a lighter orange substance on top. The amount of substance in the third test tube is almost double of the first two.

Solutions of Solids in Liquids

The dependence of solubility on temperature for a number of inorganic solids in water is shown by the solubility curves in Figure 6.4.9. Reviewing these data indicate a general trend of increasing solubility with temperature, although there are exceptions, as illustrated by the ionic compound cerium sulfate.

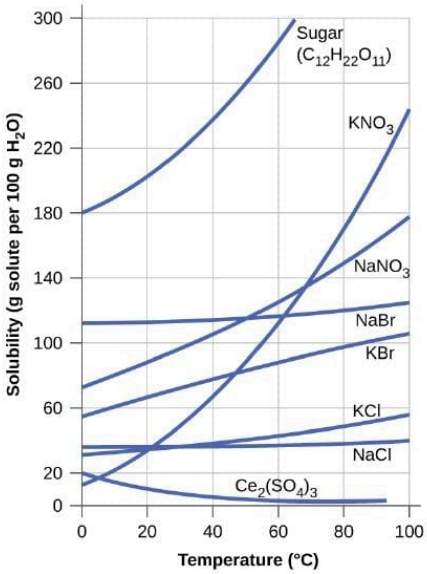


Figure 6.4.9: This graph shows how the solubility of several solids changes with temperature.

This shows a graph of the solubility of sugar C subscript 12 H subscript 22 O subscript 11, K N O subscript 3, N a N O subscript 3, N a B r, K B r, N a subscript 2 S O subscript 4, K C l, and C e subscript 2 left parenthesis S O subscript 4 right parenthesis subscript 3 in g solute per 100 g H subscript 2 O at temperatures ranging from 0 degrees Celsius to 100 degrees Celsius. At 0 degrees Celsius, solubilities are approximately 180 for sugar C subscript 12 H subscript 22 O subscript 11, 115 for K N O subscript 3, 75 for N a N O subscript 3, 115 for N a B r, 55 for K B r, 7 for N a subscript 2 S O subscript 4, 25 for K C l, and 20 for C e subscript 2 left parenthesis S O subscript 4 right parenthesis subscript 3. At 0 degrees Celsius, solubilities are approximately 180 for sugar C subscript 12 H subscript 22 O subscript 11, 115 for K N O subscript 3, 75 for N a N O subscript 3, 115 for N a B r, 55 for K B r, 7 for N a subscript 2 S O subscript 4, 25 for K C l, and 20 for C e subscript 2 left parenthesis S O subscript 4 right parenthesis subscript 3. At 100 degrees Celsius, sugar C subscript 12 H subscript 22 O subscript 11 has exceeded the upper limit of solubility indicated on the graph, 240 for K N O subscript 3, 178 for N a N O subscript 3, 123 for N a B r, 105 for K B r, 52 for N a subscript 2 S O subscript 4, 58 for K C l, and the graph for C e subscript 2 left parenthesis S O subscript 4 right parenthesis subscript 3 stops at about 92 degrees Celsius where the solubility is nearly zero. The graph for N a subscript 2 S O subscript 4 is shown in red. All others substances are shown in blue. The solubility of this substance increases until about 30 degrees Celsius and declines beyond that point with increasing temperature.

The temperature dependence of solubility can be exploited to prepare supersaturated solutions of certain compounds. A solution may be saturated with the compound at an elevated temperature (where the solute is more soluble) and subsequently cooled to a lower temperature without precipitating the solute. The resultant solution contains solute at a concentration greater than its equilibrium solubility at the lower temperature (i.e., it is supersaturated) and is relatively stable. Precipitation of the excess solute can be initiated by adding a seed crystal (see the video in the Link to Learning earlier in this module) or by mechanically agitating the solution. Some hand warmers, such as the one pictured in Figure 6.4.10, take advantage of this behavior.



Figure 6.4.10: This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is “clicked.” (credit: modification of work by “Velela”/Wikimedia Commons)

Three photos of hand warmers are shown side by side with an arrow pointing from the first photo to the second, and another arrow pointing from the second photo to the third. The first packet contains a clear colorless liquid and a small metal disc can be seen. In the second packet, the disc can’t be seen and a dispersion of white liquid is beginning. In the third packet, all of the liquid is white.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 6.4.2: This video shows the crystallization process occurring in a hand warmer.

Summary

The extent to which one substance will dissolve in another is determined by several factors, including the types and relative strengths of intermolecular attractive forces that may exist between the substances' atoms, ions, or molecules. This tendency to dissolve is quantified as substance's solubility, its maximum concentration in a solution at equilibrium under specified conditions. A saturated solution contains solute at a concentration equal to its solubility. A supersaturated solution is one in which a solute's concentration exceeds its solubility—a nonequilibrium (unstable) condition that will result in solute precipitation when the solution is appropriately perturbed. Miscible liquids are soluble in all proportions, and immiscible liquids exhibit very low mutual solubility. Solubilities for gaseous solutes decrease with increasing temperature, while those for most, but not all, solid solutes increase with temperature. The concentration of a gaseous solute in a solution is proportional to the partial pressure of the gas to which the solution is exposed, a relation known as Henry's law.

Key Equations

- $C_{\mathrm{g}} = kP_{\mathrm{g}}$

Glossary

Henry's law
: law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

immiscible
: of negligible mutual solubility; typically refers to liquid substances

miscible
: mutually soluble in all proportions; typically refers to liquid substances

partially miscible
: of moderate mutual solubility; typically refers to liquid substances

saturated
: of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

solubility
: extent to which a solute may be dissolved in water, or any solvent

supersaturated
: of concentration that exceeds solubility; a nonequilibrium state

unsaturated
: of concentration less than solubility

Answers

Exercise 6.4.1

7.25×10^{-3} g in 100.0 mL or 0.0725 g/L

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6.5: Unique Properties of Liquids

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

We stated in Section 11.0 that liquids tend to adopt the shapes of their containers. Why, then, 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.

Figure 11.3.1 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 (see the chapter opener photo). 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.

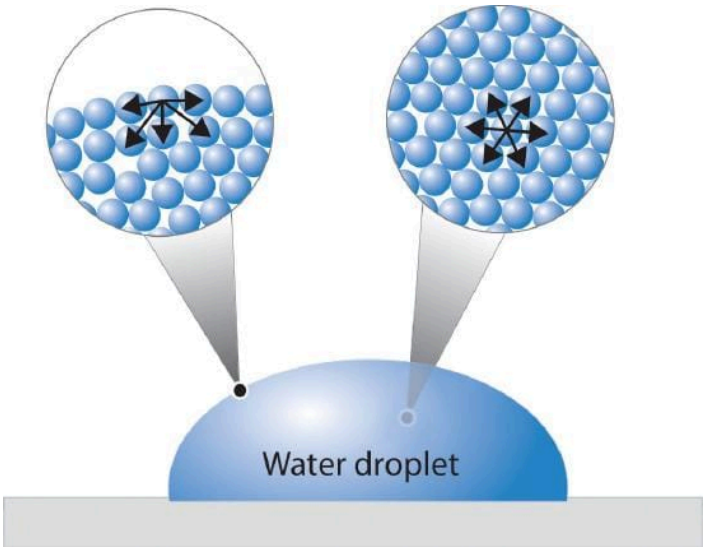


Figure 11.3.1 A Representation of Surface Tension in a Liquid Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces..

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 (part (a) in Figure 11.3.2). Many insects take advantage of this property to walk on the surface of puddles or ponds

without sinking (part (b) in Figure 11.3.2).

Figure 11.3.2 The Effects of the High Surface Tension of Liquid Water (a) A paper clip can "float" on water because of surface tension (from Christopher Rozitis.

(b) Surface tension also allows insects such as this water strider to "walk on water."

Such phenomena are manifestations of surface tensionThe energy required to increase the surface area of a liquid by a certain amount. Surface tension is measured in units of energy per area (e.g., J/m^2)., 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 11.3.1. 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, which we will discuss in more detail in Chapter 12.

Table 11.3.1 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 (Substances [surface-active agents], such as soaps and detergents, that disrupt the attractive intermolecular interactions between molecules of a polar liquid, thereby reducing the surface tension of the liquid). 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 actionThe tendency of a polar liquid to rise against gravity into a

small-diameter glass tube., which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure 11.3.3 . When a glass capillary is put into a dish of water, water is drawn up into the tube. 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 11.3.3 The Phenomenon of Capillary Action When a capillary is placed in liquid ink the ink rises up into the capillary. The smaller the diameter of the capillary, the higher the water rises. The height of the water does *not* depend on the angle at which the capillary is tilted.

Of course, you can see the same phenomina in anything with narrow channels, like bricks

Figure 11.3.4 The Phenomenon of Capillary Action: Water rises through a brick in a time lapse video

Capillary action is the net result of two opposing sets of forces: cohesive forces (the intermolecular forces that hold a liquid together., which are the intermolecular forces that hold a liquid together), and adhesive forces (the attractive intermolecular forces between a liquid and the substance comprising the surface of a capillary), 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 (part (a) in Figure 11.3.5). The upper surface of a liquid in a tube is called the meniscusThe upper surface of the liquid in a tube., 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 (part (b) in Figure 11.3.5).

Note the Pattern

Polar substances are drawn up a glass capillary and generally have a concave meniscus.

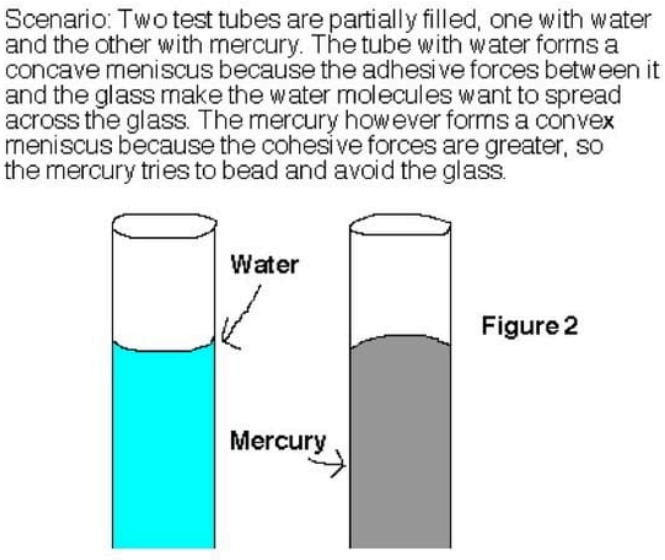
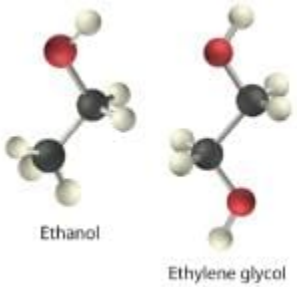


Figure 11.3.5 The Effects of Capillary Action This drawing illustrates the shape of the meniscus and the relative height of a mercury column when a glass capillary is put into liquid mercury. The meniscus is convex and the surface of the liquid inside the tube is *lower* than the level of the liquid outside the tube. Because water adheres strongly to the polar surface of glass, it has a concave meniscus, whereas mercury, which does not adhere to the glass, has a convex 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)The resistance of a liquid to flow. 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 10.3.1 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.

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.

Note the Pattern

Viscosity increases as intermolecular interactions or molecular size increases.

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. 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. 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 11.3.1

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

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 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.

Key Takeaways

- Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions.

Contributors and Attributions

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Video at 11.3.2b by Cambridge University @ YouTube

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6.6: Crystalline and Amorphous Solids

Learning Objectives

- To know the characteristic properties of crystalline and amorphous solids.

With few exceptions, the particles that compose a solid material, whether ionic, molecular, covalent, or metallic, are held in place by strong attractive forces between them. When we discuss solids, therefore, we consider the *positions* of the atoms, molecules, or ions, which are essentially fixed in space, rather than their motions (which are more important in liquids and gases). The constituents of a solid can be arranged in two general ways: they can form a regular repeating three-dimensional structure called a crystal lattice (a regular repeating three-dimensional structure) and thus producing a crystalline solid, or they can aggregate with no particular order, in which case they form an amorphous solid (a solid with no particular structural order; from the Greek *ámorphos*, meaning “shapeless”).

Crystalline solids, or *crystals*, have distinctive internal structures that in turn lead to distinctive flat surfaces, or *faces*. The faces intersect at angles that are characteristic of the substance. When exposed to x-rays, each structure also produces a distinctive pattern that can be used to identify the material (see Section 12.3). The characteristic angles do not depend on the size of the crystal; they reflect the regular repeating arrangement of the component atoms, molecules, or ions in space. When an ionic crystal is cleaved (Figure 12.1.1), for example, repulsive interactions cause it to break along fixed planes to produce new faces that intersect at the same angles as those in the original crystal. In a covalent solid such as a cut diamond, the angles at which the faces meet are also not arbitrary but are determined by the arrangement of the carbon atoms in the crystal.



Crystalline faces. The faces of crystals can intersect at right angles, as in galena (PbS) and pyrite (FeS_2), or at other angles, as in quartz.

Cleavage surfaces of an amorphous solid. Obsidian, a volcanic glass with the same chemical composition as granite (typically $KAlSi_3O_8$), tends to have curved, irregular surfaces when cleaved.



