

Map: Chemistry - The Molecular Nature of Matter and Change (Silberberg)

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CHAPTER OVERVIEW

1: Keys to the Study of Chemistry

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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CHAPTER OVERVIEW

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1: Keys to the Study of Chemistry

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1.1: Some Fundamental Definitions

Learning Objectives

- To classify matter.

Chemists study the structures, physical properties, and chemical properties of material substances. These consist of **matter**, which is anything that occupies space and has mass. Gold and iridium are matter, as are peanuts, people, and postage stamps. Smoke, smog, and laughing gas are matter. Energy, light, and sound, however, are not matter; ideas and emotions are also not matter.

The **mass** of an object is the quantity of matter it contains. Do not confuse an object's mass with its **weight**, which is a force caused by the gravitational attraction that operates on the object. Mass is a fundamental property of an object that does not depend on its location. In physical terms, the mass of an object is directly proportional to the force required to change its speed or direction. A more detailed discussion of the differences between weight and mass and the units used to measure them is included in Essential Skills 1 (Section 1.9). Weight, on the other hand, depends on the location of an object. An astronaut whose mass is 95 kg weighs about 210 lb on Earth but only about 35 lb on the moon because the gravitational force he or she experiences on the moon is approximately one-sixth the force experienced on Earth. For practical purposes, weight and mass are often used interchangeably in laboratories. Because the force of gravity is considered to be the same everywhere on Earth's surface, 2.2 lb (a weight) equals 1.0 kg (a mass), regardless of the location of the laboratory on Earth.

Under normal conditions, there are three distinct states of matter: solids, liquids, and gases. **Solids** are relatively rigid and have fixed shapes and volumes. A rock, for example, is a solid. In contrast, **liquids** have fixed volumes but flow to assume the shape of their containers, such as a beverage in a can. **Gases**, such as air in an automobile tire, have neither fixed shapes nor fixed volumes and expand to completely fill their containers. Whereas the volume of gases strongly depends on their temperature and **pressure** (the amount of force exerted on a given area), the volumes of liquids and solids are virtually independent of temperature and pressure. Matter can often change from one physical state to another in a process called a **physical change**. For example, liquid water can be heated to form a gas called steam, or steam can be cooled to form liquid water. However, such changes of state do not affect the chemical composition of the substance.

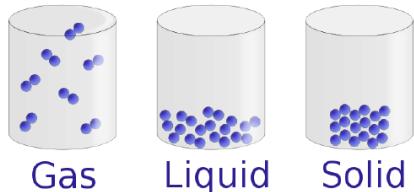


Figure 1.1.1: The Three States of Matter. Solids have a defined shape and volume. Liquids have a fixed volume but flow to assume the shape of their containers. Gases completely fill their containers, regardless of volume. Figure used with permission from Wikipedia

Pure Substances and Mixtures

A pure chemical substance is any matter that has a fixed chemical composition and characteristic properties. Oxygen, for example, is a pure chemical substance that is a colorless, odorless gas at 25°C. Very few samples of matter consist of pure substances; instead, most are mixtures, which are combinations of two or more pure substances in variable proportions in which the individual substances retain their identity. Air, tap water, milk, blue cheese, bread, and dirt are all mixtures. If all portions of a material are in the same state, have no visible boundaries, and are uniform throughout, then the material is **homogeneous**. Examples of homogeneous mixtures are the air we breathe and the tap water we drink. Homogeneous mixtures are also called solutions. Thus air is a solution of nitrogen, oxygen, water vapor, carbon dioxide, and several other gases; tap water is a solution of small amounts of several substances in water. The specific compositions of both of these solutions are not fixed, however, but depend on both source and location; for example, the composition of tap water in Boise, Idaho, is not the same as the composition of tap water in Buffalo, New York. Although most solutions we encounter are liquid, solutions can also be solid. The gray substance still used by some dentists to fill tooth cavities is a complex solid solution that contains 50% mercury and 50% of a powder that contains mostly silver, tin, and copper, with small amounts of zinc and mercury. Solid solutions of two or more metals are commonly called alloys.

If the composition of a material is not completely uniform, then it is **heterogeneous** (e.g., chocolate chip cookie dough, blue cheese, and dirt). Mixtures that appear to be homogeneous are often found to be heterogeneous after microscopic examination.

Milk, for example, appears to be homogeneous, but when examined under a microscope, it clearly consists of tiny globules of fat and protein dispersed in water. The components of heterogeneous mixtures can usually be separated by simple means. Solid-liquid mixtures such as sand in water or tea leaves in tea are readily separated by filtration, which consists of passing the mixture through a barrier, such as a strainer, with holes or pores that are smaller than the solid particles. In principle, mixtures of two or more solids, such as sugar and salt, can be separated by microscopic inspection and sorting. More complex operations are usually necessary, though, such as when separating gold nuggets from river gravel by panning. First solid material is filtered from river water; then the solids are separated by inspection. If gold is embedded in rock, it may have to be isolated using chemical methods.



Figure 1.1.2: A Heterogeneous Mixture. Under a microscope, whole milk is actually a heterogeneous mixture composed of globules of fat and protein dispersed in water. Figure used with permission from Wikipedia

Homogeneous mixtures (solutions) can be separated into their component substances by physical processes that rely on differences in some physical property, such as differences in their boiling points. Two of these separation methods are distillation and crystallization. **Distillation** makes use of differences in volatility, a measure of how easily a substance is converted to a gas at a given temperature. A simple distillation apparatus for separating a mixture of substances, at least one of which is a liquid. The most volatile component boils first and is condensed back to a liquid in the water-cooled condenser, from which it flows into the receiving flask. If a solution of salt and water is distilled, for example, the more volatile component, pure water, collects in the receiving flask, while the salt remains in the distillation flask.

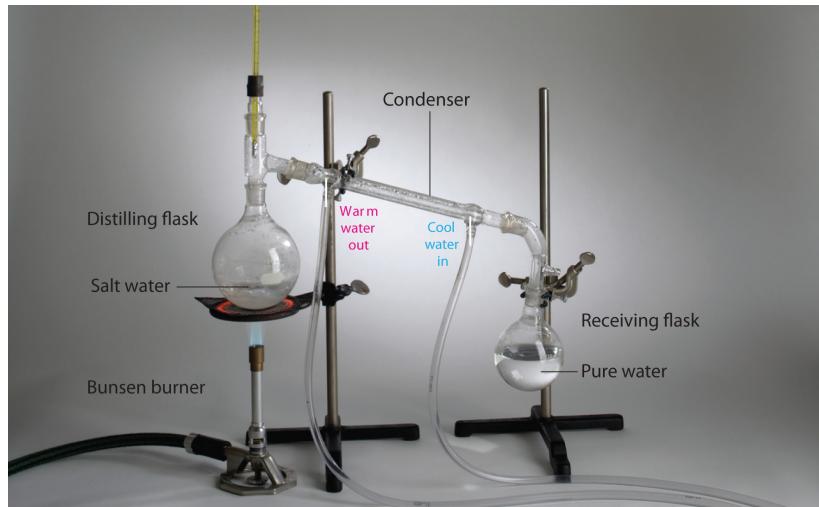


Figure 1.1.3: The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.

Mixtures of two or more liquids with different boiling points can be separated with a more complex distillation apparatus. One example is the refining of crude petroleum into a range of useful products: aviation fuel, gasoline, kerosene, diesel fuel, and lubricating oil (in the approximate order of decreasing volatility). Another example is the distillation of alcoholic spirits such as brandy or whiskey. (This relatively simple procedure caused more than a few headaches for federal authorities in the 1920s during the era of Prohibition, when illegal stills proliferated in remote regions of the United States!)

Crystallization separates mixtures based on differences in solubility, a measure of how much solid substance remains dissolved in a given amount of a specified liquid. Most substances are more soluble at higher temperatures, so a mixture of two or more

substances can be dissolved at an elevated temperature and then allowed to cool slowly. Alternatively, the liquid, called the solvent, may be allowed to evaporate. In either case, the least soluble of the dissolved substances, the one that is least likely to remain in solution, usually forms crystals first, and these crystals can be removed from the remaining solution by filtration.



Figure 1.1.4: The Crystallization of Sodium Acetate from a Concentrated Solution of Sodium Acetate in Water. The addition of a small “seed” crystal (a) causes the compound to form white crystals, which grow and eventually occupy most of the flask. Video can be found here: www.youtube.com/watch?v=BLq5NibwV5g

closeup of bulb flask containing liquid with many thin spike crystals radially emerging from the center.

Most mixtures can be separated into pure substances, which may be either elements or compounds. An **element**, such as gray, metallic sodium, is a substance that cannot be broken down into simpler ones by chemical changes; a **compound**, such as white, crystalline sodium chloride, contains two or more elements and has chemical and physical properties that are usually different from those of the elements of which it is composed. With only a few exceptions, a particular compound has the same elemental composition (the same elements in the same proportions) regardless of its source or history. The chemical composition of a substance is altered in a process called a **chemical change**. The conversion of two or more elements, such as sodium and chlorine, to a chemical compound, sodium chloride, is an example of a chemical change, often called a chemical reaction. Currently, about 118 elements are known, but millions of chemical compounds have been prepared from these 118 elements. The known elements are listed in [the periodic table](#).

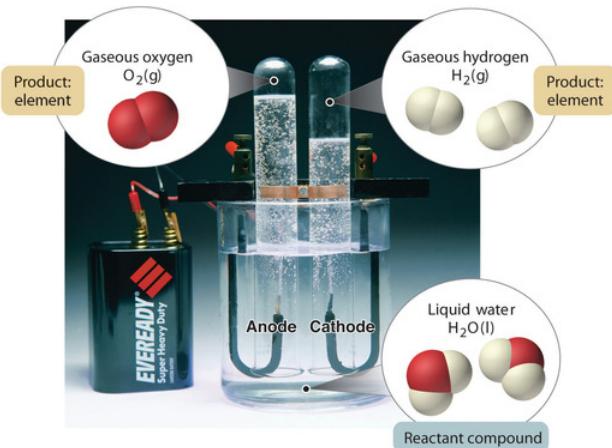


Figure 1.1.5: The Decomposition of Water to Hydrogen and Oxygen by Electrolysis. Water is a chemical compound; hydrogen and oxygen are elements.

a battery wired to an anode and cathode placed in a beaker filled with water. Two inverted test tubes are submerged in the water and placed over each of the electrodes to collect the gaseous products. Magnifying pointers show the molecular structure of water in the beaker as well as the hydrogen gas collected on the anode side and oxygen gas on the cathode side.



Different Definitions of Matter: [Different Definitions of Matter, YouTube \(opens in new window\)](#) [youtu.be]

In general, a reverse chemical process breaks down compounds into their elements. For example, water (a compound) can be decomposed into hydrogen and oxygen (both elements) by a process called electrolysis. In electrolysis, electricity provides the energy needed to separate a compound into its constituent elements (Figure 1.1.5). A similar technique is used on a vast scale to obtain pure aluminum, an element, from its ores, which are mixtures of compounds. Because a great deal of energy is required for electrolysis, the cost of electricity is by far the greatest expense incurred in manufacturing pure aluminum. Thus recycling aluminum is both cost-effective and ecologically sound.

The overall organization of matter and the methods used to separate mixtures are summarized in Figure 1.1.6.