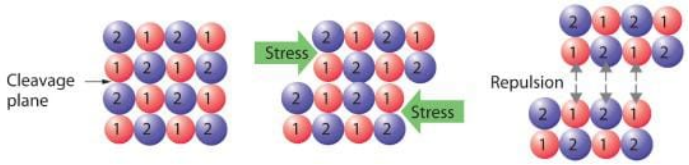
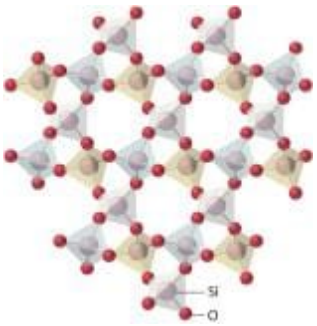


Figure 12.1.1 Cleaving a Crystal of an Ionic Compound along a Plane of Ions Deformation of the ionic crystal causes one plane of atoms to slide along another. The resulting repulsive interactions between ions with like charges cause the layers to separate.

Crystals tend to have relatively sharp, well-defined melting points because all the component atoms, molecules, or ions are the same distance from the same number and type of neighbors; that is, the regularity of the crystalline lattice creates local environments that are the same. Thus the intermolecular forces holding the solid together are uniform, and the same amount of thermal energy is needed to break every interaction simultaneously.

Amorphous solids have two characteristic properties. When cleaved or broken, they produce fragments with irregular, often curved surfaces; and they have poorly defined patterns when exposed to x-rays because their components are not arranged in a regular array. An amorphous, translucent solid is called a glassAn amorphous, translucent solid. A glass is a solid that has been cooled too quickly to form ordered crystals.. Almost any substance can solidify in amorphous form if the liquid phase is cooled rapidly enough. Some solids, however, are intrinsically amorphous, because either their components cannot fit together well enough to form a stable crystalline lattice or they contain impurities that disrupt the lattice. For example, although the chemical composition and the basic structural units of a quartz crystal and quartz glass are the same—both are SiO_2 and both consist of linked SiO_4 tetrahedra—the arrangements of the atoms in space are not. Crystalline quartz contains a highly ordered arrangement of silicon and oxygen atoms, but in quartz glass the atoms are arranged almost randomly. When molten SiO_2 is cooled rapidly (4 K/min), it forms quartz glass, whereas the large, perfect quartz crystals sold in mineral shops have had cooling times of thousands of years. In contrast, aluminum crystallizes much more rapidly. Amorphous aluminum forms only when the liquid is cooled at the extraordinary rate of 4×10^{13} K/s, which prevents the atoms from arranging themselves into a regular array.



The lattice of crystalline quartz (SiO_2). The atoms form a regular arrangement in a structure that consists of linked tetrahedra.

In an amorphous solid, the local environment, including both the distances to neighboring units and the numbers of neighbors, varies throughout the material. Different amounts of thermal energy are needed to overcome these different interactions. Consequently, amorphous solids tend to soften slowly over a wide temperature range rather than having a well-defined melting point like a crystalline solid. If an amorphous solid is maintained at a temperature just below its melting point for long periods of time, the component molecules, atoms, or ions can gradually rearrange into a more highly ordered crystalline form.

Note the Pattern

Crystals have sharp, well-defined melting points; amorphous solids do not.

Summary

Solids are characterized by an extended three-dimensional arrangement of atoms, ions, or molecules in which the components are generally locked into their positions. The components can be arranged in a regular repeating three-dimensional array (a

crystal lattice), which results in a **crystalline solid**, or more or less randomly to produce an **amorphous solid**. Crystalline solids have well-defined edges and faces, diffract x-rays, and tend to have sharp melting points. In contrast, amorphous solids have irregular or curved surfaces, do not give well-resolved x-ray diffraction patterns, and melt over a wide range of temperatures.

Key Takeaway

- Crystalline solids have regular ordered arrays of components held together by uniform intermolecular forces, whereas the components of amorphous solids are not arranged in regular arrays.

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6.7: The Solid State of Matter

Learning Objectives

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

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

When most liquids are cooled, they eventually freeze and form crystalline solids, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called amorphous solids or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged (Figure 10.37).

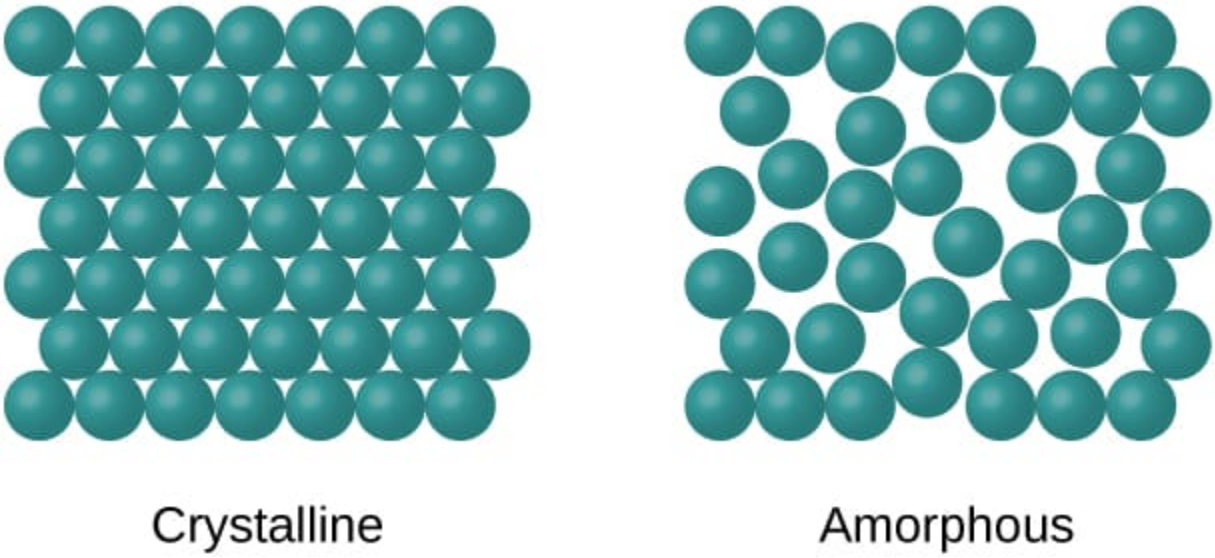


Figure 10.37 The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as silicon dioxide (shown in Figure 10.38), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

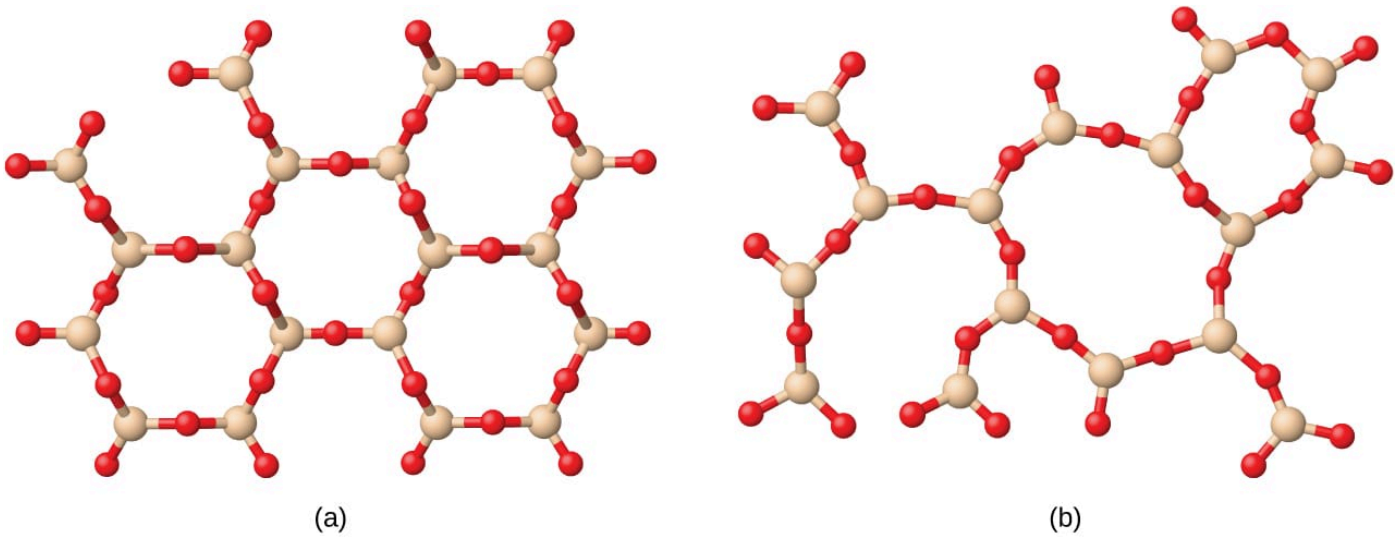


Figure 10.38 (a) Silicon dioxide, SiO_2, is abundant in nature as one of several crystalline forms of the mineral quartz. (b) Rapid cooling of molten SiO_2 yields an amorphous solid known as “fused silica”.

Crystalline solids are generally classified according to the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

Ionic Solids

Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong (Figure 10.39). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.

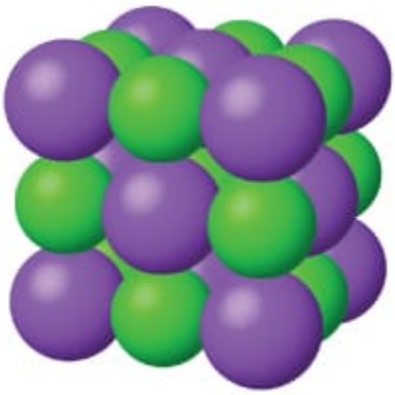


Figure 10.39 Sodium chloride is an ionic solid.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 10.40. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite

strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.

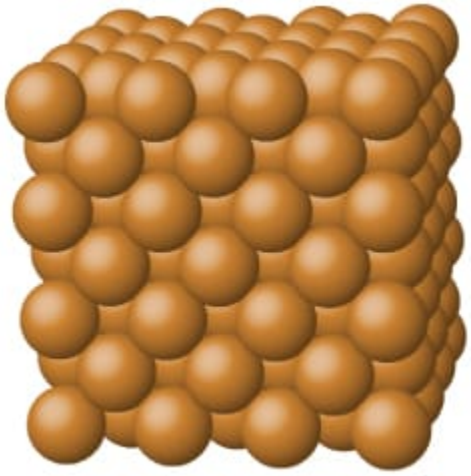


Figure 10.40 Copper is a metallic solid.

Covalent Network Solid

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in Figure 10.41. To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.

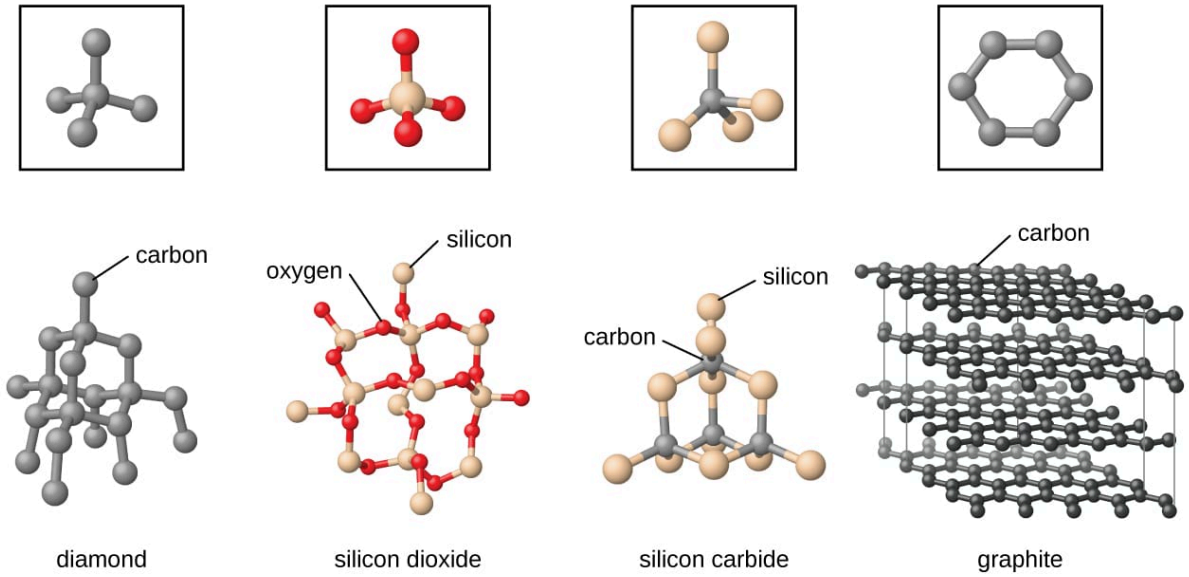


Figure 10.41 A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

Molecular Solid

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure 10.42, are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2, N_2, O_2, and F_2, have weak attractive forces and form molecular solids with very low melting points (below –200 °C). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, 0 °C) and table sugar (melting point, 185 °C).