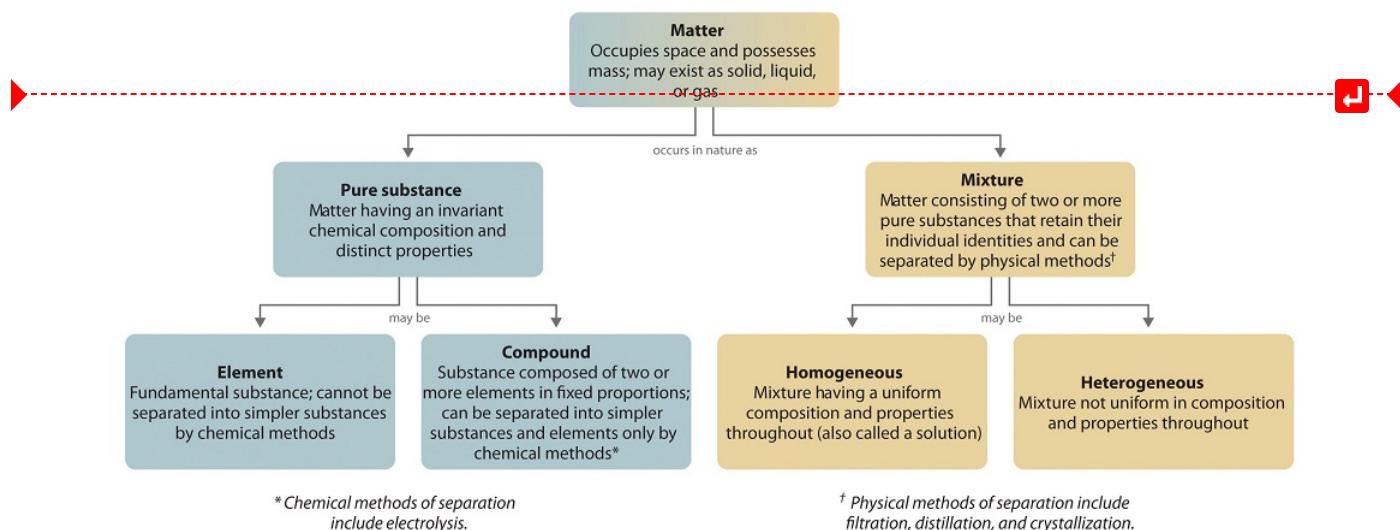


Figure 1.1.6: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

✓ Example 1.1.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

- a. filtered tea
- b. freshly squeezed orange juice
- c. a compact disc
- d. aluminum oxide, a white powder that contains a 2:3 ratio of aluminum and oxygen atoms
- e. selenium

Given: a chemical substance

Asked for: its classification

Strategy:

- A. Decide whether a substance is chemically pure. If it is pure, the substance is either an element or a compound. If a substance can be separated into its elements, it is a compound.
- B. If a substance is not chemically pure, it is either a heterogeneous mixture or a homogeneous mixture. If its composition is uniform throughout, it is a homogeneous mixture.

Solution

- a. A Tea is a solution of compounds in water, so it is not chemically pure. It is usually separated from tea leaves by filtration. **B** Because the composition of the solution is uniform throughout, it is a homogeneous mixture.
- b. A Orange juice contains particles of solid (pulp) as well as liquid; it is not chemically pure. B Because its composition is not uniform throughout, orange juice is a heterogeneous mixture.
- c. A A compact disc is a solid material that contains more than one element, with regions of different compositions visible along its edge. Hence a compact disc is not chemically pure. **B** The regions of different composition indicate that a compact disc is a heterogeneous mixture.
- d. A Aluminum oxide is a single, chemically pure compound.
- e. A Selenium is one of the known elements.

? Exercise 1.1.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

- a. white wine
- b. mercury
- c. ranch-style salad dressing
- d. table sugar (sucrose)

Answer A

solution

Answer B

element

Answer C

heterogeneous mixture

Answer D

compound



Different Definitions of Changes: [Different Definitions of Changes, YouTube](#)(*opens in new window*) [[youtub.be](#)] (*opens in new window*)

Summary

Matter can be classified according to physical and chemical properties. Matter is anything that occupies space and has mass. The three states of matter are solid, liquid, and gas. A physical change involves the conversion of a substance from one state of matter to another, without changing its chemical composition. Most matter consists of mixtures of pure substances, which can be homogeneous (uniform in composition) or heterogeneous (different regions possess different compositions and properties). Pure substances can be either chemical compounds or elements. Compounds can be broken down into elements by chemical reactions, but elements cannot be separated into simpler substances by chemical means. The properties of substances can be classified as either physical or chemical. Scientists can observe physical properties without changing the composition of the substance, whereas chemical properties describe the tendency of a substance to undergo chemical changes (chemical reactions) that change its chemical composition. Physical properties can be intensive or extensive. Intensive properties are the same for all samples; do not depend on sample size; and include, for example, color, physical state, and melting and boiling points. Extensive properties depend on the amount of material and include mass and volume. The ratio of two extensive properties, mass and volume, is an important intensive property called density.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)



Learning Objectives

- To separate physical from chemical properties and changes

All matter has physical and chemical properties. **Physical properties** are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). **Chemical properties** describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion. All samples of a pure substance have the same chemical and physical properties. For example, pure copper is always a reddish-brown solid (a physical property) and always dissolves in dilute nitric acid to produce a blue solution and a brown gas (a chemical property).

Physical properties can be extensive or intensive. **Extensive properties** vary with the amount of the substance and include mass, weight, and volume. **Intensive properties**, in contrast, do not depend on the amount of the substance; they include color, melting point, boiling point, electrical conductivity, and physical state at a given temperature. For example, elemental sulfur is a yellow crystalline solid that does not conduct electricity and has a melting point of 115.2 °C, no matter what amount is examined (Figure 1.1.1). Scientists commonly measure intensive properties to determine a substance's identity, whereas extensive properties convey information about the amount of the substance in a sample.

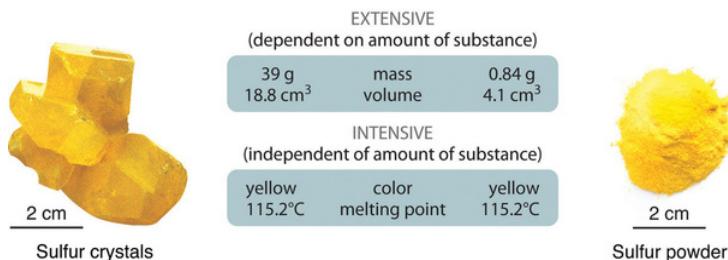


Figure 1.1.1: The Difference between Extensive and Intensive Properties of Matter. Because they differ in size, the two samples of sulfur have different extensive properties, such as mass and volume. In contrast, their intensive properties, including color, melting point, and electrical conductivity, are identical.

Although mass and volume are both extensive properties, their ratio is an important intensive property called **density** (ρ). Density is defined as mass per unit volume and is usually expressed in grams per cubic centimeter (g/cm³). As mass increases in a given volume, density also increases. For example, lead, with its greater mass, has a far greater density than the same volume of air, just as a brick has a greater density than the same volume of Styrofoam. At a given temperature and pressure, the density of a pure substance is a constant:

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

$$\rho = \frac{m}{V}$$

Pure water, for example, has a density of 0.998 g/cm³ at 25 °C. The average densities of some common substances are in Table 1.1.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will “float” (Figure 1.1.2).

Table 1.1.1: Densities of Common Substances

Substance	Density at 25 °C (g/cm ³)	Substance	Density at 25 °C (g/cm ³)
blood	1.035	corn oil	0.922
body fat	0.918	mayonnaise	0.910
whole milk	1.030	honey	1.420



Figure 1.1.2: Water and oil. Since the oil has a lower density than water, it floats on top. (CC-BY SA 3.0; [Victor Blacus](#)).

Physical Property and Change

Physical changes are changes in which no chemical bonds are broken or formed. This means that the same types of compounds or elements that were there at the beginning of the change are there at the end of the change. Because the ending materials are the same as the beginning materials, the properties (such as color, boiling point, etc) will also be the same. Physical changes involve moving molecules around, but not changing them. Some types of physical changes include:

- Changes of state (changes from a solid to a liquid or a gas and vice versa)
- Separation of a mixture
- Physical deformation (cutting, denting, stretching)
- Making solutions (special kinds of mixtures) .

As an ice cube melts, its shape changes as it acquires the ability to flow. However, its composition does not change. **Melting** is an example of a **physical change** (Figure 1.1.3), since some properties of the material change, but the identity of the matter does not. Physical changes can further be classified as reversible or irreversible. The melted ice cube may be refrozen, so melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolving is also a reversible physical change. When salt is dissolved into water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.



Figure 1.1.3: Ice Melting is a physical change. When solid water (H_2O) as ice melts into a liquid (water), it appears changed. However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass.

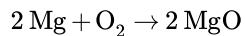
Chemical Properties and Change

Chemical changes occur when bonds are broken and/or formed between molecules or atoms. This means that one substance with a certain set of properties (such as melting point, color, taste, etc) is turned into a different substance with different properties. Chemical changes are frequently harder to reverse than physical changes.

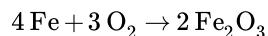
One good example of a chemical change is burning paper. In contrast to the act of ripping paper, the act of burning paper actually results in the formation of new chemicals (carbon dioxide and water, to be exact). Another example of chemical change occurs when water is formed. Each molecule contains two atoms of hydrogen and one atom of oxygen chemically bonded.

Another example of a chemical change is what occurs when natural gas is burned in your furnace. This time, before the reaction we have a molecule of methane, CH_4 , and two molecules of oxygen, O_2 , while after the reaction we have two molecules of water, H_2O , and one molecule of carbon dioxide, CO_2 . In this case, not only has the appearance changed, but the structure of the molecules has also changed. The new substances do not have the same chemical properties as the original ones. Therefore, this is a chemical change.

The combustion of magnesium metal is also chemical change (Magnesium + Oxygen \rightarrow Magnesium Oxide):



as is the rusting of iron (Iron + Oxygen \rightarrow Iron Oxide/ Rust):



Using the components of composition and properties, we have the ability to distinguish one sample of matter from the others.



Different Definitions of Changes: [Different Definitions of Changes, YouTube](#)(opens in new window) [youtu.be]



Different Definitions of Properties: [Different Definitions of Properties, YouTube](#)(opens in new window) [youtu.be]

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2. Cracolice, Peters. Basics of introductory Chemistry An active Learning Approach. Second ed. Belmont, CA 94001:Brooks/Cole, 2007.

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1.3: The Scientific Approach- Developing a Model

Learning Objectives

- To identify the components of the scientific method

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

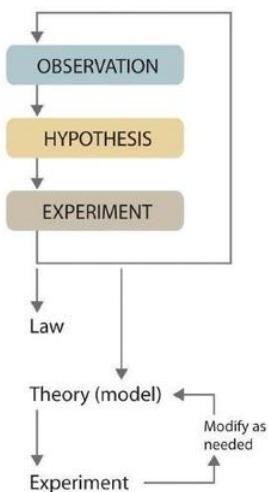


Figure 1.3.1: The Scientific Method. As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

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

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

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

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

After a hypothesis has been formed, scientists conduct experiments to test its validity. **Experiments** are systematic observations or measurements, preferably made under controlled conditions—that is, under conditions in which a single variable changes. For example, in the dinosaur extinction scenario, iridium concentrations were measured worldwide and compared. A properly designed and executed experiment enables a scientist to determine whether the original hypothesis is valid. Experiments often demonstrate that the hypothesis is incorrect or that it must be modified. More experimental data are then collected and analyzed, at which point

a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in a **law**, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply says what happens; it does not address the question of why.

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

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

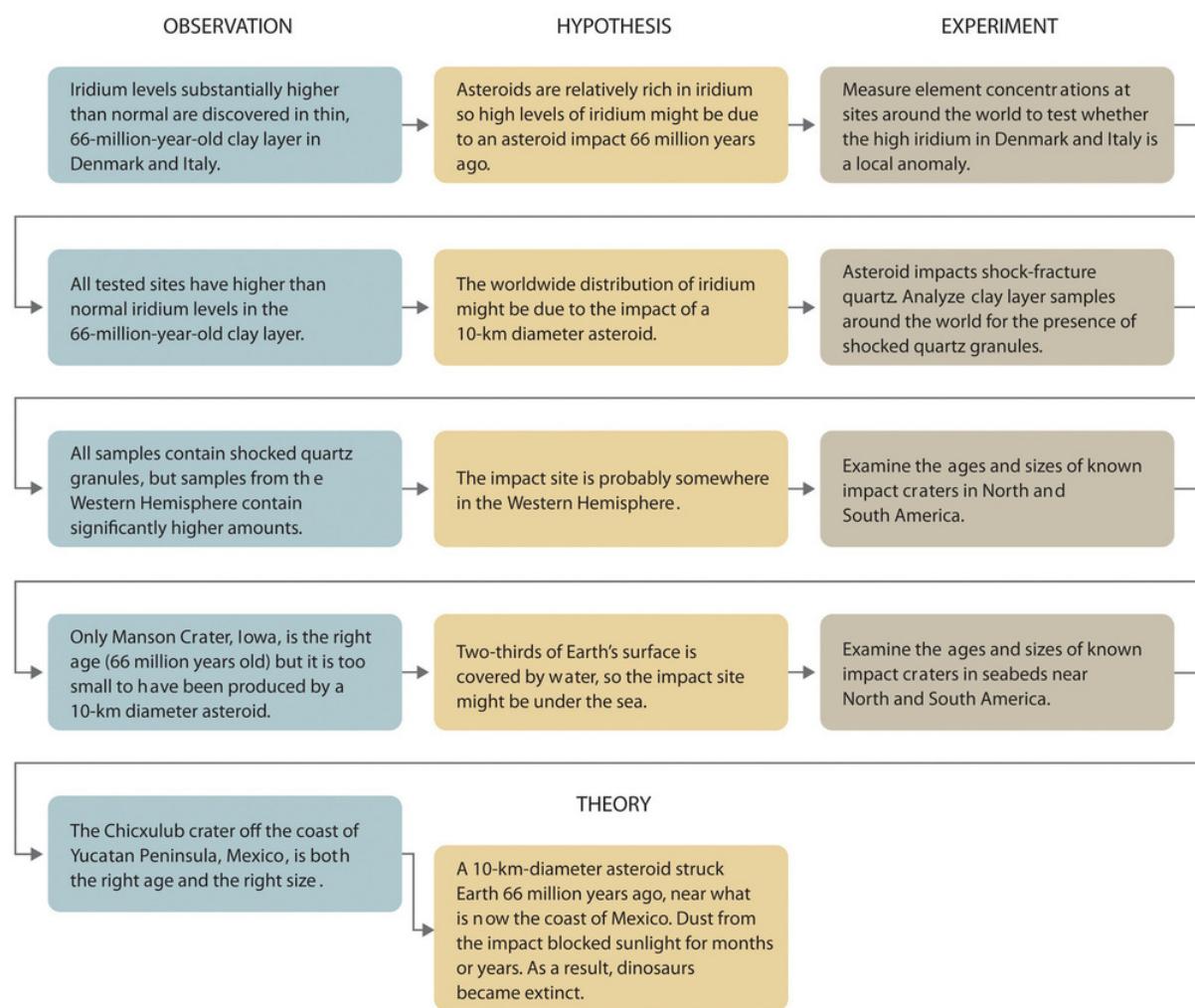


Figure 1.3.2: A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth

✓ Example 1.3.1

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

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

Given: components of the scientific method

Asked for: statement classification

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

Solution

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

? Exercise 1.3.1

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

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

Answer a

experiment

Answer b

law

Answer c

theory

Answer d

hypothesis

Answer e

qualitative observation

Answer f

quantitative observation

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

others in the field, rather than by making direct observations.

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

Summary

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



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

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1.4: Measurement and Chemical Problem Solving

Learning Objectives

- To identify the basic units of measurement of the seven fundamental properties
- Describe the names and abbreviations of the *SI base units* and the *SI decimal prefixes*.
- Define the *liter* and the *metric ton* in these units.
- Explain the meaning and use of *unit dimensions*; state the dimensions of *volume*.
- State the quantities that are needed to define a *temperature scale*, and show how these apply to the *Celsius*, *Kelvin*, and *Fahrenheit* temperature scales.
- Explain how a Torricellian *barometer* works.

Have you ever estimated a distance by “stepping it off”—that is, by counting the number of steps required to take you a certain distance? Or perhaps you have used the width of your hand, or the distance from your elbow to a fingertip to compare two dimensions. If so, you have engaged in what is probably the first kind of measurement ever undertaken by primitive mankind. The results of a measurement are always expressed on some kind of a *scale* that is defined in terms of a particular kind of *unit*. The first scales of distance were likely related to the human body, either directly (the length of a limb) or indirectly (the distance a man could walk in a day).

Ångström	1E-8 cm
Astronomical unit	1.49598 km
Bolt (U.S., cloth)	120 ft
Cable (nautical)	720 ft
Chain (engineer's)	100 ft
Chain (surveyor's)	0.1 furong
Cubit	18 in
Ell	45 in
Foot (U.S.)	12 in
Foot (British)	0.46 pace
Furlong	1/8 mile
Hand	4 in
Inch (U.S.)	1/12 ft
Inch (British)	1/36 yard
League	3 miles
Light year	9.46612 km
Mile (U.S., statute)	5280 ft
Mile (nautical)	1.853 km
Nail (British)	2.25 in
Pace (British)	30 in
Parsec	3.084E13 km
Point (printer's)	1/72 in
Rope (British)	20 ft
Span	9 in

Figure 1.4.1: Current and past units of distance

Table showing various forms of units for measuring distance used in the past and the present. Left column shows unit and right column shows value of unit measurement in terms of more commonly used units.

As civilization developed, a wide variety of measuring scales came into existence, many for the same quantity (such as length), but adapted to particular activities or trades. Eventually, it became apparent that in order for trade and commerce to be possible, these scales had to be defined in terms of standards that would allow measures to be verified, and, when expressed in different units (bushels and pecks, for example), to be correlated or converted.

History of Units

Over the centuries, hundreds of measurement units and scales have developed in the many civilizations that achieved some literate means of recording them. Some, such as those used by the Aztecs, fell out of use and were largely forgotten as these civilizations died out. Other units, such as the various systems of measurement that developed in England, achieved prominence through extension of the Empire and widespread trade; many of these were confined to specific trades or industries. The examples shown here are only some of those that have been used to measure length or distance. The history of measuring units provides a fascinating reflection on the history of industrial development.

The most influential event in the history of measurement was undoubtedly the French Revolution and the Age of Rationality that followed. This led directly to the metric system that attempted to do away with the confusing multiplicity of measurement scales by reducing them to a few fundamental ones that could be combined in order to express any kind of quantity. The metric system spread rapidly over much of the world, and eventually even to England and the rest of the U.K. when that country established closer economic ties with Europe in the latter part of the 20th Century. The United States is presently the only major country in which “metrication” has made little progress within its own society, probably because of its relative geographical isolation and its vibrant internal economy.

Science, being a truly international endeavor, adopted metric measurement very early on; engineering and related technologies have been slower to make this change, but are gradually doing so. Even within the metric system, however, a variety of units were employed to measure the same fundamental quantity; for example, energy could be expressed within the metric system in units of ergs, electron-volts, joules, and two kinds of calories. This led, in the mid-1960s, to the adoption of a more basic set of units, the *Système International (SI)* units that are now recognized as the standard for science and, increasingly, for technology of all kinds.

The Seven SI Base Units and Decimal Prefixes

In principle, any physical quantity can be expressed in terms of only seven base units (Table 1.4.1), with each base unit defined by a standard described in the [NIST Web site](#).

Table 1.4.1: The Seven Base Units

Property	Unit	Symbol
length	meter	m
mass	kilogram	kg
time	second	s
temperature (absolute)	kelvin	K
amount of substance	mole	mol
electric current	ampere	A
luminous intensity	candela	cd

A few special points about some of these units are worth noting:

- The base unit of **mass** is unique in that a decimal prefix (Table 1.4.2) is built into it; i.e., the base SI unit is not the *gram*.
- The base unit of **time** is the only one that is not metric. Numerous attempts to make it so have never garnered any success; we are still stuck with the 24:60:60 system that we inherited from ancient times. The ancient Egyptians of around 1500 BC invented the 12-hour day, and the 60:60 part is a remnant of the base-60 system that the Sumerians used for their astronomical calculations around 100 BC.
- Of special interest to Chemistry is the **mole**, the base unit for expressing the **quantity of matter**. Although the number is not explicitly mentioned in the official definition, chemists define the mole as Avogadro's number (approximately 6.02×10^{23}) of anything.

Owing to the wide range of values that quantities can have, it has long been the practice to employ prefixes such as milli and mega to indicate decimal fractions and multiples of metric units. As part of the SI standard, this system has been extended and formalized (Table 1.4.2).

Table 1.4.2: Prefixes used to scale up or down base units

Prefix	Abbreviation	Multiplier	Prefix	Abbreviation	Multiplier
--------	--------------	------------	--------	--------------	------------

Prefix	Abbreviation	Multiplier	Prefix	Abbreviation	Multiplier
peta	P	10^{15}	deci	d	10^{-1}
tera	T	10^{12}	centi	c	10^{-2}
giga	G	10^9	milli	m	10^{-3}
mega	M	10^6	micro	μ	10^{-6}
kilo	k	10^3	nano	n	10^{-9}
hecto	h	10^2	pico	p	10^{-12}
deca	da	10	femto	f	10^{-15}

◀ Pseudo-Si Units

There is a category of units that are “honorary” members of the SI in the sense that it is acceptable to use them along with the base units defined above. These include such mundane units as the hour, minute, and degree (of angle), etc., but the three shown here are of particular interest to chemistry, and you will need to know them.

Pseudo-Si Units

liter (litre)	L	$1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$
metric ton	t	$1 \text{ t} = 10^3 \text{ kg}$
united atomic mass unit (amu)	u	$1 \text{ u} = 1.66054 \times 10^{-27} \text{ kg}$

Derived Units and Dimensions

Most of the physical quantities we actually deal with in science and also in our daily lives, have units of their own: volume, pressure, energy and electrical resistance are only a few of hundreds of possible examples. It is important to understand, however, that all of these can be expressed in terms of the SI base units; they are consequently known as *derived units*. In fact, most physical quantities can be expressed in terms of one or more of the following five fundamental units:

- mass (M)
- length (L)
- time (T)
- electric charge (Q)
- temperature (Θ theta)

Consider, for example, the unit of *volume*, which we denote as V. To measure the volume of a rectangular box, we need to multiply the lengths as measured along the three coordinates:

$$V = x \cdot y \cdot z$$

We say, therefore, that volume has the dimensions of length-cubed:

$$\dim\{V\} = L^3$$

Thus the units of volume will be m^3 (in the SI) or cm^3 , ft^3 (English), etc. Moreover, any formula that calculates a volume must contain within it the L^3 dimension; thus the volume of a sphere is $4/3\pi r^3$. The *dimensions* of a unit are the powers which M, L, t, Q and Θ must be given in order to express the unit. Thus,

$$\dim\{V\} = M^0 L^3 T^0 Q^0 \Theta^0$$

as given above.

There are several reasons why it is worthwhile to consider the dimensions of a unit.

1. Perhaps the most important use of dimensions is to help us understand the relations between various units of measure and thereby get a better understanding of their physical meaning. For example, a look at the dimensions of the frequently confused electrical terms resistance and resistivity should enable you to explain, in plain words, the difference between them.
2. By the same token, the dimensions essentially tell you how to calculate any of these quantities, using whatever specific units you wish. (Note here the distinction between dimensions and units.)
3. Just as you cannot add apples to oranges, an expression such as $a = b + cx^2$ is meaningless unless the dimensions of each side are identical. (Of course, the two sides should work out to the same units as well.)
4. Many quantities must be dimensionless—for example, the variable x in expressions such as $\log x$, e^x , and $\sin x$. Checking through the dimensions of such a quantity can help avoid errors.

The formal, detailed study of dimensions is known as *dimensional analysis* and is a topic in any basic physics course.

✓ Example 1.4.1

Find the dimensions of energy.

Solution

When mechanical work is performed on a body, its energy increases by the amount of work done, so the two quantities are equivalent and we can concentrate on work. The latter is the product of the force applied to the object and the distance it is displaced. From Newton's law, force is the product of mass and acceleration, and the latter is the rate of change of velocity, typically expressed in meters per second per second. Combining these quantities and their dimensions yields the result shown in Table 1.4.1.