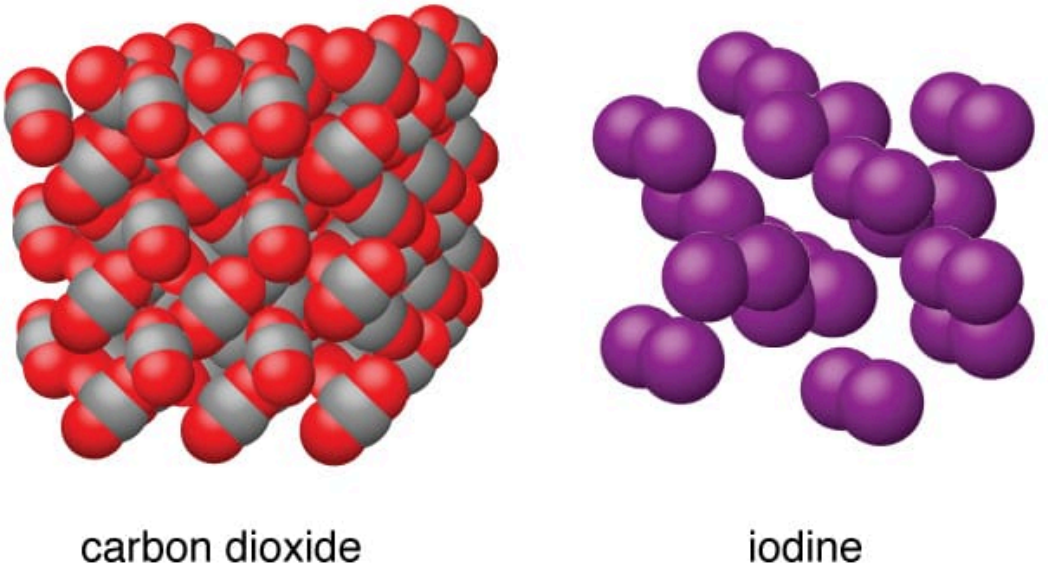


Figure 10.42 Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of –78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

Properties of Solids

A crystalline solid, like those listed in Table 10.4, has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

Table 10.4

How Sciences Interconnect

Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in Figure 10.43. You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.

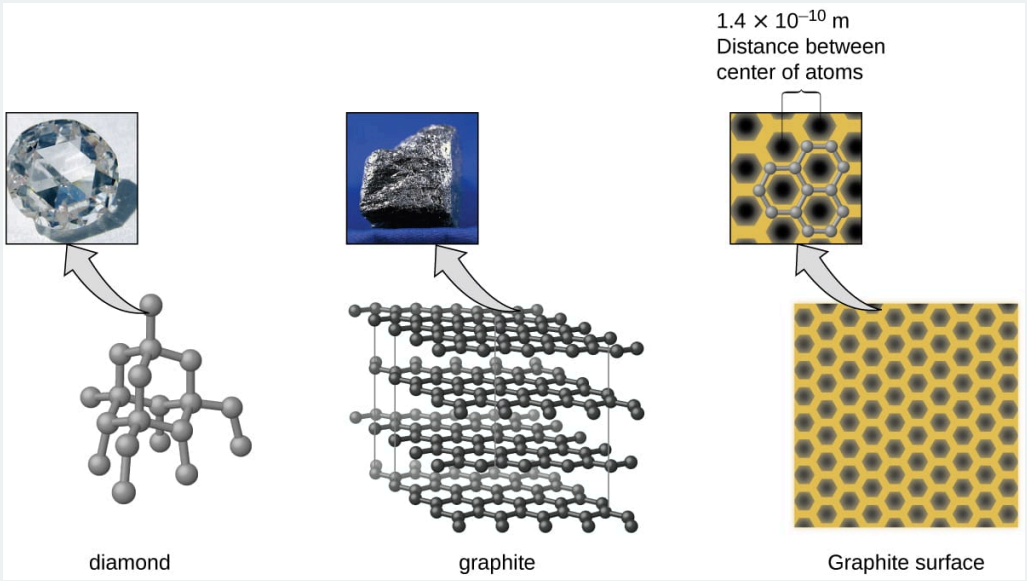


Figure 10.43 Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in Figure 10.44, is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.

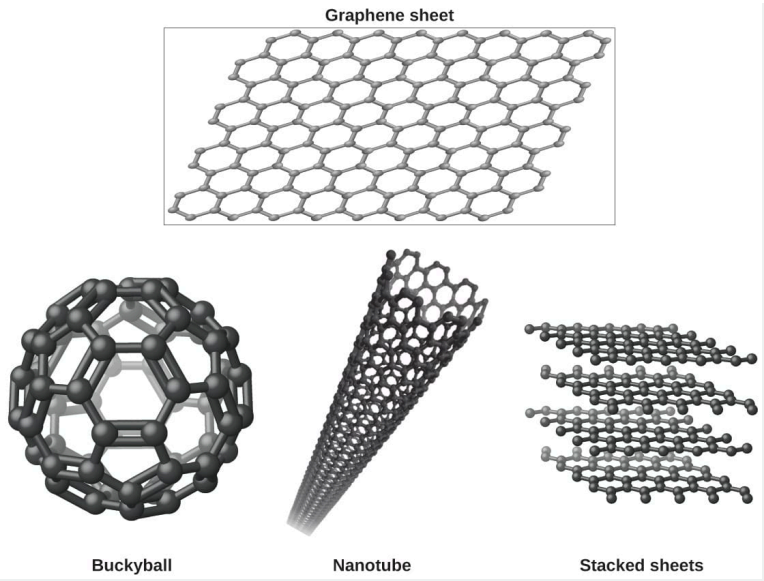


Figure 10.44 Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.

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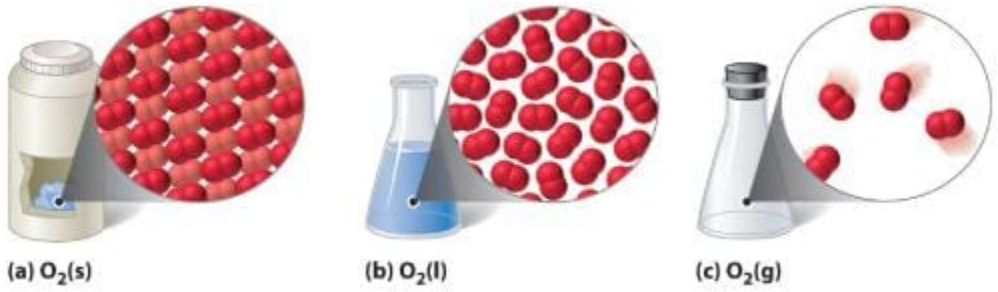
6.8: Gaseous Elements and Compounds

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 10.1.1 compares the three states of matter and illustrates the differences at the molecular level.

Figure 10.1.1 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 vaporThe distinction between a gas and a vapor is subtle: the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions (25°C, 1.0 atm). Nitrogen (N_2) and oxygen (O_2) are thus 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 10.1.1

Table 10.1.1 Properties of Water at 1.0 atm

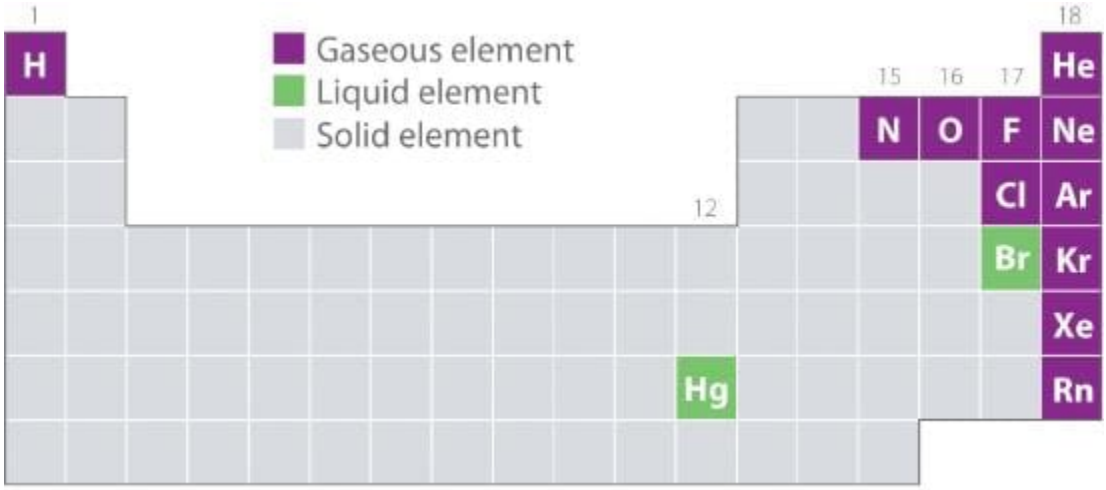
Temperature	State	Density (g/cm^3)
≤0°C	solid (ice)	0.9167 (at 0.0°C)
0°C–100°C	liquid (water)	0.9997 (at 4.0°C)
≥100°C	vapor (steam)	0.005476 (at 127°C)

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 10.1.2 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 10.1.2 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.

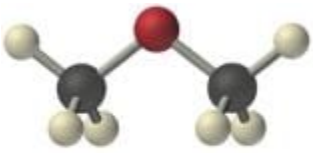
Many of the elements and compounds we have encountered so far are typically found as gases; some of the more common ones are listed in Table 10.1.2 . Gaseous substances include many binary hydrides, such as the hydrogen halides (HX); hydrides of the chalcogens; hydrides of the group 15 elements N, P, and As; hydrides of the group 14 elements C, Si, and Ge; and diborane (B_2H_6). In addition, many of the simple covalent oxides of the nonmetals are gases, such as CO, CO_2, NO, NO_2, SO_2, SO_3, and ClO_2. Many low-molecular-mass organic compounds are gases as well, including all the hydrocarbons with four or fewer carbon atoms and simple molecules such as dimethyl ether [$(CH_3)_2O$], methyl chloride (CH_3Cl), formaldehyde (CH_2O), and acetaldehyde (CH_3CHO). Finally, refrigerants, such as the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFCs) are gases which can be easily liquified by compression and in turn the liquids can be turned into gases by decreasing the pressure on the liquids. The phase change from liquid to gas in tubes inside the refrigerator cools, while the compression in coils at the bottom or back of the refrigerator warms the room. Ammonia and SO_2 are other compressible gases that have been used as refrigerants but cannot be used in houses because of their poisonous nature. Ammonia is still used as a refrigerant in large commercial settings because of its efficiency and low cost.

Table 10.1.2 Some Common Substances That Are Gases at 25°C and 1.0 atm

Elements	Compounds	
He (helium)	HF (hydrogen fluoride)	C_2H_4 (ethylene)
Ne (neon)	HCl (hydrogen chloride)	C_2H_2 (acetylene)
Ar (argon)	HBr (hydrogen bromide)	C_3H_8 (propane)
Kr (krypton)	HI (hydrogen iodide)	C_4H_{10} (butane)
***HCN boils at 26°C at 1 atm, so it is included in this table.**		

Elements	Compounds	
Xe (xenon)	HCN (hydrogen cyanide)*	CO (carbon monoxide)
Rn (radon)	H_2S (hydrogen sulfide)	CO_2 (carbon dioxide)
H_2 (hydrogen)	NH_3 (ammonia)	NO (nitric oxide)
N_2 (nitrogen)	PH_3 (phosphine)	N_2O (nitrous oxide)
O_2 (oxygen)	CH_4 (methane)	NO_2 (nitrogen dioxide)
O_3 (ozone)	C_2H_6 (ethane)	SO_2 (sulfur dioxide)
F_2 (fluorine)		
Cl_2 (chlorine)		
***HCN boils at 26°C at 1 atm, so it is included in this table.**		

All of the gaseous substances mentioned previously (other than the monatomic noble gases) contain covalent or polar covalent bonds and are nonpolar or polar molecules. In contrast, the strong electrostatic attractions in ionic compounds, such as NaBr (boiling point = 1390°C) or LiF (boiling point = 1673°C), prevent them from existing as gases at room temperature and pressure. In addition, the lightest members of any given family of compounds are most likely gases, and the boiling points of polar compounds are generally greater than those of nonpolar compounds of similar molecular mass. Therefore, in a given series of compounds, the lightest and least polar members are the ones most likely to be gases. With relatively few exceptions, however, compounds with more than about five atoms from period 2 or below are too heavy to exist as gases under normal conditions.



Dimethyl ether

Note the Pattern

Gaseous substances often contain covalent or polar covalent bonds, exist as nonpolar or slightly polar molecules, have relatively low molecular masses, and contain five or fewer atoms from periods 1 or 2.

While gases have a wide array of uses, a particularly grim use of a gaseous substance is believed to have been employed by the Persians on the Roman city of Dura in eastern Syria in the third century AD. The Persians dug a tunnel underneath the city wall to enter and conquer the city. Archeological evidence suggests that when the Romans responded with counter-tunnels to stop the siege, the Persians ignited bitumen and sulfur crystals to produce a dense, poisonous gas. It is likely that bellows or chimneys distributed the toxic fumes. The remains of about 20 Roman soldiers were discovered at the base of the city wall at the entrance to a tunnel that was less than 2 m high and 11 m long. Because it is highly unlikely that the Persians could have slaughtered so many Romans at the entrance to such a confined space, archeologists speculate that the ancient Persians used chemical warfare to successfully conquer the city.

Example 10.1.1

Which compounds would you predict to be gases at room temperature and pressure?

1. cyclohexene
2. lithium carbonate
3. cyclobutane
4. vanadium(III) oxide
5. benzoic acid ($C_6H_5CO_2H$)

Given: compounds

Asked for: physical state

Strategy:

A Decide whether each compound is ionic or covalent. An ionic compound is most likely a solid at room temperature and pressure, whereas a covalent compound may be a solid, a liquid, or a gas.