Table 1.4.3: Dimensions of units commonly used in Chemistry

Q	M	L	t	quantity	SI unit, other typical units
1	-	-	-	electric charge	coulomb
-	1	-	-	mass	kilogram, gram, metric ton, pound
-	-	1	-	length	meter, foot, mile
-	-	-	1	time	second, day, year
-	-	3	-	volume	liter, cm^3 , quart, fluidounce
-	1	-3	-	density	kg m^{-3} , g cm^{-3}
-	1	1	-2	force	newton, dyne
-	1	-1	-2	pressure	pascal, atmosphere, torr

Q	M	L	t	quantity	SI unit, other typical units
-	1	2	-2	energy	joule, erg, calorie, electron-volt
-	1	2	-3	power	watt
1	1	2	-2	electric potential	volt
1	-	-	-1	electric current	ampere
1	1	1	-2	electric field intensity	volt m ⁻¹
-2	1	2	-1	electric resistance	ohm
2	1	3	-1	electric resistivity	-
2	-1	-2	1	electric conductance	siemens, mho

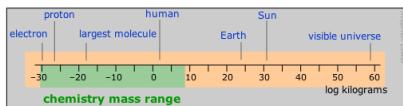
Dimensional analysis is widely employed when it is necessary to convert one kind of unit into another, and chemistry students often use it in "chemical arithmetic" calculations, in which context it is also known as the "Factor-Label" method. In this section, we will look at some of the quantities that are widely encountered in Chemistry, and at the units in which they are commonly expressed. In doing so, we will also consider the actual range of values these quantities can assume, both in nature in general, and also within the subset of nature that chemistry normally addresses. In looking over the various units of measure, it is interesting to note that their unit values are set close to those encountered in everyday human experience

Mass is not weight

These two quantities are widely confused. Although they are often used synonymously in informal speech and writing, they have different dimensions: *weight* is the *force* exerted on a mass by the local gravitational field:

$$f = ma = mg \quad (1.4.1)$$

where g is the acceleration of gravity. While the nominal value of the latter quantity is 9.80 m s^{-2} at the Earth's surface, its exact value varies locally. Because it is a force, the SI unit of weight is properly the *newton*, but it is common practice (except in physics classes!) to use the terms "weight" and "mass" interchangeably, so the units *kilograms* and *grams* are acceptable in almost all ordinary laboratory contexts.



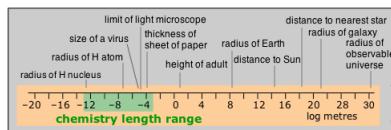
Numeric scale in terms of log kilogram. Range is negative 30 to 60 with intervals of 10. The range from negative 30 to 8 is highlighted in green to show chemistry mass range.

Please note that in this diagram and in those that follow, the numeric scale represents the *logarithm* of the number shown. For example, the mass of the electron is 10^{-30} kg .

The range of masses spans 90 orders of magnitude, more than any other unit. The range that chemistry ordinarily deals with has greatly expanded since the days when a microgram was an almost inconceivably small amount of material to handle in the laboratory; this lower limit has now fallen to the atomic level with the development of tools for directly manipulating these particles. The upper level reflects the largest masses that are handled in industrial operations, but in the recently developed fields of geochemistry and environmental chemistry, the range can be extended indefinitely. Flows of elements between the various regions of the environment (atmosphere to oceans, for example) are often quoted in teragrams.

Length

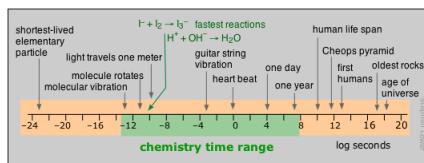
Chemists tend to work mostly in the moderately-small part of the distance range. Those who live in the lilliputian world of crystal- and molecular structures and atomic radii find the *picometer* a convenient currency, but one still sees the older non-SI unit called the *Ångstrom* used in this context: $1\text{\AA} = 10^{-10} \text{ m} = 100\text{pm}$. Nanotechnology, the rage of the present era, also resides in this realm. The largest polymeric molecules and colloids define the top end of the particulate range; beyond that, in the normal world of doing things in the lab, the *centimeter* and occasionally the *millimeter* commonly rule.



Numeric scale in terms of log meters. Range is negative 20 to 30 with intervals of 4. The range from negative 12 to negative 4 is highlighted in green to show chemistry length range.

Time

For humans, time moves by the heartbeat; beyond that, it is the motions of our planet that count out the hours, days, and years that eventually define our lifetimes. Beyond the few thousands of years of history behind us, those years-to-the-powers-of-tens that are the fare for such fields as evolutionary biology, geology, and cosmology, cease to convey any real meaning for us. Perhaps this is why so many people are not very inclined to accept their validity.

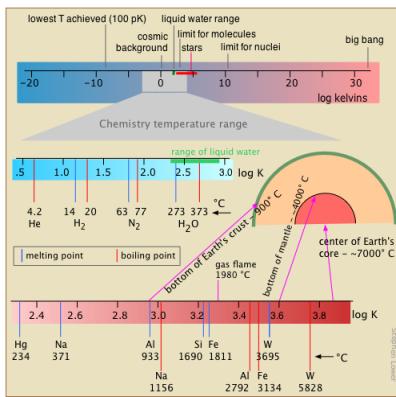


Numeric scale in terms of log seconds. Range is negative 24 to 20 with intervals of 4. The range from negative 12 to 8 is highlighted in green to show chemistry time range.

Most of what actually takes place in the chemist's test tube operates on a far shorter time scale, although there is no limit to how slow a reaction can be; the upper limits of those we can directly study in the lab are in part determined by how long a graduate student can wait around before moving on to gainful employment. Looking at the microscopic world of atoms and molecules themselves, the time scale again shifts us into an unreal world where numbers tend to lose their meaning. You can gain some appreciation of the duration of a nanosecond by noting that this is about how long it takes a beam of light to travel between your two outstretched hands. In a sense, the material foundations of chemistry itself are defined by time: neither a new element nor a molecule can be recognized as such unless it lasts long enough to have its "picture" taken through measurement of its distinguishing properties.

Temperature

Temperature, the measure of thermal intensity, spans the narrowest range of any of the base units of the chemist's measurement toolbox. The reason for this is tied into temperature's meaning as a measure of the intensity of thermal kinetic energy. Chemical change occurs when atoms are jostled into new arrangements, and the weakness of these motions brings most chemistry to a halt as absolute zero is approached. At the upper end of the scale, thermal motions become sufficiently vigorous to shake molecules into atoms, and eventually, as in stars, strip off the electrons, leaving an essentially reaction-less gaseous fluid, or plasma, of bare nuclei (ions) and electrons.



Numeric scale in terms of log Kelvins. Range is negative 20 to 30 with intervals of 10. The range from negative 3 to 4 is highlighted to show chemistry temperature range. This range is magnified further to show two numeric scales, one highlighting the lower range and the other the upper range. Melting and boiling points of different compounds are also shown on the scale.

The degree is really an *increment* of temperature, a fixed fraction of the distance between two defined reference points on a *temperature scale*.

Although rough means of estimating and comparing temperatures have been around since AD 170, the first mercury thermometer and temperature scale were introduced in Holland in 1714 by Gabriel Daniel Fahrenheit. Fahrenheit established three fixed points on his thermometer. Zero degrees was the temperature of an ice, water, and salt mixture, which was about the coldest temperature that could be reproduced in a laboratory of the time. When he omitted salt from the slurry, he reached his second fixed point when the water-ice combination stabilized at "the thirty-second degree." His third fixed point was "found at the ninety-sixth degree, and the spirit expands to this degree when the thermometer is held in the mouth or under the armpit of a living man in good health."

After Fahrenheit died in 1736, his thermometer was recalibrated using 212 degrees, the temperature at which water boils, as the upper fixed point. Normal human body temperature registered 98.6 rather than 96. In 1743, the Swedish astronomer Anders Celsius devised the aptly-named *centigrade* scale that places exactly 100 degrees between the two reference points defined by the freezing and boiling points of water.

When we say that the temperature is so many degrees, we must specify the particular scale on which we are expressing that temperature. A temperature scale has two defining characteristics, both of which can be chosen arbitrarily:

- The temperature that corresponds to 0° on the scale;
- The magnitude of the *unit increment* of temperature—that is, the size of the *degree*.

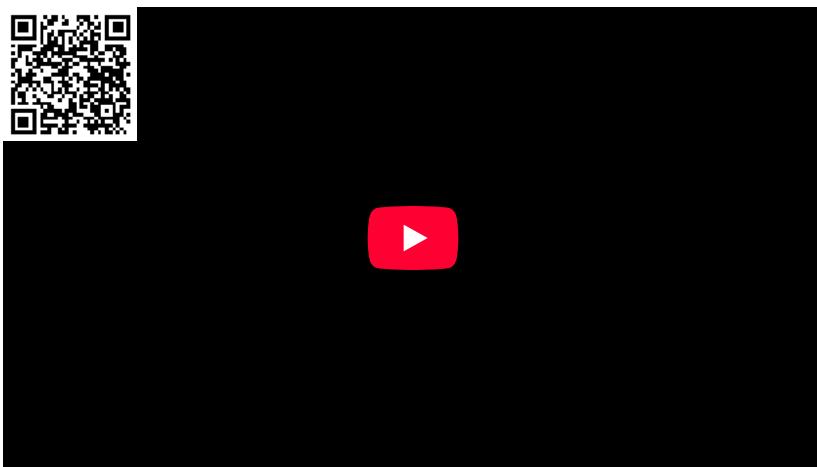
To express a temperature given on one scale in terms of another, it is necessary to take both of these factors into account. The key to temperature conversions is easy if you bear in mind that between the so-called ice- and steam-points of water there are 180 Fahrenheit degrees, but only 100 Celsius degrees, making the $F^\circ/100/180 = 5/9$ the magnitude of the C° . Note the distinction between " ${}^\circ C$ " (a *temperature*) and " C° " (a *temperature increment*). Because the ice point is at 32°F, the two scales are offset by this amount. If you remember this, there is no need to memorize a conversion formula; you can work it out whenever you need it.

Near the end of the 19th Century when the physical significance of temperature began to be understood, the need was felt for a temperature scale whose zero really means zero—that is, the complete absence of thermal motion. This gave rise to the *absolute temperature scale* whose zero point is $-273.15\text{ }^\circ C$, but which retains the same degree magnitude as the Celsius scale. This eventually got renamed after Lord Kelvin (William Thompson); thus the Celsius degree became the *kelvin*. Thus we can now express an increment such as five C° as "five kelvins"

The "other" Absolute Scale

In 1859 the Scottish engineer and physicist William J. M. Rankine proposed an absolute temperature scale based on the Fahrenheit degree. Absolute zero (0° Ra) corresponds to -459.67° F . The Rankine scale has been used extensively by those same American and English engineers who delight in expressing heat capacities in units of BTUs per pound per F° .

The importance of absolute temperature scales is that absolute temperatures can be entered directly in all the fundamental formulas of physics and chemistry in which temperature is a variable.



Units of Temperature: [Units of Temperature, YouTube](#)(opens in new window) [youtu.be] (opens in new window)

Pressure

Pressure is the measure of the *force* exerted on a unit area of surface. Its SI units are therefore newtons per square meter, but we make such frequent use of pressure that a derived SI unit, the *pascal*, is commonly used:

$$1 \text{ Pa} = 1 \text{ N m}^{-2}$$

The concept of pressure first developed in connection with studies relating to the atmosphere and vacuum that were carried out in the 17th century.

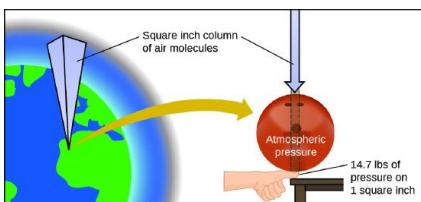
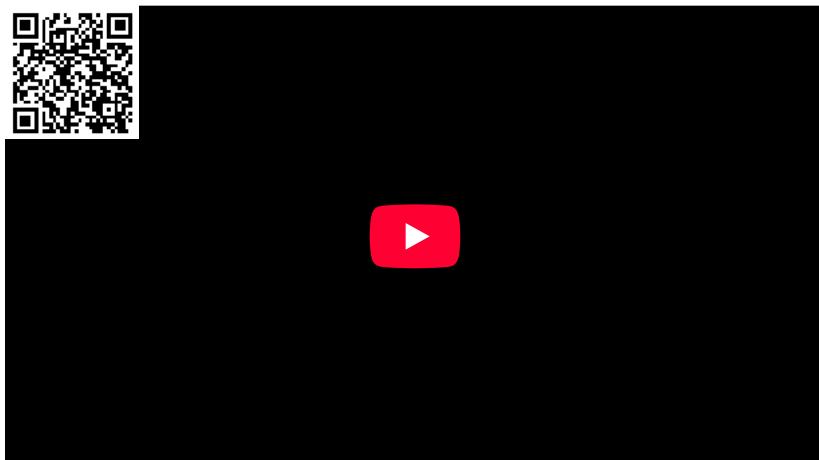


Diagram of Earth with a square inch column of air molecules extending to the atmosphere. This column points to an arrow pointing down on a bowling ball resting on a human thumbnail placed on top of a table.

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car below. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is twice the usual pressure, and the sensation is unpleasant.



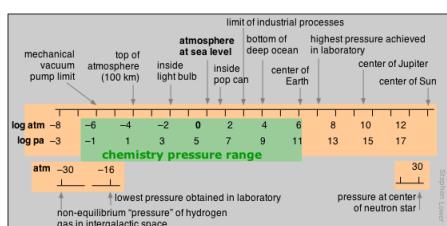
Video 1.4.1: A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased. A smaller scale demonstration of this phenomenon is briefly explained.

The molecules of a gas are in a state of constant thermal motion, moving in straight lines until experiencing a collision that exchanges momentum between pairs of molecules and sends them bouncing off in other directions. This leads to a completely random distribution of the molecular velocities both in speed and direction—or it would in the absence of the Earth's gravitational field which exerts a tiny downward force on each molecule, giving motions in that direction a very slight advantage. In an ordinary container this effect is too small to be noticeable, but in a very tall column of air the effect adds up: the molecules in each vertical layer experience more downward-directed hits from those above it. The resulting force is quickly randomized, resulting in an increased pressure in that layer which is then propagated downward into the layers below.

At sea level, the total mass of the sea of air pressing down on each 1-cm^2 of surface is about 1034 g, or 10340 kg m^{-2} . The force (weight) that the Earth's gravitational acceleration g exerts on this mass is

$$f = ma = mg = (10340 \text{ kg})(9.81 \text{ m s}^{-2}) = 1.013 \times 10^5 \text{ kg m s}^{-2} = 1.013 \times 10^5 \text{ N}$$

resulting in a pressure of $1.013 \times 10^5 \text{ N m}^{-2} = 1.013 \times 10^5 \text{ Pa}$. The actual pressure at sea level varies with atmospheric conditions, so it is customary to define standard atmospheric pressure as $1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$ or 101.325 kPa . Although the standard atmosphere is not an SI unit, it is still widely employed. In meteorology, the *bar*, exactly $1.000 \times 10^5 = 0.967 \text{ atm}$, is often used.



Numeric scale given in terms of log atm and log pascals respectively. Range is negative 8 to 12 with intervals of 2 atm and negative 3 to 17 with intervals of 2 pascals. The range from negative 6 to 6 atm and negative 1 to 11 pascals is highlighted to show chemistry pressure range.

The Barometer

In the early 17th century, the Italian physicist and mathematician Evangelista Torricelli invented a device to measure atmospheric pressure. The *Torricellian barometer* consists of a vertical glass tube closed at the top and open at the bottom. It is filled with a liquid, traditionally mercury, and is then inverted, with its open end immersed in the container of the same liquid. The liquid level in the tube will fall until its own weight is balanced by the vertical force transmitted hydrostatically to the column by the downward force of the atmosphere acting on the liquid surface in the open container. Torricelli was also the first to recognize that the space above the mercury constituted a vacuum, and is credited with being the first to create a vacuum.

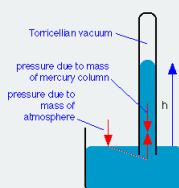
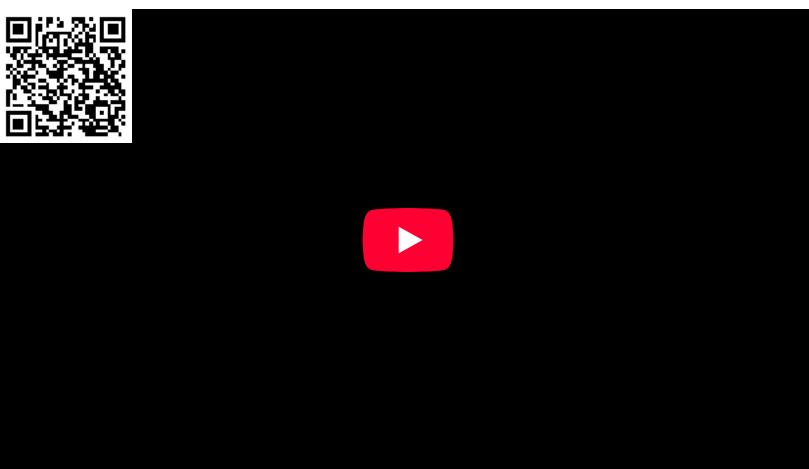


Diagram showing a barometer setup with arrows pointing on the surface of the liquid to indicate pressure due to atmosphere as well as arrow pointing up in the vertical tube to show height of liquid in the tube.

One standard atmosphere will support a column of mercury that is 760 mm high, so the “millimeter of mercury”, now more commonly known as the torr, has long been a common pressure unit in the sciences: 1 atm = 760 torr.



International System of Units (SI Units): [International System of Units \(SI Units\)](#), [YouTube](#)(opens in new window) [youtu.be]

Summary

The natural sciences begin with **observation**, and this usually involves **numerical measurements** of quantities such as length, volume, density, and temperature. Most of these quantities have **units** of some kind associated with them, and these units must be retained when you use them in calculations. Measuring units can be defined in terms of a very small number of fundamental ones that, through "dimensional analysis", provide insight into their derivation and meaning, and must be understood when converting between different unit systems.

Contributions

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- 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>.

Learning Objectives

- To be introduced to the dimensional analysis and how it can be used to aid basic chemistry problem solving.
- To use dimensional analysis to identify whether an equation is set up correctly in a numerical calculation
- To use dimensional analysis to facilitate the conversion of units.

Dimensional analysis is amongst the most valuable tools physical scientists use. Simply put, it is the conversion between an amount in one unit to the corresponding amount in a desired unit using various conversion factors. This is valuable because certain measurements are more accurate or easier to find than others.

A Macroscopic Example: Party Planning

If you have every planned a party, you have used dimensional analysis. The amount of beer and munchies you will need depends on the number of people you expect. For example, if you are planning a Friday night party and expect 30 people you might estimate you need to go out and buy 120 bottles of sodas and 10 large pizza's. How did you arrive at these numbers? The following indicates the type of dimensional analysis solution to party problem:

$$(30 \cancel{\text{humans}}) \times \left(\frac{4 \text{ sodas}}{1 \cancel{\text{human}}} \right) = 120 \text{ sodas} \quad (\text{Eq1})$$
$$(30 \cancel{\text{humans}}) \times \left(\frac{0.333 \text{ pizzas}}{1 \cancel{\text{human}}} \right) = 10 \text{ pizzas} \quad (1.4.2)$$

Notice that the units that canceled out are lined out and only the desired units are left (discussed more below). Finally, in going to buy the soda, you perform another dimensional analysis: should you buy the sodas in six-packs or in cases?

$$(120 \text{ sodas}) \times \left(\frac{1 \text{ six pack}}{6 \text{ sodas}} \right) = 20 \text{ six packs} \quad (1.4.3)$$

$$(120 \text{ sodas}) \times \left(\frac{1 \text{ case}}{24 \text{ sodas}} \right) = 5 \text{ cases} \quad (1.4.4)$$

Realizing that carrying around 20 six packs is a real headache, you get 5 cases of soda instead.

In this party problem, we have used dimensional analysis in two different ways:

- In the first application (Equations 1.4.1 and Equation 1.4.2), dimensional analysis was used to calculate how much soda is needed. This is based on knowing: (1) how much soda we need for one person and (2) how many people we expect; likewise for the pizza.
- In the second application (Equations 1.4.3 and 1.4.4), dimensional analysis was used to **convert units** (i.e. from individual sodas to the equivalent amount of six packs or cases)

Using Dimensional Analysis to Convert Units

Consider the conversion in Equation 1.4.3:

$$(120 \text{ sodas}) \times \left(\frac{1 \text{ six pack}}{6 \text{ sodas}} \right) = 20 \text{ six packs} \quad (1.4.5)$$

If we ignore the numbers for a moment, and just look at the units (i.e. **dimensions**), we have:

$$\text{soda} \times \left(\frac{\text{six pack}}{\text{ sodas}} \right)$$

We can treat the dimensions in a similar fashion as other numerical analyses (i.e. any number divided by itself is 1). Therefore:

$$\text{soda} \times \left(\frac{\text{six pack}}{\text{sodas}} \right) = \cancel{\text{soda}} \times \left(\frac{\text{six pack}}{\cancel{\text{sodas}}} \right)$$

So, the dimensions of the numerical answer will be "six packs".

How can we use dimensional analysis to be sure we have set up our equation correctly? Consider the following alternative way to set up the above unit conversion analysis:

$$120 \cancel{\text{soda}} \times \left(\frac{6 \text{ sodas}}{\cancel{\text{six pack}}} \right) = 720 \frac{\text{sodas}^2}{1 \text{ six pack}}$$

- While it is correct that there are 6 sodas in one six pack, the above equation yields a value of 720 with units of **sodas²/six pack**.
- These rather bizarre units indicate that the equation has been setup **incorrectly** (and as a consequence you will have a ton of extra soda at the party).

Using Dimensional Analysis in Calculations

In the above case it was relatively straightforward keeping track of units during the calculation. What if the calculation involves powers, etc? For example, the equation relating kinetic energy to mass and velocity is:

$$E_{\text{kinetics}} = \frac{1}{2} \text{mass} \times \text{velocity}^2 \quad (1.4.6)$$

An example of units of mass is kilograms (kg) and velocity might be in meters/second (m/s). What are the dimensions of E_{kinetic} ?

$$(kg) \times \left(\frac{m}{s} \right)^2 = \frac{kg \cdot m^2}{s^2}$$

The $\frac{1}{2}$ factor in Equation 1.4.6 is neglected since pure numbers have no units. Since the velocity is squared in Equation 1.4.6, the **dimensions** associated with the numerical value of the velocity are also squared. We can double check this by knowing the Joule (J) is a measure of energy, and as a composite unit can be decomposed thusly:

$$1 \text{ J} = kg \frac{m^2}{s^2}$$

Units of Pressure

Pressure (P) is a measure of the Force (F) per unit area (A):

$$P = \frac{F}{A}$$

Force, in turn, is a measure of the acceleration (a) on a mass (m):

$$F = m \times a$$

Thus, pressure (P) can be written as:

$$P = \frac{m \times a}{A}$$

What are the units of pressure from this relationship? (Note: acceleration is the change in velocity per unit time)

$$P = \frac{kg \times \frac{m}{s^2}}{m \cdot s}$$

We can simplify this description of the units of Pressure by dividing numerator and denominator by m :

$$P = \frac{\frac{kg}{s^2}}{m} = \frac{kg}{m \cdot s^2}$$

In fact, these are the units of a the composite *Pascal* (Pa) unit and is the **SI measure** of pressure.