B Among the covalent compounds, those that are relatively nonpolar and have low molecular masses are most likely gases at room temperature and pressure.

Solution:

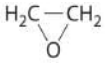
A Lithium carbonate is Li_2CO_3, containing Li^+ and CO_3^{2-} ions, and vanadium(III) oxide is V_2O_3, containing V^{3+} and O^{2-} ions. Both are primarily ionic compounds that are expected to be solids. The remaining three compounds are all covalent.

B Benzoic acid has more than four carbon atoms and is polar, so it is not likely to be a gas. Both cyclohexene and cyclobutane are essentially nonpolar molecules, but cyclobutane (C_4H_8) has a significantly lower molecular mass than cyclohexene (C_6H_{10}), which again has more than four carbon atoms. We therefore predict that cyclobutane is most likely a gas at room temperature and pressure, while cyclohexene is a liquid. In fact, with a boiling point of only 12°C, compared to 83°C for cyclohexene, cyclobutane is indeed a gas at room temperature and pressure.

Exercise

Which compounds would you predict to be gases at room temperature and pressure?

1. *n*-butanol
2. ammonium fluoride (NH_4F)
3. ClF
4. ethylene oxide



5. $HClO_4$

Answer: c; d

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). Many inorganic and organic compounds with four or fewer nonhydrogen atoms are also gases at room temperature and pressure. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms.

Key Takeaway

- The molecules in gaseous substances often contain covalent or polar covalent bonds, are nonpolar or slightly polar molecules, and have relatively low molecular masses.

Contributors and Attributions

- Anonymous

Modified by Joshua Halpern

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6.9: Gas Pressure

Learning Objectives

- To describe and measure the pressure of a gas.

At the macroscopic level, a complete physical description of a sample of a gas requires four quantities: *temperature* (expressed in kelvins), *volume* (expressed in liters), *amount* (expressed in moles), and *pressure* (in atmospheres). As we explain in this section and Section 10.3, these variables are *not* independent. If we know the values of any *three* of these quantities, we can calculate the fourth and thereby obtain a full physical description of the gas. Temperature, volume, and amount have been discussed in previous chapters. We now discuss pressure and its units of measurement.

Units of Pressure

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. The air in a balloon, for example, exerts a force against the interior surface of the balloon, and a liquid injected into a mold exerts a force against the interior surface of the mold, just as a chair exerts a force against the floor because of its mass and the effects of gravity. If the air in a balloon is heated, the increased kinetic energy of the gas eventually causes the balloon to burst because of the increased pressure(*P*)The amount of force (F)(A)P = F/A of the gas, the force (*F*) per unit area (*A*) of surface:

$$P = \frac{F}{A}$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 10.2.1 that applying the same force to a smaller area produces a higher pressure. When we use a hose to wash a car, for example, we can increase the pressure of the water by reducing the size of the opening of the hose with a thumb.

The units of pressure are derived from the units used to measure force and area. In the English system, the units of force are pounds and the units of area are square inches, so we often see pressure expressed in pounds per square inch (lb/in^2, or psi), particularly among engineers. For scientific measurements, however, the SI units for force are preferred. The SI unit for pressure, derived from the SI units for force (newtons) and area (square meters), is the newton per square meter (N/m^2), which is called the pascal (Pa)The SI unit for pressure. The pascal is newtons per square meter: N/m^2, after the French mathematician Blaise Pascal (1623–1662):

$$1\ \ Pa = 1\ \ N/m^2$$

To convert from pounds per square inch to pascals, multiply psi by 6894.757 [1 Pa = 1 psi (6894.757)].

Blaise Pascal (1623–1662)

In addition to his talents in mathematics (he invented modern probability theory), Pascal did research in physics and was an author and a religious philosopher as well. His accomplishments include invention of the first syringe and the first digital calculator and development of the principle of hydraulic pressure transmission now used in brake systems and hydraulic lifts.

Example 10.2.1

Assuming a paperback book has a mass of 2.00 kg, a length of 27.0 cm, a width of 21.0 cm, and a thickness of 4.5 cm, what pressure does it exert on a surface if it is

1. lying flat?
2. standing on edge in a bookcase?

Given: mass and dimensions of object

Asked for: pressure

Strategy:

A Calculate the force exerted by the book and then compute the area that is in contact with a surface.

B Substitute these two values into Equation 10.2.1 to find the pressure exerted on the surface in each orientation.

Solution:

The force exerted by the book does *not* depend on its orientation. Recall from Section 9.1 that the force exerted by an object is $F = ma$, where m is its mass and a is its acceleration. In Earth's gravitational field, the acceleration is due to gravity (9.8067 m/s^2 at Earth's surface). In SI units, the force exerted by the book is therefore

$F = ma$ = (2.00 kg)(9.8067 m/s^2) = 19.6 (kg·m)/s^2 = 19.6 N

1. **A** We calculated the force as 19.6 N. When the book is lying flat, the area is (0.270 m)(0.210 m) = 0.0567 m^2. **B** The pressure exerted by the text lying flat is thus $P = \dfrac{19.6\ N}{0.0567\ m^2} = 3.46 \times 10^2\ \ Pa$
2. **A** If the book is standing on its end, the force remains the same, but the area decreases: $(21.0\ cm)\,(4.5\ cm) = (0.210\ m)\,(0.045\ m) = 9.5 \times \times 10^{-3}\ \ m^2$

   B The pressure exerted by the book in this position is thus

   $$P = \frac{19.6\ N}{9.5 \times 10^{-3}\ m^2} = 2.1 \times 10^3\ \ Pa$$

   Thus the *pressure* exerted by the book varies by a factor of about six depending on its orientation, although the *force* exerted by the book does not vary.

Exercise

What pressure does a 60.0 kg student exert on the floor

1. when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?
2. as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answers:

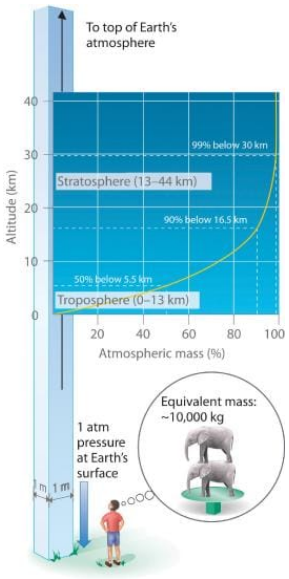
1. 3.27 × 10^4 Pa (4.74 lb/in.^{2})
2. 5.9 × 10^6 Pa (8.5 × 10^2 lb/in.^{2})

Atmospheric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface, and half of it is within the first 5.5 km (Figure 9.3). Every point on Earth's surface experiences a net pressure called *atmospheric pressure*. The pressure exerted by the atmosphere is considerable: a 1.0 m^2 column, measured from sea level to the top of the atmosphere, has a mass of about 10,000 kg, which gives a pressure of about 100 kPa:

$$Pressure = \frac{\left(1.0 \times 10^4\ kg\right)\left(9,807\ \cancel{m}/s^2\right)}{1.0\ \cancel{m^2}} = 0.98 \times 10^5\ \ Pa = 98\ \ kPa$$

Figure 10.2.1 Atmospheric Pressure

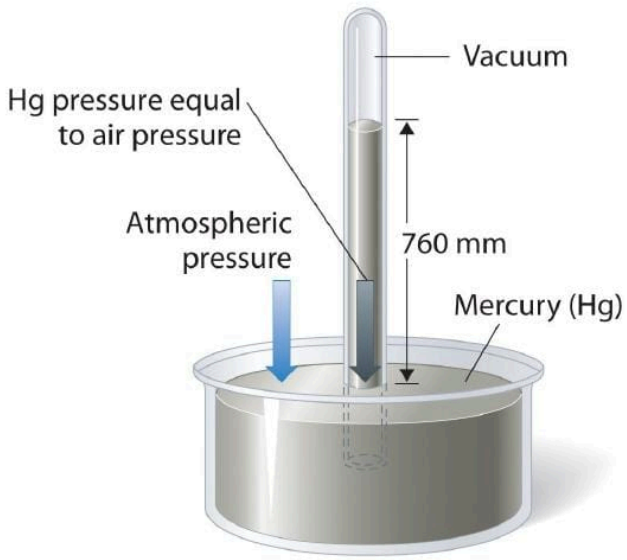


Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface, resulting in a pressure at the surface of 1.01×10^5 N/m^2. This corresponds to a pressure of 101 kPa = 760 mmHg = 1 atm.

In English units, this is about 14 lb/in.^{2}, but we are so accustomed to living under this pressure that we never notice it. Instead, what we notice are *changes* in the pressure, such as when our ears pop in fast elevators in skyscrapers or in airplanes during rapid changes in altitude. We make use of atmospheric pressure in many ways. We can use a drinking straw because sucking on it removes air and thereby reduces the pressure inside the straw. The atmospheric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

Atmospheric pressure can be measured using a barometer (a device used to measure atmospheric pressure), which was invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). A barometer may be constructed from a long glass tube that is closed at one end. It is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside (Figure 10.2.1). Why doesn't all the mercury run out? Gravity is certainly exerting a downward force on the mercury in the tube, but it is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a *vacuum*), there is no pressure pushing down on the column. Thus the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere. Under normal weather conditions at sea level, the two forces are balanced when the top of the mercury column is approximately 760 mm above the level of the mercury in the dish, as shown in Figure 10.2.2 This value varies with meteorological conditions and altitude. In Denver, Colorado, for example, at an elevation of about 1 mile, or 1609 m (5280 ft), the height of the mercury column is 630 mm rather than 760 mm.

Figure 10.2.2 A Mercury Barometer



The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the mercury column.

Mercury barometers have been used to measure atmospheric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg) often called the torr (a unit of pressure). One torr is the same as 1 mmHg, after Torricelli. Standard atmospheric pressure is the atmospheric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm). Also referred to as standard atmospheric pressure, it is the atmospheric pressure required to support a column of mercury exactly 760 mm tall. These units are also related to the pascal as follows:

$$1\ \ atm = 760\ \ mmHg = 760\ \ torr = 1.01325 \times \times 10^{5}\ \ Pa = 101.325\ \ kPa$$

Thus a pressure of 1 atm equals 760 mmHg exactly and is approximately equal to 100 kPa.

While mercury barometers were the workhorses for pressure measurement into the last quarter of the 20th century, they have been replaced by electronic gauges. One motivation was safety. Mercury and mercury vapor are heavy metal poisons.

The oldest and simplest replacement for mercury barometers are aneroid gauges. The simplest version of an aneroid gauge (Figure 6.2.3) has a thin metal diaphram which expands and contracts. The diaphragm is connected to a dial by a mechanical linkage. Aneroid gauges can either be absolute or differential. Differential aneroid gauges compare the pressure in the gauge housing to that being measured. A common use for aneroid gauges was airplane altimeters.

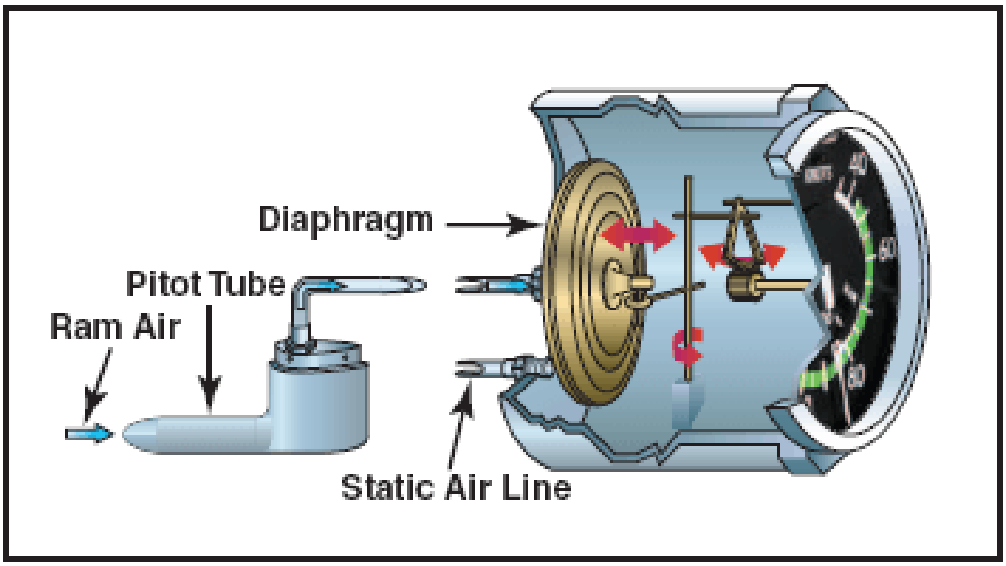


Figure 6.2.2 An Aneroid Barometer *An Aneroid Barometer uses the expansion/contraction of a metal diaphragm to move the indicator dial. This drawing from the Wikipedia shows a simple aneroid barometer used for an airplane altimeter.*

Most modern pressure sensors are based on strain gauge which convert pressure into a strain on a semiconductor element. The strain is converted into an electrical signal by the piezoelectric effect as a change in resistance monitored by a resistance bridge. Alternatively pressure is related to the change in frequency of a quartz crystal oscillator. Modern balances are also based on this later principle.

A very accurate type of pressure sensor uses a metal diaphragm as one part of a capacitor. As the pressure changes the diaphragm moves altering the capacitance. Handbooks are available from sensor manufacturers with details including OMEGA and WIKA.