Performing Dimensional Analysis

The use of units in a calculation to ensure that we obtain the final proper units is called **dimensional analysis**. For example, if we observe experimentally that an object's potential energy is related to its mass, its height from the ground, and to a gravitational force, then when multiplied, the units of mass, height, and the force of gravity must give us units corresponding to those of energy.

Energy is typically measured in joules, calories, or electron volts (eV), defined by the following expressions:

- $1 \text{ J} = 1 (\text{kg} \cdot \text{m}^2)/\text{s}^2 = 1 \text{ coulomb-volt}$
- $1 \text{ cal} = 4.184 \text{ J}$
- $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

Performing dimensional analysis begins with finding the appropriate **conversion factors**. Then, you simply multiply the values together such that the units cancel by having equal units in the numerator and the denominator. To understand this process, let us walk through a few examples.

✓ Example 1.4.1

Imagine that a chemist wants to measure out 0.214 mL of benzene, but lacks the equipment to accurately measure such a small volume. The chemist, however, is equipped with an analytical balance capable of measuring to $\pm 0.0001 \text{ g}$. Looking in a reference table, the chemist learns the density of benzene ($\rho = 0.8765 \text{ g/mL}$). How many grams of benzene should the chemist use?

Solution

$$0.214 \text{ mL} \times \left(\frac{0.8765 \text{ g}}{1 \text{ mL}} \right) = 0.187571 \text{ g}$$

Notice that the mL are being divided by mL, an equivalent unit. We can cancel these out, which results with the 0.187571 g. However, this is not our final answer, since this result has too many **significant figures** and must be rounded down to three significant digits. This is because 0.214 mL has three significant digits and the conversion factor had four significant digits. Since 5 is greater than or equal to 5, we must round the preceding 7 up to 8.

Hence, the chemist should weigh out 0.188 g of benzene to have 0.214 mL of benzene.

✓ Example 1.4.2

To illustrate the use of dimensional analysis to solve energy problems, let us calculate the kinetic energy in joules of a 320 g object traveling at 123 cm/s.

Solution

To obtain an answer in joules, we must convert grams to kilograms and centimeters to meters. Using Equation 1.4.6, the calculation may be set up as follows:

$$\text{KE} = \frac{1}{2}mv^2 = \frac{1}{2}(g)(\cancel{kg})(\cancel{g}) \left(\frac{\cancel{kg}}{1000 \text{ g}} \right) \left(\frac{\cancel{m}}{\cancel{cm}} \right)^2 = \frac{1}{2} \frac{\cancel{kg} \cdot \cancel{m}^2}{\cancel{kg} \cdot \cancel{m}^2} (\cancel{s}^2) = \frac{1}{2} \frac{320 \text{ g}}{1000 \text{ g}} \text{ kg} \cdot \cancel{m}^2 \cdot \cancel{s}^2$$

Alternatively, the conversions may be carried out in a stepwise manner:

Step 1: convert g to kg

$$320 \text{ g} \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 0.320 \text{ kg}$$

Step 2: convert cm to m

$$123 \text{ cm} \left(\frac{1 \text{ m}}{100 \text{ cm}} \right) = 1.23 \text{ m}$$

Now the natural units for calculating joules is used to get final results

$$\begin{aligned} KE &= \frac{1}{2}0.320 \text{ kg}(1.23 \text{ m})^2 \\ &= \frac{1}{2}0.320 \text{ kg} \left(1.513 \frac{\text{m}^2}{\text{s}^2} \right) = 0.242 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} = 0.242 \text{ J} \end{aligned}$$

Of course, steps 1 and 2 can be done in the opposite order with no effect on the final results. However, this second method involves an additional step.

✓ Example 1.4.3

Now suppose you wish to report the number of kilocalories of energy contained in a 7.00 oz piece of chocolate in units of kilojoules per gram.

Solution

To obtain an answer in kilojoules, we must convert 7.00 oz to grams and kilocalories to kilojoules. Food reported to contain a value in Calories actually contains that same value in kilocalories. If the chocolate wrapper lists the caloric content as 120 Calories, the chocolate contains 120 kcal of energy. If we choose to use multiple steps to obtain our answer, we can begin with the conversion of kilocalories to kilojoules:

$$120 \text{ kcal} \left(\frac{1000 \text{ cal}}{1 \text{ kcal}} \right) \left(\frac{4.184 \text{ J}}{1 \text{ cal}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = 502 \text{ kJ}$$

We next convert the 7.00 oz of chocolate to grams:

$$7.00 \text{ oz} \left(\frac{28.35 \text{ g}}{1 \text{ oz}} \right) = 199 \text{ g}$$

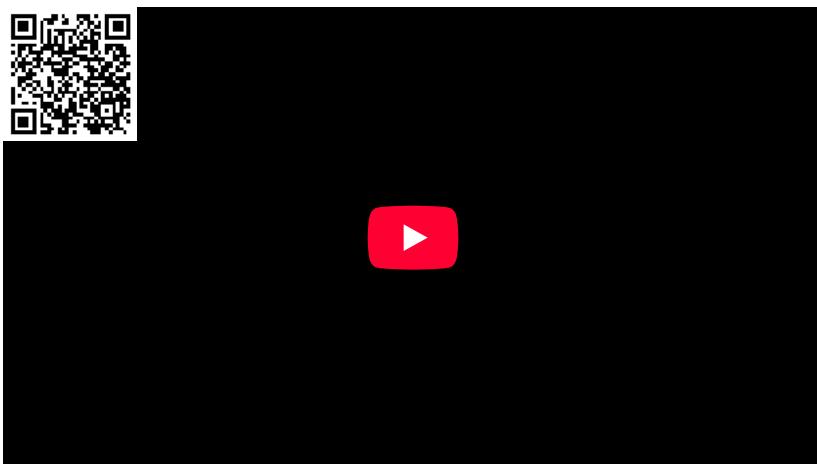
The number of kilojoules per gram is therefore

$$\frac{502 \text{ kJ}}{199 \text{ g}} = 2.52 \text{ kJ/g}$$

Alternatively, we could solve the problem in one step with all the conversions included:

$$\left(\frac{120 \text{ kcal}}{7.00 \text{ oz}} \right) \left(\frac{1000 \text{ cal}}{1 \text{ kcal}} \right) \left(\frac{4.184 \text{ J}}{1 \text{ cal}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \left(\frac{1 \text{ oz}}{28.35 \text{ g}} \right) = 2.53 \text{ kJ/g}$$

The discrepancy between the two answers is attributable to rounding to the correct number of significant figures for each step when carrying out the calculation in a stepwise manner. Recall that all digits in the calculator should be carried forward when carrying out a calculation using multiple steps. In this problem, we first converted kilocalories to kilojoules and then converted ounces to grams.



Converting Between Units: Converting Between Units, YouTube([opens in new window](#)) [youtu.be]

Summary

Dimensional analysis is used in numerical calculations, and in converting units. It can help us identify whether an equation is set up correctly (i.e. the resulting units should be as expected). Units are treated similarly to the associated numerical values, i.e., if a variable in an equation is supposed to be squared, then the associated dimensions are squared, etc.

Contributors and Attributions

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1.5: Uncertainty in Measurement- Significant Figures

Learning Objectives

- To introduce the fundamental mathematical skills you will need to complete basic chemistry questions and problems

Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal of scientists is to obtain measured values that are both accurate and precise.

Suppose, for example, that the mass of a sample of gold was measured on one balance and found to be 1.896 g. On a different balance, the same sample was found to have a mass of 1.125 g. Which was correct? Careful and repeated measurements, including measurements on a calibrated third balance, showed the sample to have a mass of 1.895 g. The masses obtained from the three balances are in the following table:

Masses Obtained from the three balances

Balance 1	Balance 2	Balance 3
1.896 g	1.125 g	1.893 g
1.895 g	1.158 g	1.895 g
1.894 g	1.067 g	1.895 g

Whereas the measurements obtained from balances 1 and 3 are reproducible (precise) and are close to the accepted value (accurate), those obtained from balance 2 are neither. Even if the measurements obtained from balance 2 had been precise (if, for example, they had been 1.125, 1.124, and 1.125), they still would not have been accurate. We can assess the precision of a set of measurements by calculating the average deviation of the measurements as follows:

1. Calculate the average value of all the measurements:

$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}} \quad (1.5.1)$$

2. Calculate the deviation of each measurement, which is the absolute value of the difference between each measurement and the average value:

$$\text{deviation} = |\text{measurement} - \text{average}| \quad (1.5.2)$$

where $| |$ means absolute value (i.e., convert any negative number to a positive number).

3. Add all the deviations and divide by the number of measurements to obtain the average deviation:

$$\text{average} = \frac{\text{sum of deviations}}{\text{number of measurements}} \quad (1.5.3)$$

Then we can express the precision as a percentage by dividing the average deviation by the average value of the measurements and multiplying the result by 100. In the case of balance 2, the average value is

$$\frac{1.125 \text{ g} + 1.158 \text{ g} + 1.067 \text{ g}}{3} = 1.117 \text{ g}$$

The deviations are

- $|1.125 \text{ g} - 1.117 \text{ g}| = 0.008 \text{ g}$
- $|1.158 \text{ g} - 1.117 \text{ g}| = 0.041 \text{ g}$ and
- $|1.067 \text{ g} - 1.117 \text{ g}| = 0.050 \text{ g}$

So the average deviation is

$$\frac{0.008 \text{ g} + 0.041 \text{ g} + 0.050 \text{ g}}{3} = 0.033 \text{ g}$$

The precision of this set of measurements is therefore

$$\frac{0.033 \text{ g}}{1.117 \text{ g}} \times 100 = 3.0\%$$

When a series of measurements is precise but not accurate, the error is usually systematic. Systematic errors can be caused by faulty instrumentation or faulty technique.

✓ Example 1.5.1

The following archery targets show marks that represent the results of four sets of measurements. Which target shows

- a. a precise but inaccurate set of measurements?
- b. an accurate but imprecise set of measurements?
- c. a set of measurements that is both precise and accurate?
- d. a set of measurements that is neither precise nor accurate?



(a)



(b)



(c)



(d)

✓ Example 1.5.2

- a. A 1-carat diamond has a mass of 200.0 mg. When a jeweler repeatedly weighed a 2-carat diamond, he obtained measurements of 450.0 mg, 459.0 mg, and 463.0 mg. Were the jeweler's measurements accurate? Were they precise?
- b. A single copper penny was tested three times to determine its composition. The first analysis gave a composition of 93.2% zinc and 2.8% copper, the second gave 92.9% zinc and 3.1% copper, and the third gave 93.5% zinc and 2.5% copper. The actual composition of the penny was 97.6% zinc and 2.4% copper. Were the results accurate? Were they precise?

Solution

a. The expected mass of a 2-carat diamond is $2 \times 200.0 \text{ mg} = 400.0 \text{ mg}$. The average of the three measurements is 457.3 mg, about 13% greater than the true mass. These measurements are not particularly accurate.

The deviations of the measurements are 7.3 mg, 1.7 mg, and 5.7 mg, respectively, which give an average deviation of 4.9 mg and a precision of

$$\frac{4.9 \text{ mg}}{457.3 \text{ mg}} \times 100 = 1.1\%$$

These measurements are rather *precise*.

b. The average values of the measurements are 93.2% zinc and 2.8% copper versus the true values of 97.6% zinc and 2.4% copper. Thus these measurements are not very accurate, with errors of -4.5% and +17% for zinc and copper, respectively. (The sum of the measured zinc and copper contents is only 96.0% rather than 100%, which tells us that either there is a significant error in one or both measurements or some other element is present.)

The deviations of the measurements are 0.0%, 0.3%, and 0.3% for both zinc and copper, which give an average deviation of 0.2% for both metals. We might therefore conclude that the measurements are equally precise, but that is not the case. Recall that precision is the average deviation divided by the average value times 100. Because the average value of the zinc measurements is much greater than the average value of the copper measurements (93.2% versus 2.8%), the copper measurements are much less precise.

$$\text{precision (Zn)} = \frac{0.2\%}{93.2\%} \times 100 = 0.2\%$$

$$\text{precision (Cu)} = \frac{0.2\%}{2.8\%} \times 100 = 7\%$$

Significant Figures

No measurement is free from error. Error is introduced by the limitations of instruments and measuring devices (such as the size of the divisions on a graduated cylinder) and the imperfection of human senses (i.e., detection). Although errors in calculations can be enormous, they do not contribute to uncertainty in measurements. Chemists describe the estimated degree of error in a measurement as the uncertainty of the measurement, and they are careful to report all measured values using only significant figures, numbers that describe the value without exaggerating the degree to which it is known to be accurate. Chemists report as significant all numbers known with absolute certainty, plus one more digit that is understood to contain some uncertainty. The uncertainty in the final digit is usually assumed to be ± 1 , unless otherwise stated.

💡 Significant Figure Rules

The following rules have been developed for counting the number of significant figures in a measurement or calculation:

1. Any nonzero digit is significant.
2. Any zeros between nonzero digits are significant. The number 2005, for example, has four significant figures.
3. Any zeros used as a placeholder preceding the first nonzero digit are not significant. So 0.05 has one significant figure because the zeros are used to indicate the placement of the digit 5. In contrast, 0.050 has two significant figures because the last two digits correspond to the number 50; the last zero is not a placeholder. As an additional example, 5.0 has two significant figures because the zero is used not to place the 5 but to indicate 5.0.
4. When a number does not contain a decimal point, zeros added after a nonzero number may or may not be significant. An example is the number 100, which may be interpreted as having one, two, or three significant figures. (Note: treat all trailing zeros in exercises and problems in this text as significant unless you are specifically told otherwise.)
5. Integers obtained either by counting objects or from definitions are exact numbers, which are considered to have infinitely many significant figures. If we have counted four objects, for example, then the number 4 has an infinite number of significant figures (i.e., it represents 4.000...). Similarly, 1 foot (ft) is defined to contain 12 inches (in), so the number 12 in the following equation has infinitely many significant figures:

$$1 \text{ ft} = 1, \text{ in}$$

An effective method for determining the number of significant figures is to convert the measured or calculated value to scientific notation because any zero used as a placeholder is eliminated in the conversion. When 0.0800 is expressed in scientific notation as 8.00×10^{-2} , it is more readily apparent that the number has three significant figures rather than five; in scientific notation, the number preceding the exponential (i.e., N) determines the number of significant figures.

✓ Example 1.5.3

Give the number of significant figures in each. Identify the rule for each.

- a. 5.87
- b. 0.031
- c. 52.90
- d. 00.2001
- e. 500
- f. 6 atoms

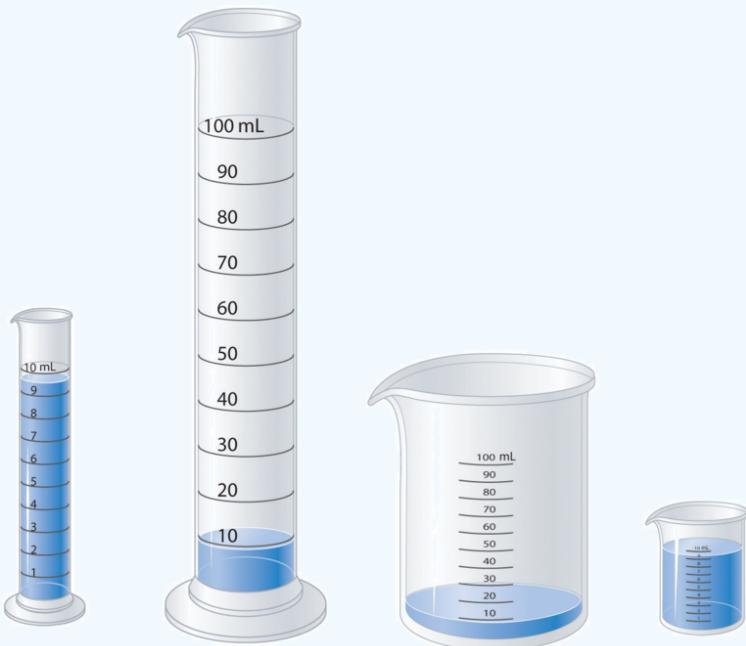
Solution

- a. three (rule 1)
- b. two (rule 3); in scientific notation, this number is represented as 3.1×10^{-2} , showing that it has two significant figures.
- c. four (rule 3)
- d. four (rule 2); this number is 2.001×10^{-1} in scientific notation, showing that it has four significant figures.

- e. one, two, or three (rule 4)
- f. infinite (rule 5)

✓ Example 1.5.4

Which measuring apparatus would you use to deliver 9.7 mL of water as accurately as possible? To how many significant figures can you measure that volume of water with the apparatus you selected?



Answer

Use the 10 mL graduated cylinder, which will be accurate to two significant figures.

Mathematical operations are carried out using all the digits given and then rounding the final result to the correct number of significant figures to obtain a reasonable answer. This method avoids compounding inaccuracies by successively rounding intermediate calculations. After you complete a calculation, you may have to round the last significant figure up or down depending on the value of the digit that follows it. If the digit is 5 or greater, then the number is rounded up. For example, when rounded to three significant figures, 5.215 is 5.22, whereas 5.213 is 5.21. Similarly, to three significant figures, 5.005 kg becomes 5.01 kg, whereas 5.004 kg becomes 5.00 kg. The procedures for dealing with significant figures are different for addition and subtraction versus multiplication and division.

When we add or subtract measured values, the value with the fewest significant figures to the right of the decimal point determines the number of significant figures to the right of the decimal point in the answer. Drawing a vertical line to the right of the column corresponding to the smallest number of significant figures is a simple method of determining the proper number of significant figures for the answer:

$$3240.7 + 21.236 = 3261.9\mid 36$$

The line indicates that the digits 3 and 6 are not significant in the answer. These digits are not significant because the values for the corresponding places in the other measurement are unknown (3240.7??). Consequently, the answer is expressed as 3261.9, with five significant figures. Again, numbers greater than or equal to 5 are rounded up. If our second number in the calculation had been 21.256, then we would have rounded 3261.956 to 3262.0 to complete our calculation.

When we multiply or divide measured values, the answer is limited to the smallest number of significant figures in the calculation; thus,

$$42.9 \times 8.323 = 357.057 = 357.$$

Although the second number in the calculation has four significant figures, we are justified in reporting the answer to only three significant figures because the first number in the calculation has only three significant figures. An exception to this rule occurs when multiplying a number by an integer, as in 12.793×12 . In this case, the number of significant figures in the answer is determined by the number 12.973, because we are in essence adding 12.973 to itself 12 times. The correct answer is therefore 155.516, an increase of one significant figure, not 155.52.

When you use a calculator, it is important to remember that the number shown in the calculator display often shows more digits than can be reported as significant in your answer. When a measurement reported as 5.0 kg is divided by 3.0 L, for example, the display may show 1.666666667 as the answer. We are justified in reporting the answer to only two significant figures, giving 1.7 kg/L as the answer, with the last digit understood to have some uncertainty.

In calculations involving several steps, slightly different answers can be obtained depending on how rounding is handled, specifically whether rounding is performed on intermediate results or postponed until the last step. Rounding to the correct number of significant figures should always be performed at the end of a series of calculations because rounding of intermediate results can sometimes cause the final answer to be significantly in error.

✓ Example 1.5.5

Complete the calculations and report your answers using the correct number of significant figures.

- a. $87.25 \text{ mL} + 3.0201 \text{ mL}$
- b. $26.843 \text{ g} + 12.23 \text{ g}$
- c. 6×12.011
- d. $2(1.008) \text{ g} + 15.99 \text{ g}$
- e. $137.3 + 2(35.45)$
- f. $\frac{118.7}{2} \text{ g} - 35.5 \text{ g}$
- g. $47.23 \text{ g} - \frac{207.2}{5.92} \text{ g}$
- h. $\frac{77.604}{6.467} - 4.8$
- i. $\frac{24.86}{2.0} - 3.26(0.98)$
- j. $(15.9994 \times 9) + 2.0158$

Solution

- a. 90.27 mL
- b. 39.07 g
- c. 72.066 (See rule 5 under “Significant Figures.”)
- d. $2(1.008) \text{ g} + 15.99 \text{ g} = 2.016 \text{ g} + 15.99 \text{ g} = 18.01 \text{ g}$
- e. $137.3 + 2(35.45) = 137.3 + 70.90 = 208.2$
- f. $59.35 \text{ g} - 35.5 \text{ g} = 23.9 \text{ g}$
- g. $47.23 \text{ g} - 35.0 \text{ g} = 12.2 \text{ g}$
- h. $12.00 - 4.8 = 7.2$
- i. $12 - 3.2 = 9$
- j. $143.9946 + 2.0158 = 146.0104$

In practice, chemists generally work with a calculator and carry all digits forward through subsequent calculations. When working on paper, however, we often want to minimize the number of digits we have to write out. Because successive rounding can compound inaccuracies, intermediate roundings need to be handled correctly. When working on paper, always round an intermediate result so as to retain at least one more digit than can be justified and carry this number into the next step in the calculation. The final answer is then rounded to the correct number of significant figures at the very end.

In the worked examples in this text, we will often show the results of intermediate steps in a calculation. In doing so, we will show the results to only the correct number of significant figures allowed for that step, in effect treating each step as a separate calculation. This procedure is intended to reinforce the rules for determining the number of significant figures, but in some cases it may give a final answer that differs in the last digit from that obtained using a calculator, where all digits are carried through to the last step.



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CHAPTER OVERVIEW

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CHAPTER OVERVIEW

2: The Components of Matter

In this chapter, you will learn how to describe the composition of chemical compounds. We introduce *chemical nomenclature*—the language of chemistry—that will enable you to recognize and name the most common kinds of compounds. An understanding of chemical nomenclature not only is essential for your study of chemistry but also has other benefits—for example, it helps you understand the labels on products found in the supermarket and the pharmacy. You will also be better equipped to understand many of the important environmental and medical issues that face society. By the end of this chapter, you will be able to describe what happens chemically when a doctor prepares a cast to stabilize a broken bone, and you will know the composition of common substances such as laundry bleach, the active ingredient in baking powder, and the foul-smelling compound responsible for the odor of spoiled fish. Finally, you will be able to explain the chemical differences among different grades of gasoline.

- [2.1: Elements, Compounds, and Mixtures - An Atomic Overview](#)
- [2.2: The Observations That Led to an Atomic View of Matter](#)
- [2.3: The Observations That Led to the Nuclear Atom Model](#)
- [2.4: The Atomic Theory Today](#)
- [2.5: Elements - A First Look at the Periodic Table](#)
- [2.6: Compounds - Introduction to Bonding](#)
- [2.7: Compounds - Formulas, Names, and Masses](#)
- [2.8: Mixtures - Classification and Separation](#)
- [2.E: The Components of Matter \(Exercises\)](#)

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2.2: The Observations That Led to an Atomic View of Matter

Learning Objectives

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

Long before the end of the 19th century, it was well known that applying a high voltage to a gas contained at low pressure in a sealed tube (called a gas discharge tube) caused electricity to flow through the gas, which then emitted light (Figure 2.2.1). Researchers trying to understand this phenomenon found that an unusual form of energy was also emitted from the cathode, or negatively charged electrode; this form of energy was called a cathode ray.

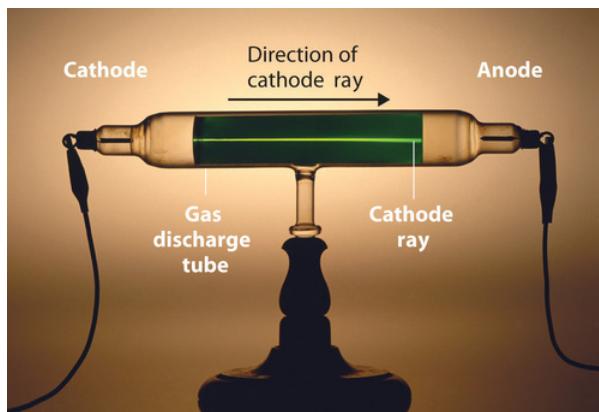


Figure 2.2.1: A Gas Discharge Tube Producing Cathode Rays. When a high voltage is applied to a gas contained at low pressure in a gas discharge tube, electricity flows through the gas, and energy is emitted in the form of light. Image used with Permission (CC BY-SA-NC).