Below atmospheric pressures another type of gauge is used based on measuring temperature change of a hot wire as a function of pressure. This is best suited to pressures below atmospheric. Older types called thermocouple or Pirani gauges measure only up to a few Torr. Modern variations called convection gauges can measure up to atmospheric pressure

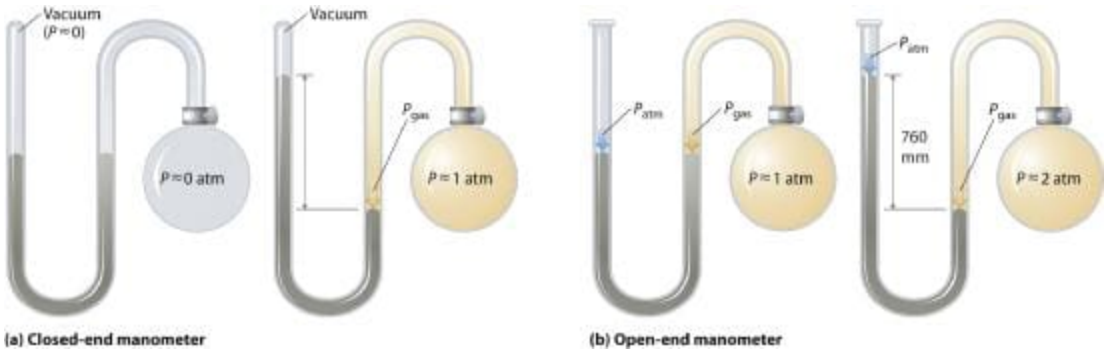
A summary of the various types of pressure gauge in use today can be found in a technical note at the Kurt Lesker site

Pressure gauges specify whether the measurement is absolute (relative to zero pressure) or gauge (relative to the standard atmosphere). One must be careful about which kind a gauge is when buying or using one..

Manometers

Barometers measure atmospheric pressure, but manometers measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in part (a) in Figure 10.2.3. When the bulb contains no gas (i.e., when its interior is a near vacuum), the heights of the two columns of mercury are the same because the space above the mercury on the left is a near vacuum (it contains only traces of mercury vapor). If a gas is released into the bulb on the right, it will exert a pressure on the mercury in the right column, and the two columns of mercury will no longer be the same height. The *difference* between the heights of the two columns is equal to the pressure of the gas.

Figure 10.2.3 The Two Types of Manometer



(a) Closed-end manometer (b) Open-end manometer

(a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum (P ≈ 0), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere (P ≈ 1 atm), and the difference in the heights of the two columns gives the difference between atmospheric pressure and the pressure of the gas in the bulb.

If the tube is open to the atmosphere instead of closed, as in the open-end manometer shown in part (b) in Figure 10.2.3, then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the atmospheric pressure. If the gas in the bulb has a *higher* pressure, the mercury in the open tube will be forced up by the gas pushing down on the mercury in the other arm of the U-shaped tube. The pressure of the gas in the bulb is therefore the sum of the atmospheric pressure (measured with a barometer) and the difference in the heights of the two columns. If the gas in the bulb has a pressure *less* than that of the atmosphere, then the height of the mercury will be greater in the arm attached to the bulb. In this case, the pressure of the gas in the bulb is the atmospheric pressure minus the difference in the heights of the two columns.

Example 10.2.3

Suppose you want to construct a closed-end manometer to measure gas pressures in the range 0.000–0.200 atm. Because of the toxicity of mercury, you decide to use water rather than mercury. How tall a column of water do you need? (At 25°C, the density of water is 0.9970 g/cm^3; the density of mercury is 13.53 g/cm^3.)

Given: pressure range and densities of water and mercury

Asked for: column height

Strategy:

A Calculate the height of a column of mercury corresponding to 0.200 atm in millimeters of mercury. This is the height needed for a mercury-filled column.

B From the given densities, use a proportion to compute the height needed for a water-filled column.

Solution:

A In millimeters of mercury, a gas pressure of 0.200 atm is

$$P = \left(0.200 \ \cancel{atm}\right)\left(\frac{760 \ mmHg}{1 \ \cancel{atm}}\right) = 152 \ \ mmHg$$

Using a mercury manometer, you would need a mercury column at least 152 mm high.

B Because water is less dense than mercury, you need a *taller* column of water to achieve the same pressure as a given column of mercury. The height needed for a water-filled column corresponding to a pressure of 0.200 atm is proportional to the ratio of the density of mercury (d_{Hg})(d_{H2O})

$$(height_{H_2O})\,(d_{H_2O}) = (height_{Hg})\,(d_{Hg})$$

$$height_{H_2O} = (height_{Hg})\,\frac{d_{Hg}}{d_{H_2O}}$$

$$= (152\ mmHg)\left(\frac{13.53\ \cancel{g/cm^2}}{0.9970\ \cancel{g/cm^2}}\right)$$

$$= 2.06 \times 10^3\ mm\ H_2O$$

This answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

Exercise

Suppose you want to design a barometer to measure atmospheric pressure in an environment that is always hotter than 30°C. To avoid using mercury, you decide to use gallium, which melts at 29.76°C; the density of liquid gallium at 25°C is 6.114 g/cm^3. How tall a column of gallium do you need if P = 1.00 atm?

Answer: 1.68 m

The answer to Example 4 also tells us the maximum depth of a farmer's well if a simple suction pump will be used to get the water out. If a column of water 2.06 m high corresponds to 0.200 atm, then 1.00 atm corresponds to a column height of

$$\frac{h}{2.06\ m} = \frac{1.00\ \cancel{atm}}{0.200\ \cancel{atm}}$$

$$h = 10.3\ m$$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on atmospheric pressure to force the liquid up a tube. If 1 atm pressure corresponds to a 10.3 m (33.8 ft) column of water, then it is physically impossible for atmospheric pressure to raise the water in a well higher than this. Until electric pumps were invented to push water mechanically from greater depths, this factor greatly limited where people could live because obtaining water from wells deeper than about 33 ft was difficult.

Summary

Four quantities must be known for a complete physical description of a sample of a gas: *temperature*, *volume*, *amount*, and *pressure*. **Pressure** is force per unit area of surface; the SI unit for pressure is the **pascal (Pa)**, defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area on which the force is exerted. The pressure exerted by Earth's atmosphere, called *atmospheric pressure*, is about 101 kPa or 14.7 lb/in.^{2} at sea level. Atmospheric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to atmospheric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard atmospheric pressure**, the pressure required to support a column of mercury 760 mm tall, is yet another unit of pressure: 1 **atmosphere (atm)**. A **manometer** is an apparatus used to measure the pressure of a sample of a gas.

Key Takeaways

- Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer.

Key Equation

Definition of pressure

Equation 10.2.1: $P = F/A$

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6.10: The Ideal Gas Law

Learning Objectives

- To use the ideal gas law to describe the behavior of a gas.

Motivating the Ideal Gas Law

In a gas, molecules freely move, filling any volume that they occupy. The kinetic energy of the molecules greatly exceeds any potential energy of attraction or repulsion between molecules and the size of the molecules are miniscule compared to the average space between them. Contrast this with solids, where the molecules are held in place by the attractive forces and the comparatively small kinetic energy only results in the molecules jiggling in place when thermally excited. Again, in a solid, the molecules are packed so closely together that the volume of the solid is essentially that of the sum of the molecular volumes of all of the molecules in it. Liquids represent a situation where molecular attraction and kinetic energy are balanced and the spacing between molecules is higher than in solids but much less than in gases.

At high temperatures and low pressures, where the kinetic energy and the spacing between molecules are both large, one may neglect both the miniscule attractive forces and molecular volume. Under such conditions the properties of the gas, the pressure, P, volume, V, number of moles, n, and the temperature, T are independent of the mixture of molecules in the gas. In that limit the behavior of the gas is called ideal, and governed by the ideal gas law

No gases are truly ideal, but while no model is perfect, some are useful, and under most commonly encountered conditions, the ideal gas law is very useful indeed to describe the behavior of gases. It is also easy to predict that the conditions where the ideal gas law would have trouble describing the behavior of a gas would be low temperature (small molecular kinetic energy) and high pressure (little space between molecules). The behavior of gases under such conditions becomes increasingly like that of liquids and will be discussed in the next chapter.

The Ideal Gas Law

The ideal gas law

$$PV = nRT$$

relates the pressure, volume, temperature and number of moles in a gas to each other. R is a constant called the gas constant. The ideal gas law is what is called an equation of state because it is a complete description of the gas's thermodynamic state. No other information is needed to calculate any other thermodynamic variable, and, since the equation relates four variables, a knowledge of any three of them is sufficient.

Pressure, volume and number of moles, the latter sometime called extent, share an important property, they can never be negative. What would a negative volume be, or an absolute negative pressure or extent? The concepts do not even exist. This means that temperature in the ideal gas law is similarly limited. **It can never be negative.**

We can determine what zero temperature on the ideal gas scale is by holding the number of moles and the pressure constant and extrapolate the temperature measured in Celcius to what its value would be at zero volume

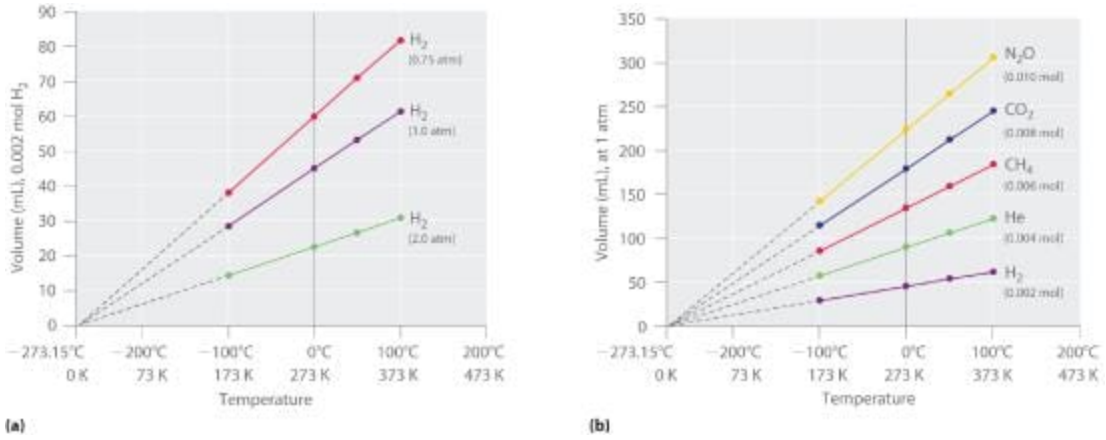


Figure 10.3.1 *The Relationship between Volume and Temperature (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to –100°C, and the broken lines show the extrapolation of the data to V = 0. The temperature scale is given in both degrees Celsius and Kelvin. 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 extrapolated temperature corresponding to zero volume at constant pressure and amount is -273.15 °C, which is called absolute zero because no lower temperature is possible (unless, of course you can come up with a negative volumes, but you cannot). For convenience we set the degrees on the Kelvin scale to the size of the degree on the Celcius scale. In other words

$1\ \ K = 1^oC$

Note the Pattern

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

$$R = 0.08206\ \ L \cdot atm/\left(K \cdot \cdot mol\right)$$

Because the product *PV* has the units of energy, as described in Section 8.1 and Essential Skills 4 (Section 9.9), *R* can also have units of J/(K·mol) or cal/(K·mol):

$$R = 8.3145\ \ J/\left(K \cdot mol\right) = 1.9872 cal/\left(K \cdot mol\right)$$

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and 1 atm pressure, referred to as standard temperature and pressure (STP) The conditions 0°C (273.15 K) and 1 atm pressure for a gas.

This can be confusing because as discussed in the previous chapter,the standard state for enthalpies of reaction and formation is 298K. Be sure to use the appropriate standard state for enthalpies (298 K) and gas problems (273.15 K)

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 10.3.1:

$$V = \frac{nRT}{P} = \frac{\left(1.000\ \cancel{mol}\right)\left(0.082057\ L \cdot \cancel{atm}/\cancel{K} \cdot \cancel{mol}\right)\left(273.15\ \cancel{K}\right)}{1.000\ \cancel{atm}} = 22.31\ \ L$$

Thus the volume of 1 mol of an ideal gas at 0°C and 1 atm pressure is 22.41 L, approximately equivalent to the volume of three basketballs. The quantity 22.41 L is called the standard molar volumeThe volume of 1 mol of an ideal gas at STP (0°C and 1 atm pressure), which is 22.41 L. of an ideal gas. The molar volumes of several real gases at STP are given in Table 10.3.1, 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 STP.

Table 10.3.1 *Molar Volumes of Selected Gases at Standard Temperature (0°C) and Pressure (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 10.3.1

The balloon that Charles used for hisflight 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 10.3.1) for *n*, we obtain

$$n = \frac{PV}{RT}$$

B *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.082057 (L·atm)/(K·mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$745 \ \cancel{\text{mmHg}} \times \frac{1 \text{ atm}}{760 \ \cancel{\text{mmHg}}} = 0.980 \text{ atm} \tag{6.10.1}$$

$$T = 273 + 30 = 303\text{K} \tag{6.10.2}$$

Substituting these values into the expression we derived for *n*, we obtain

$$n = \frac{PV}{RT} = \frac{0.980 \cancel{\text{ atm}} \times 31150 \cancel{\text{ L}}}{0.08206 \frac{\cancel{\text{atm}} \cdot \cancel{\text{L}}}{\text{mol} \cdot \cancel{\text{K}}} \times 303 \cancel{\text{ K}}} = 1.23 \times 10^3 \text{ mol} \tag{6.10.3}$$

Exercise

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, 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 6.

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

$$\frac{n}{V} = \frac{P}{RT} \tag{10.3.6}$$

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):

$$n = \frac{m}{M} \tag{10.3.7}$$

Substituting this expression for *n* into Equation 10.4.12 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{10.3.8}$$

Because *m*/*V* is the density *d* of a substance, we can replace *m*/*V* by *d* and rearrange to give

$$d = \frac{m}{V} = \frac{MP}{RT} \tag{10.3.9}$$

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 10.3.2

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 10.3.9 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

\((4)(12.011) + (10)(1.0079) = 58.123 \; g/mol \notag \)

Using 0.082057 (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:

$$P = 750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.987 \text{ atm}$$

B Substituting these values into Equation 10.3.9 gives

$$d = \frac{58.123 \text{ g/mol} \times 0.987 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} = 2.35 \text{ g/L}$$

Exercise

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 10.3.9 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 re-weighed. 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 10.

Example 10.3.3

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 10.3.8 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 10.3.8 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P}$$

Density is the mass of the gas divided by its volume:

$$d = \frac{m}{V} = \frac{0.289\text{g}}{0.17\text{L}} = 1.84\text{g/L}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K$$

$$P = 727\text{mmHg} \times \frac{1\text{atm}}{760\text{mmHg}} = 0.957\text{atm}$$

The molar mass of the unknown gas is thus

$$d = \frac{1.84\text{ g/L} \times 0.08206\frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 291\text{ K}}{0.957\text{ atm}} = 45.9\text{g/mol}$$

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:

$$M(\text{NO}) = 14 + 16 = 30\text{ g/mol}$$

$$M(\text{N}_2\text{O}) = (2)(14) + 16 = 44\text{ g/mol}$$

$$M(\text{NO}_2) = 14 + (2)(16) = 46\text{ g/mol}$$

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

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

Summary

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.

Key Takeaways

- 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.

Key Equations

Ideal gas law

Equation 10.3.1: $PV = nRT$

where $R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}}$

Density of a gas

Equation 10.3.9: $d = \frac{MP}{RT}$

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6.11: Gas Mixtures

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:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{10.5.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

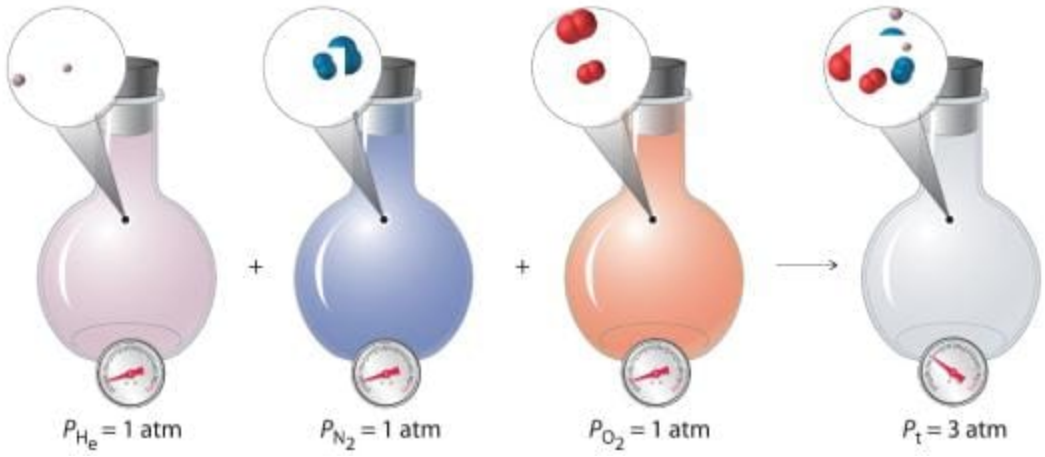
With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure 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 pressureThe pressure a gas in a mixture would exert if it were the only one present (at the same temperature and volume)., 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 pressuresA law that states that the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases.. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots = \sum_{i=1}^{n} P_i \tag{10.5.2}$$

where P_t is the total pressure and the other terms are the partial pressures of the individual gases (Figure 10.5.1).

Figure 10.5.1 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:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right) \tag{10.5.3}$$

More generally, for a mixture of *i* components, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{10.5.4a}$$

$$P_{tot} = \sum_{i=1}^{n} n_i\left(\frac{RT}{V}\right) \tag{10.5.4b}$$

Equation 10.5.4. restates Equation 10.5.3 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 10.27 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 11.

Example 10.5.1

For reasons that we will examine in Chapter 15, 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

$$n_{\text{He}} = \frac{326.4\ \text{g}}{4.003\ \text{g/mol}} = 81.54\ \text{mol}$$

The number of moles of O_2 is

$$n_{\text{O}_2} = \frac{51.2\ \text{g}}{32.00\ \text{g/mol}} = 1.60\ \text{mol}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}}RT}{V} = \frac{81.54\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 196.2\ \text{atm}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{V} = \frac{1.60\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 3.85\ \text{atm}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85)\ \text{atm} = 200.1\ \text{atm}$$

Exercise

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_t = 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*)The ratio of the number of moles of any component of a mixture to the total number of moles of all species present in the mixture. 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_t):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{10.5.6}$$

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: $P_A = n_ART/V$ and $P_t = n_tRT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_ART/V}{n_{tot}RT/V} = \frac{n_A}{n_{tot}} = x_A \tag{10.5.7}$$

Rearranging this equation gives

$$P_A = x_AP_{tot} \tag{10.5.8}$$

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. Recall from Chapter 7 (Table 7.6.1) that 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 10.5.4, 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 10.5.2

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_{N_2}	597	568
P_{O_2}	158	116
P_{H_2O}	0.3	28
P_{CO_2}	5	48
P_{Ar}	8	8
P_t	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 10.5.8.

Solution:

The mole fraction of any gas A is given by

$$x_A = \frac{P_A}{P_{tot}}$$

where P_A is the partial pressure of A and P_t is the total pressure. In this case,

$$x_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063$$

The following table gives the values of P_A and X_A for exhaled air.

P_A		X_A
N_2	$\left(568 \ \cancel{mmHg}\right) \frac{1 \ atm}{760 \ \cancel{mmHg}} = 0.747 \ atm$	$\frac{0.747 \ \cancel{atm}}{1.01 \ \cancel{atm}} = 0.740$
O_2	$\left(116 \ \cancel{mmHg}\right) \frac{1 \ atm}{760 \ \cancel{mmHg}} = 0.153 \ atm$	$\frac{0.153 \ \cancel{atm}}{1.01 \ \cancel{atm}} = 0.151$
H_2O	$\left(28 \ \cancel{mmHg}\right) \frac{1 \ atm}{760 \ \cancel{mmHg}} = 0.037 \ atm$	$\frac{0.031 \ \cancel{atm}}{1.01 \ \cancel{atm}} = 0.031$
CO_2	$\left(48 \ \cancel{mmHg}\right) \frac{1 \ atm}{760 \ \cancel{mmHg}} = 0.063 \ atm$	$\frac{0.063 \ \cancel{atm}}{1.01 \ \cancel{atm}} = 0.061$
Ar	$\left(8 \ \cancel{mmHg}\right) \frac{1 \ atm}{760 \ \cancel{mmHg}} = 0.011 \ atm$	$\frac{0.011 \ \cancel{atm}}{1.01 \ \cancel{atm}} = 0.011$

Exercise

We saw in Example 10 that 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: $P_{\mathrm{CO_2}} = 86\ \mathrm{atm}$, $P_{\mathrm{N_2}} = 2.7\ \mathrm{atm}$

Summary

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.

Key Takeaways

- The partial pressure of each gas in a mixture is proportional to its mole fraction.

Key Equations

Mole fraction

Equation 10.5.7: $X_A = \dfrac{molesA}{totalmoles} = \dfrac{n_A}{n_t}$

Relationship between partial pressure and mole fraction

Equation 10.5.8: $P_A = X_A P_t$

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6.12: Kinetic Theory of Gases

Learning Objectives

- State the major concepts behind the kinetic theory of gases.
- Relate the general properties of gases to the kinetic theory.

Gases were among the first substances studied in terms of the modern scientific method, which was developed in the 1600s. It did not take long to recognize that gases all shared certain physical behaviors, suggesting that all gases could be described by one all-encompassing theory. Today, that theory is the **kinetic theory of gases**. The kinetic theory of gases is based on the following statements:

1. Gases consist of tiny particles of matter that are in constant motion.
2. Gas particles are constantly colliding with each other and the walls of a container. These collisions are elastic—that is, there is no net loss of energy from the collisions.
3. Gas particles are separated by large distances, with the size of a gas particle tiny compared to the distances that separate them.
4. There are no interactive forces (i.e., attraction or repulsion) between the particles of a gas.
5. The average speed of gas particles is dependent on the temperature of the gas.

Figure 6.12.1 shows a representation of how we mentally picture the gas phase.

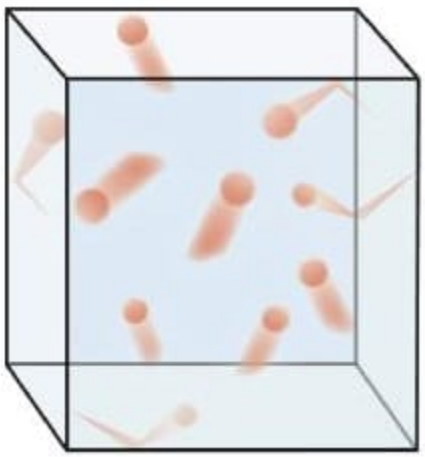


Figure 6.12.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion, with a lot of distance between the particles.

This model of gases explains some of the physical properties of gases. Because most of a gas is empty space, a gas has a low density and can expand or contract under the appropriate influence. The fact that gas particles are in constant motion means that two or more gases will always mix, as the particles from the individual gases move and collide with each other.

An **ideal gas** is a gas that exactly follows the statements of the kinetic theory. Unfortunately, *real gases* are not ideal. Many gases deviate slightly from agreeing perfectly with the kinetic theory of gases. However, most gases adhere to the statements, and the kinetic theory of gases is well accepted by the scientific community.

- The physical behavior of gases is explained by the kinetic theory of gases.
- An ideal gas adheres exactly to the kinetic theory of gases.

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6.13: Real Gases

Learning Objectives

- To recognize the differences between the behavior of an ideal gas and a real gas.

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 11.1.1). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (part (b) in Figure 11.1.1). Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure 11.1.2 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.

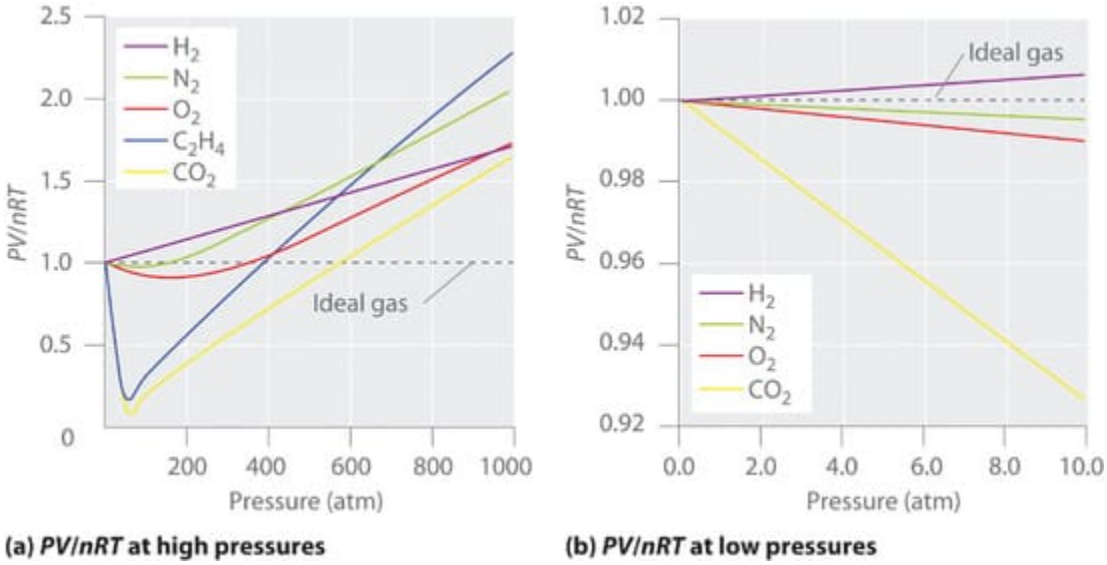


Figure 11.1.1 Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures (a) In these plots of *PV*/*nRT* versus *P* at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.

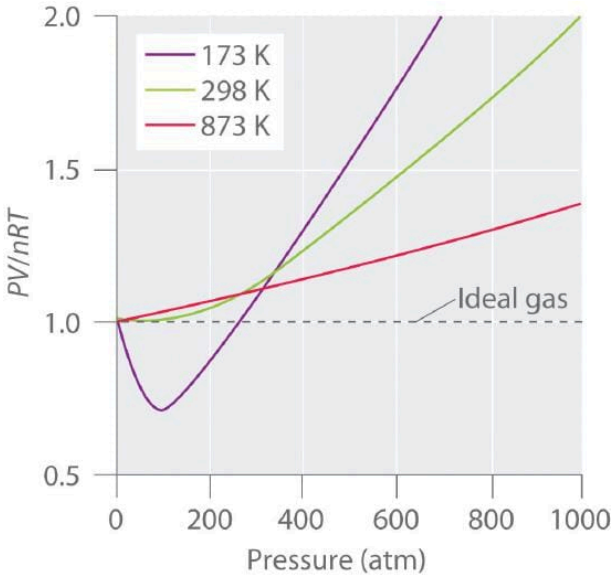


Figure 11.1.2 The Effect of Temperature on the Behavior of Real Gases A plot of *PV*/*nRT* versus *P* for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

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 11.1.3). 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.

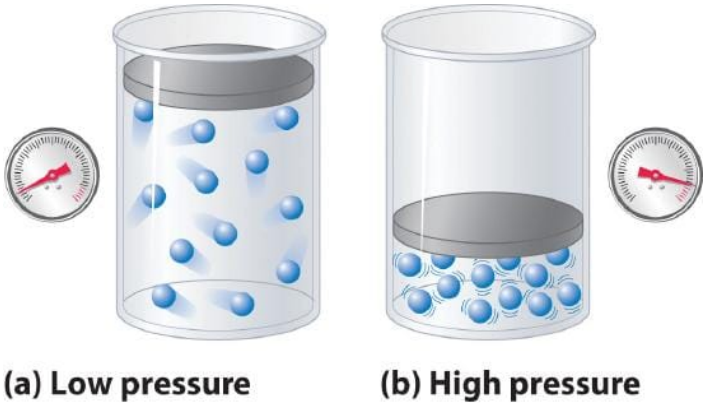


Figure 11.1.3 The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume 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 (Figure 11.1.3). Thus as shown in Figure 11.1.2, 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.

Note the Pattern

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 equationA modification of the ideal gas law designed to describe the behavior of real gases by explicitly including the effects of molecular volume and intermolecular forces.,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{11.1.1}$$

a and *b* are empirical constants that are different for each gas. The values of *a* and *b* are listed in Table 11.1.5 for several common gases. The pressure term $P + (an^2/V^2)$ 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 10.1.4 . The volume term $V – nb$ corrects for the volume occupied by the gaseous molecules.

Table 11.1.1 van der Waals Constants for Some Common Gases

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

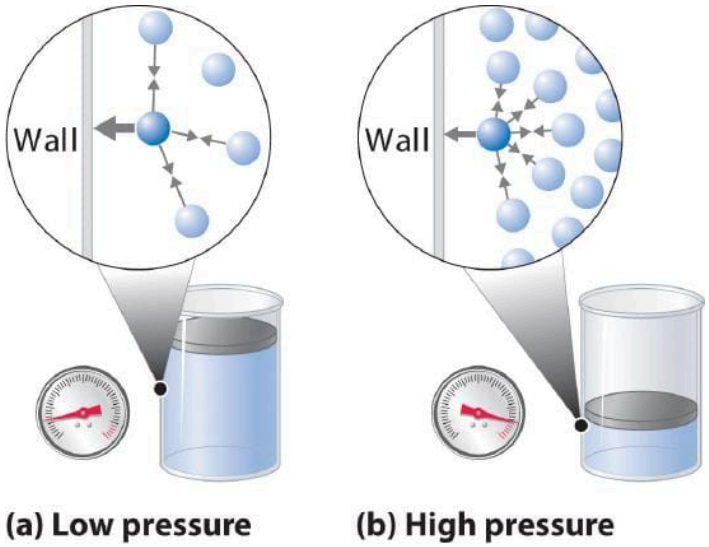


Figure 11.1.4 The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to 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 11.1.1

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.0 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 11.1.1 . 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):

$$\left(500 \cancel{g}\right)\left(\frac{1\ mol}{70.906\ \cancel{g}} = 7.05 mol\ Cl_2\right)$$

Using the ideal gas law and the temperature in kelvins (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} = \frac{\left(7.05\ \cancel{mol}\right)\left[0.08206\left(\cancel{L}\cdot atm\right)/\left(\cancel{K}\cdot\cancel{mol}\right)\right]\left(298\ \cancel{K}\right)}{4.0\ \cancel{L}} = 43\ \ atm$$

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 11.1.1 . Solving for *P* gives

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

$$= \frac{\left(7.05\ \cancel{mol}\right)\left[0.08206\left(\cancel{L}\cdot atm\right)/\left(\cancel{K}\cdot\cancel{mol}\right)\right]\left(298\ \cancel{K}\right)}{4.0\ \cancel{L} - 7.05\ \cancel{mol}\left(0.0542\ \cancel{L}/\cancel{mol}\right)} - \frac{6.260^2\ \cancel{L^2}\cdot atm/\cancel{mol^2}\left(7.05\ \cancel{mol^2}\right)}{4.0\ \cancel{L^2}}$$

$$= 47.7\ \ atm - 19.4\ \ atm = 28\ \ atm\ \ (2\ \ significant\ \ figures)$$

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

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

1. ideal gas law.
2. van der Waals equation.

Answer: a. 77 atm; b. 67 atm

Liquefaction of Gases

LiquefactionThe condensation of gases into a liquid form. 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. In Chapter 11.2 , we will consider in more detail the nature of the intermolecular forces that allow gases to liquefy.

Note the Pattern

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 (an ultracold liquid formed from the liquefaction of gases., 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 11.1.5 A Liquid Natural Gas Transport Ship

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure 11.1.5). 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**.

Key Takeaways

- Molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

Key Equation

van der Waals equation

Equation 11.1.1: $\left(p+\frac{an^2}{V^2}\right)(V-b)=nRT$<mi/>

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6.14: Overview of Chromatography

The first uses of chromatography involved separating the colored components of plants in the early 1900's. The pigments in a plant can be separated into yellow, orange and green colors (xanthophylls, carotenes and chlorophylls respectively) through this method. The Greek name for color is *chroma*, and *graphein* is 'to write,' so chromatography can be thought of as "color writing."

The general idea of chromatography can be demonstrated with food dyes in your kitchen. Commercial green food dye does not contain any green colored components at all, and chromatography can show that green food dye is actually a mixture of blue and yellow dyes. If a drop of green food dye is placed in the middle of a paper towel followed by a few drops of water, the water will creep outwards as it wets the paper (Figure 2.1). As the water expands, the dye will travel with it. If you let the dye expand long enough, you'll see that the edges will be tinted with blue (Figure 2.1d). This is the beginning of the separation of the blue and yellow components in the green dye by the paper and water.

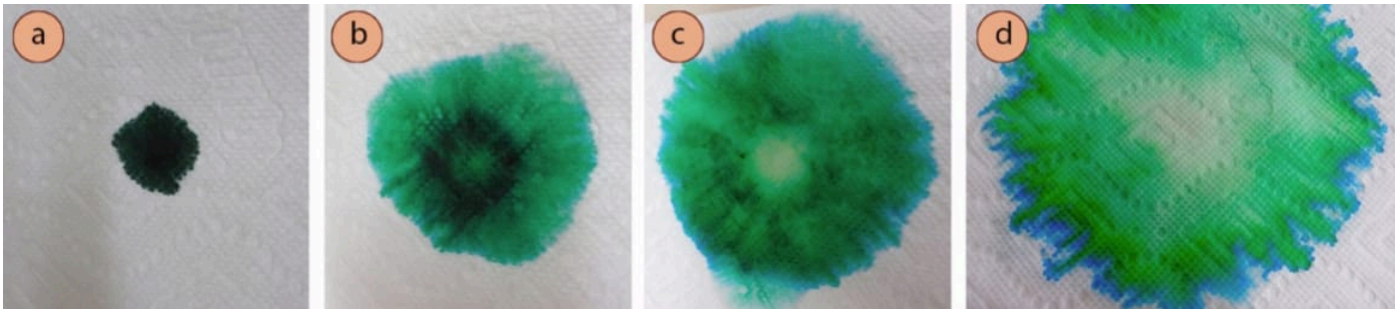


Figure 2.1: Time-lapse sequence of a drop of green food dye on a paper towel, followed by a drop of water.

A complete separation of the green food dye can be accomplished using paper chromatography. A dilute sample is deposited on the bottom edge of a piece of paper, the paper is rolled in a cylinder, stapled, and placed vertically in a closed container containing a small amount of solvent[1] (Figure 2.2a). The solvent is allowed to wick up the paper through capillary action (called "**elution**," Figure 2.2b), and through this method complete separation of the blue and yellow components can be achieved (Figure 2.2d).

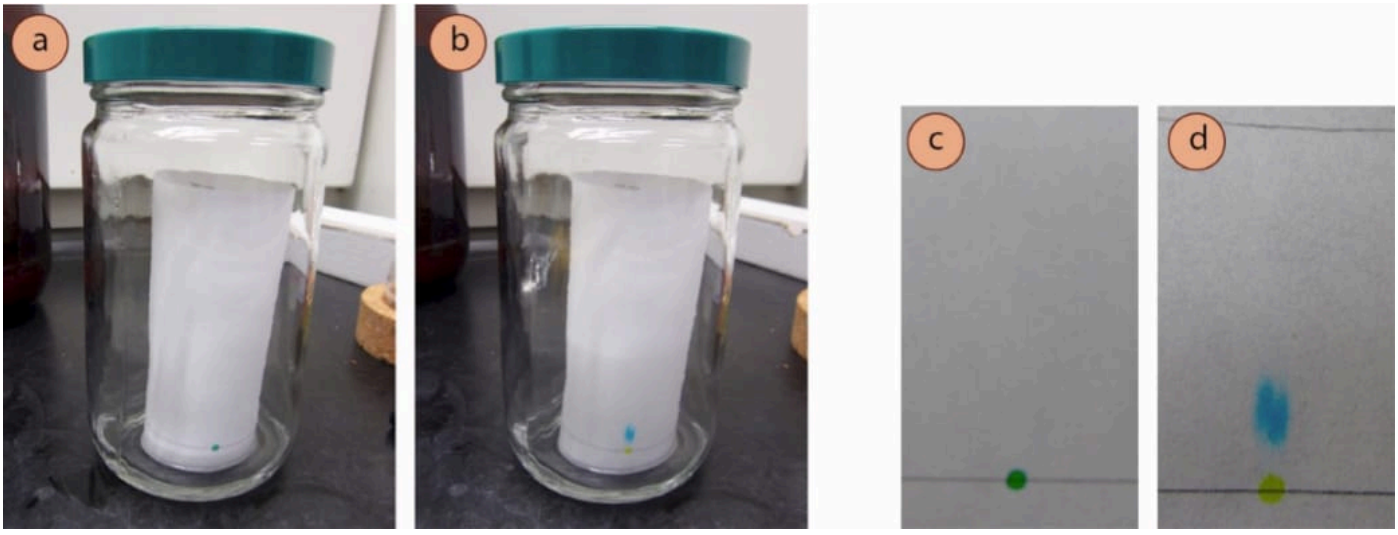


Figure 2.2: Paper chromatography of diluted green food dye: a) Before elution, b) After elution, c) Zoom in before elution, d) Zoom in after elution.

[1]The solvent used in this separation is a solution made from a 1:3:1 volume ratio of $6\ \mathrm{M}\ \mathrm{NH_4OH}$:1-pentanol:ethanol.

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6.15: General Separation Theory

The main chromatographic techniques (thin layer chromatography, column chromatography, and gas chromatography) follow the same general principles in terms of how they are able to separate mixtures.

In all chromatographic methods, a sample is first applied onto a stationary material that either **absorbs** or **adsorbs** the sample: adsorption is when molecules or ions in a sample adhere to a surface, while absorption is when the sample particles penetrate into the interior of another material. A paper towel absorbs water because the water molecules form intermolecular forces (in this case hydrogen bonds) with the cellulose in the paper towel. In chromatography, a sample is typically adsorbed onto a surface, and can form a variety of intermolecular forces with this surface.

After adsorption, the sample is then exposed to a liquid or gas traveling in one direction. The sample may overcome its intermolecular forces with the stationary surface and transfer into the moving material, due to some attraction or sufficient thermal energy. The sample will later readsorb to the stationary material, and transition between the two materials in a constant equilibrium (Equation 6.15.1). If there is to be any separation between components in a mixture, it is crucial that there are many equilibrium "steps" in the process (summarized in Figure 2.3).

$$\mathrm{X}_{(\mathrm{stationary})} \leftrightharpoons \mathrm{X}_{(\mathrm{mobile})} \tag{6.15.1}$$

The material the sample adsorbs onto is referred to as the "**stationary phase**" because it retains the sample's position. The moving material is called the "**mobile phase**" because it can cause the sample to move from its original position.

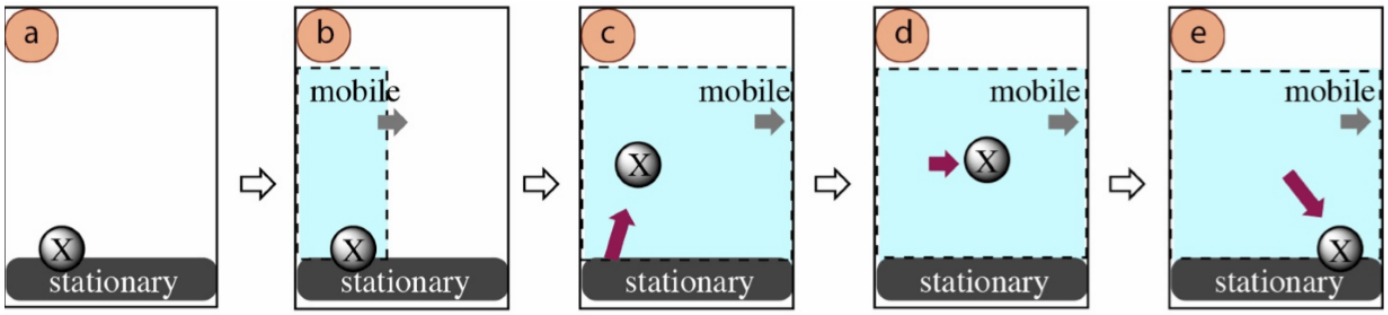


Figure 2.3: Generic chromatography sequence for compound X: a) Adsorption, b) Exposure to a mobile phase, c) Sample X breaks its attachment to the stationary phase, d) Movement with the mobile phase, e) Reattachment to the stationary phase. Steps c-e are equilibrium steps and constantly repeated.

The main principle that allows chromatography to separate components of a mixture is that components will spend different amounts of time interacting with the stationary and mobile phases. A compound that spends a large amount of time mobile will move quickly away from its original location, and will separate from a compound that spends a larger amount of time stationary. The main principle that determines the amount of time spent in the phases is the **strength of intermolecular forces** experienced in each phase. If a compound has strong intermolecular forces with the stationary phase it will remain adsorbed for a longer amount of time than a compound that has weaker intermolecular forces. This causes compounds with different strengths of intermolecular forces to move at different rates.

How these general ideas apply to each chromatographic technique (thin layer chromatography, column chromatography, and gas chromatography) will be explained in greater detail in each section.

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INDEX

A

amorphous solid
6.7: The Solid State of Matter

atomic mass
1.11: Molar Mass

atomic mass units
1.11: Molar Mass

atomic spectra
2.3: Atomic Spectra

atomic theory
1.6: Atomic Theory

atoms
1.6: Atomic Theory

Author tag:OpenStax
3.1: Prelude to Chemical Bonding and Molecular Geometry
3.2: Ionic Bonding
3.3: Covalent Bonding
4.1: Hybrid Atomic Orbitals
6.4: Solubility
6.7: The Solid State of Matter

autonumheader:yes2
4.1: Hybrid Atomic Orbitals
6.7: The Solid State of Matter

Avogadro's hypothesis
1.10: Measurement and Scale - The Mole Concept

Avogadro's number
1.10: Measurement and Scale - The Mole Concept

B

bond length
3.3: Covalent Bonding

C

chromatography
6.14: Overview of Chromatography

conversion factor
1.5: Converting Units

covalent bond
3.3: Covalent Bonding

covalent network solid
6.7: The Solid State of Matter

crystalline solid
6.7: The Solid State of Matter

D

dimensional analysis
1.5: Converting Units

E

electron
1.6: Atomic Theory

electronegativity
3.3: Covalent Bonding

exact number
1.5: Converting Units

F

fingerprint region
5.4: Interpreting Infrared Spectra
5.6: The Fingerprint Region

formula mass
1.11: Molar Mass

G

g/mol
1.11: Molar Mass

gas
6.12: Kinetic Theory of Gases

gases
6.12: Kinetic Theory of Gases

gimli flier
1.5: Converting Units

grams per mole
1.11: Molar Mass
1.12: Mole-Mass Conversions

H

Henry's law
6.4: Solubility

hybrid orbital
4.1: Hybrid Atomic Orbitals

hybridization
4.1: Hybrid Atomic Orbitals

hypothesis:yes
6.10: The Ideal Gas Law
6.11: Gas Mixtures
6.13: Real Gases
6.2: Intermolecular forces
6.3: Vapor Pressure
6.5: Unique Properties of Liquids
6.6: Crystalline and Amorphous Solids
6.8: Gaseous Elements and Compounds
6.9: Gas Pressure

I

ideal gas
6.12: Kinetic Theory of Gases

immiscible
6.4: Solubility

inert pair effect
3.2: Ionic Bonding

interstitial sites
6.7: The Solid State of Matter

ionic bond
3.2: Ionic Bonding

ionic solid
6.7: The Solid State of Matter

isotopic atomic mass
1.11: Molar Mass

K

kinetic theory
6.12: Kinetic Theory of Gases

kinetic theory of gases
6.12: Kinetic Theory of Gases

L

limiting reactant
1.16: Calculations Involving a Limiting Reactant

M

matter
1.6: Atomic Theory

metallic solid
6.7: The Solid State of Matter

miscible
6.4: Solubility

molar
1.13: Concentration and Molarity

molar mass
1.11: Molar Mass
1.12: Mole-Mass Conversions

molarity
1.13: Concentration and Molarity

mole
1.11: Molar Mass

molecular mass
1.11: Molar Mass

molecular solid
6.7: The Solid State of Matter

molecules per mole
1.12: Mole-Mass Conversions

N

neutron
1.6: Atomic Theory

nonpolar covalent bond
3.3: Covalent Bonding

P

partially miscible
6.4: Solubility

polar covalent bond
3.3: Covalent Bonding

polyatomic ions
1.8: Polyatomic Ions

proton
1.6: Atomic Theory

pure covalent bond
3.3: Covalent Bonding

Q

quantum theory
2.2: Quantum Theory

R

ratio
1.12: Mole-Mass Conversions

S

saturated
1.13: Concentration and Molarity
6.4: Solubility

scale
1.10: Measurement and Scale - The Mole Concept
Separation Theory
6.15: General Separation Theory
significant figures
1.4: Significant Figures
solubility
6.4: Solubility
sp hybrid orbital
4.1: Hybrid Atomic Orbitals
sp2 hybrid orbital
4.1: Hybrid Atomic Orbitals
sp3 hybrid orbital
4.1: Hybrid Atomic Orbitals
sp3d hybrid orbital
4.1: Hybrid Atomic Orbitals
sp3d2 hybrid orbital
4.1: Hybrid Atomic Orbitals
supersaturated
6.4: Solubility

U

unit conversion
1.12: Mole-Mass Conversions
unsaturated
6.4: Solubility

V

vacancy
6.7: The Solid State of Matter

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GLOSSARY

S

Sample Word 1 | Sample Definition 1

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By Page

- AUCHE 110 - General Chemistry I - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Review - *Undeclared*
    - 1.1: The Scientific Method - *Undeclared*
    - 1.2: SI Units - *Undeclared*
    - 1.3: Measurements - *Undeclared*
    - 1.4: Significant Figures - *CC BY-NC-SA 4.0*
    - 1.5: Converting Units - *CC BY-NC-SA 4.0*
    - 1.6: Atomic Theory - *CC BY-NC-SA 4.0*
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    - 1.8: Polyatomic Ions - *CC BY-SA 4.0*
    - 1.9: An Introduction to the Periodic Table - *Undeclared*
    - 1.10: Measurement and Scale - The Mole Concept - *CC BY-SA 4.0*
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    - 1.12: Mole-Mass Conversions - *CC BY-SA 4.0*
    - 1.13: Concentration and Molarity - *CC BY-SA 4.0*
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    - 1.15: Stoichiometric Calculations- Amounts of Reactants and Products - *Undeclared*
    - 1.16: Calculations Involving a Limiting Reactant - *Undeclared*
  - 2: Atomic Structure and Periodic Trends - *Undeclared*
    - 2.1: Electromagnetic Radiation - *CC BY-NC-SA 4.0*
    - 2.2: Quantum Theory - *CC BY-NC-SA 4.0*
    - 2.3: Atomic Spectra - *CC BY-NC-SA 4.0*
    - 2.4: The Bohr Atom - *CC BY-NC-SA 4.0*
    - 2.5: Two Ideas Leading to a New Quantum Mechanics - *CC BY-NC-SA 4.0*
    - 2.6: Wave Mechanics and Quantum Numbers - *CC BY-NC-SA 4.0*
    - 2.7: Electron Spin- A Fourth Quantum Number - *CC BY-NC-SA 4.0*
    - 2.8: Orbital Shapes and Energies - *CC BY-NC-SA 4.0*
    - 2.9: Polyelectronic Atoms - *CC BY-NC-SA 4.0*
    - 2.10: The History of the Periodic Table - *CC BY-NC-SA 4.0*
    - 2.11: Electron Configurations - *CC BY-NC-SA 4.0*
    - 2.12: Magnetic Properties - *CC BY-NC-SA 4.0*
    - 2.13: Sizes of Atoms and Ions - *CC BY-NC-SA 4.0*
    - 2.14: Ionization Energy - *CC BY-NC-SA 4.0*
    - 2.15: Electron Affinity - *CC BY-NC-SA 4.0*
    - 2.16: Electronegativity - *CC BY-NC-SA 4.0*
    - 2.17: Periodic Properties of the Elements - *CC BY-NC-SA 4.0*
  - 3: Lewis Structures and Molecular Shapes - *Undeclared*
    - 3.1: Prelude to Chemical Bonding and Molecular Geometry - *CC BY 4.0*
    - 3.2: Ionic Bonding - *CC BY 4.0*
    - 3.3: Covalent Bonding - *CC BY 4.0*
    - 3.4: Lewis Theory- An Overview - *CC BY-NC-SA 4.0*
    - 3.5: Writing Lewis Structures - *CC BY-NC-SA 4.0*
    - 3.6: Resonance - *CC BY-NC-SA 4.0*
    - 3.7: Exceptions to the Octet Rule - *CC BY-NC-*

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- 3.8: Shapes of Molecules - *CC BY-NC-SA 4.0*
- 4: Bonding Theories - *Undeclared*
  - 4.1: Hybrid Atomic Orbitals - *CC BY 4.0*
  - 4.2: Multiple Covalent Bonds - *CC BY-NC-SA 4.0*
- 5: Functional Groups and IR Spectroscopy - *Undeclared*
  - 5.1: Organic Structural Representations- Bond-Line Notation - *Undeclared*
  - 5.2: Functional Groups and Classes of Organic Compounds - *CC BY-NC-SA 4.0*
  - 5.3: IR Spectroscopy Background - *CC BY-NC 4.0*
  - 5.4: Interpreting Infrared Spectra - *CC BY-SA 4.0*
  - 5.5: Identifying the Presence of Particular Groups - *CC BY-NC 4.0*
  - 5.6: The Fingerprint Region - *CC BY-NC 4.0*
- 6: States of Matter and Intermolecular Forces - *Undeclared*
  - 6.1: Overview of States of Matter - *CC BY-NC-SA 4.0*
  - 6.2: Intermolecular forces - *CC BY-NC-SA 4.0*
  - 6.3: Vapor Pressure - *CC BY-NC-SA 4.0*
  - 6.4: Solubility - *CC BY 4.0*
  - 6.5: Unique Properties of Liquids - *CC BY-NC-SA 4.0*
  - 6.6: Crystalline and Amorphous Solids - *CC BY-NC-SA 4.0*
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  - 6.9: Gas Pressure - *CC BY-NC-SA 4.0*
  - 6.10: The Ideal Gas Law - *CC BY-NC-SA 4.0*
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  - 6.13: Real Gases - *CC BY-NC-SA 4.0*
  - 6.14: Overview of Chromatography - *CC BY-NC-ND 4.0*
  - 6.15: General Separation Theory - *CC BY-NC-ND 4.0*
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  - Index - *Undeclared*
  - Glossary - *Undeclared*
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    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Review - *Undeclared*
    - 1.1: The Scientific Method - *Undeclared*
    - 1.2: SI Units - *Undeclared*
    - 1.3: Measurements - *Undeclared*
    - 1.4: Significant Figures - *CC BY-NC-SA 4.0*
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    - 1.15: Stoichiometric Calculations- Amounts of Reactants and Products - *Undeclared*
    - 1.16: Calculations Involving a Limiting Reactant - *Undeclared*
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    - 2.3: Atomic Spectra - *CC BY-NC-SA 4.0*
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    - 2.13: Sizes of Atoms and Ions - *CC BY-NC-SA 4.0*
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    - 2.16: Electronegativity - *CC BY-NC-SA 4.0*
    - 2.17: Periodic Properties of the Elements - *CC BY-NC-SA 4.0*
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    - 3.3: Covalent Bonding - *CC BY 4.0*
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  - 4.2: Multiple Covalent Bonds - *CC BY-NC-SA 4.0*
- 5: Functional Groups and IR Spectroscopy - *Undeclared*
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  - 5.2: Functional Groups and Classes of Organic Compounds - *CC BY-NC-SA 4.0*
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  - 6.10: The Ideal Gas Law - *CC BY-NC-SA 4.0*
  - 6.11: Gas Mixtures - *CC BY-NC-SA 4.0*
  - 6.12: Kinetic Theory of Gases - *CC BY-NC-SA 4.0*
  - 6.13: Real Gases - *CC BY-NC-SA 4.0*
  - 6.14: Overview of Chromatography - *CC BY-NC-ND 4.0*
  - 6.15: General Separation Theory - *CC BY-NC-ND 4.0*
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  - Index - *Undeclared*
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