In 1897, the British physicist J. J. Thomson (1856–1940) proved that atoms were not the most basic form of matter. He demonstrated that cathode rays could be deflected, or bent, by magnetic or electric fields, which indicated that cathode rays consist of charged particles (Figure 2.2.2). More important, by measuring the extent of the deflection of the cathode rays in magnetic or electric fields of various strengths, Thomson was able to calculate the mass-to-charge ratio of the particles. These particles were emitted by the negatively charged cathode and repelled by the negative terminal of an electric field. Because like charges repel each other and opposite charges attract, Thomson concluded that the particles had a net negative charge; these particles are now called electrons. Most relevant to the field of chemistry, Thomson found that the mass-to-charge ratio of cathode rays is independent of the nature of the metal electrodes or the gas, which suggested that electrons were fundamental components of all atoms.

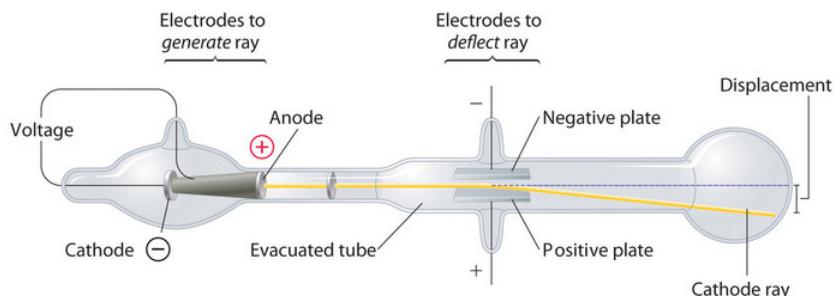


Figure 2.2.2: Deflection of Cathode Rays by an Electric Field. As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged. Image used with Permission (CC BY-SA-NC).

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

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

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

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



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

Radioactivity

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

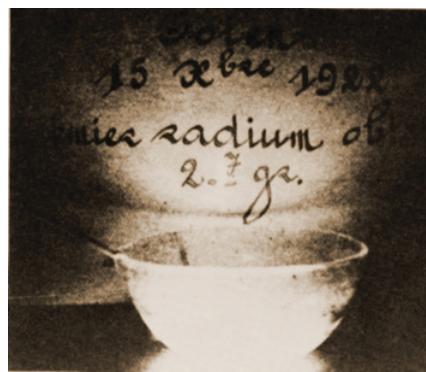


Figure 2.2.3: Radium bromide illuminated by its own radioactive glow. This 1922 photo was taken in the dark in the Curie laboratory.

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

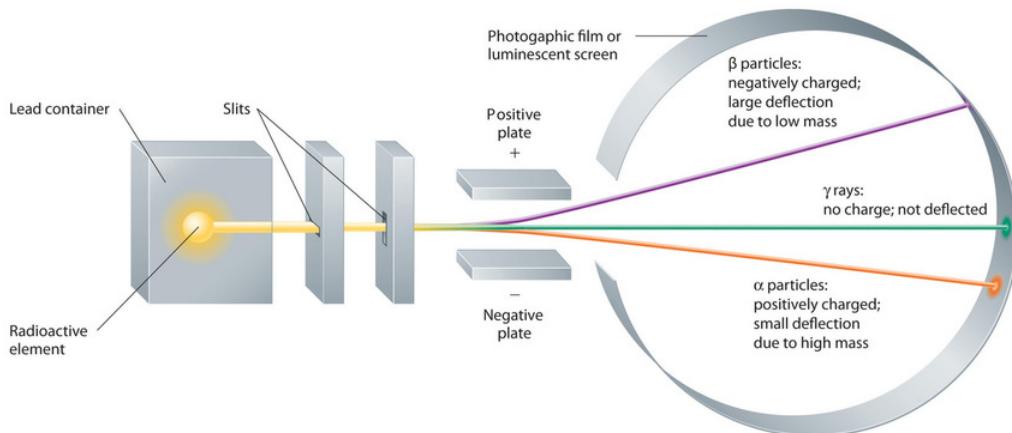


Figure 2.2.4: Effect of an Electric Field on α Particles, β Particles, and γ Rays. A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown to scale.) Image used with Permission (CC BY-SA-NC).

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

These three kinds of radiation— α particles, β particles, and γ rays—are readily distinguished by the way they are deflected by an electric field and by the degree to which they penetrate matter. As Figure 2.2.3 illustrates, α particles and β particles are deflected in opposite directions; α particles are deflected to a much lesser extent because of their higher mass-to-charge ratio. In contrast, γ rays have no charge, so they are not deflected by electric or magnetic fields. Figure 2.2.5 shows that α particles have the least penetrating power and are stopped by a sheet of paper, whereas β particles can pass through thin sheets of metal but are absorbed by lead foil or even thick glass. In contrast, γ -rays can readily penetrate matter; thick blocks of lead or concrete are needed to stop them.

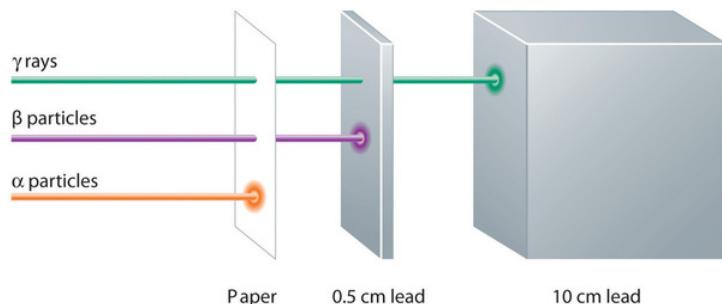


Figure 2.2.5: Relative Penetrating Power of the Three Types of Radiation. A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead or concrete is needed to absorb them. Image used with Permission (CC BY-SA-NC).

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

The Atomic Model

Once scientists concluded that all matter contains negatively charged electrons, it became clear that atoms, which are electrically neutral, must also contain positive charges to balance the negative ones. Thomson proposed that the electrons were embedded in a uniform sphere that contained both the positive charge and most of the mass of the atom, much like raisins in plum pudding or chocolate chips in a cookie (Figure 2.2.6).

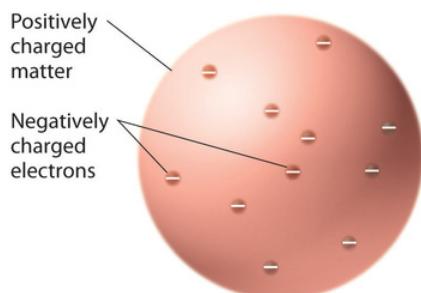


Figure 2.2.6: Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom. In this model, the electrons are embedded in a uniform sphere of positive charge. Image used with Permission (CC BY-SA-NC).

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

In a single famous experiment, however, Rutherford showed unambiguously that Thomson's model of the atom was incorrect. Rutherford aimed a stream of α particles at a very thin gold foil target (Figure 2.2.7a) and examined how the α particles were scattered by the foil. Gold was chosen because it could be easily hammered into extremely thin sheets, minimizing the number of atoms in the target. If Thomson's model of the atom were correct, the positively-charged α particles should crash through the uniformly distributed mass of the gold target like cannonballs through the side of a wooden house. They might be moving a little slower when they emerged, but they should pass essentially straight through the target (Figure 2.2.7b). To Rutherford's amazement, a small fraction of the α particles were deflected at large angles, and some were reflected directly back at the source (Figure 2.2.7c). According to Rutherford, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

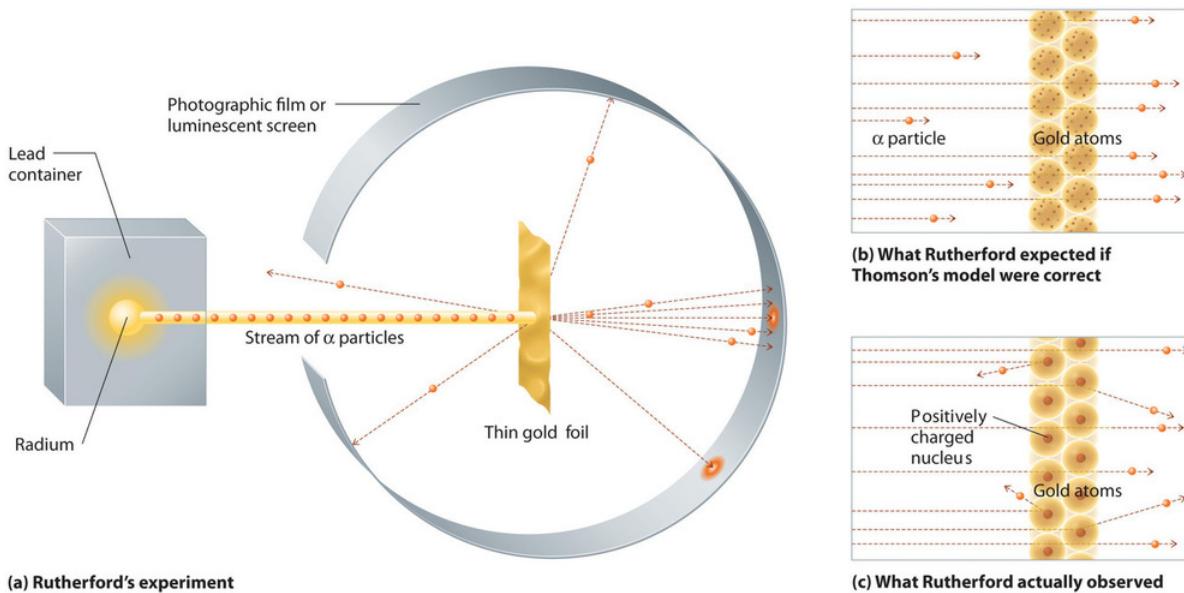


Figure 2.2.7: A Summary of Rutherford's Experiments. (a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles should have passed straight through the gold foil. (c) However, a small number of α particles were deflected in various directions, including right back at the source. This could be true only if the positive charge were much more massive than the α particle. It suggested that the mass of the gold atom is concentrated in a very small region of space, which he called the nucleus. Image used with Permission (CC BY-SA-NC).

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



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

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

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

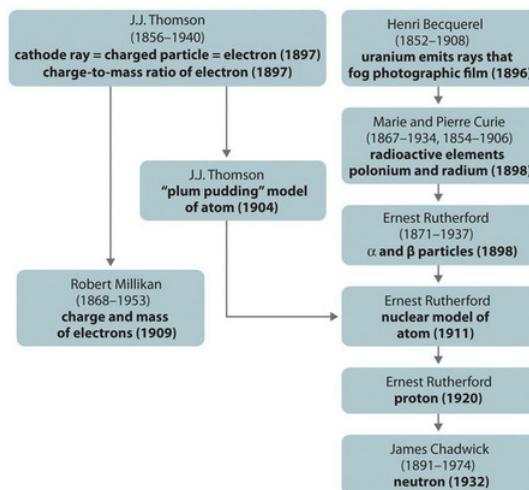


Figure 2.2.8: A Summary of the Historical Development of Models of the Components and Structure of the Atom. The dates in parentheses are the years in which the key experiments were performed. Image used with Permission (CC BY-SA-NC).

The historical development of the different models of the atom's structure is summarized in Figure 2.2.8. Rutherford established that the nucleus of the hydrogen atom was a positively charged particle, for which he coined the name proton in 1920. He also suggested that the nuclei of elements other than hydrogen must contain electrically neutral particles with approximately the same mass as the proton. The neutron, however, was not discovered until 1932, when James Chadwick (1891–1974, a student of Rutherford; Nobel Prize in Physics, 1935) discovered it. As a result of Rutherford's work, it became clear that an α particle contains two protons and neutrons, and is therefore the nucleus of a helium atom.

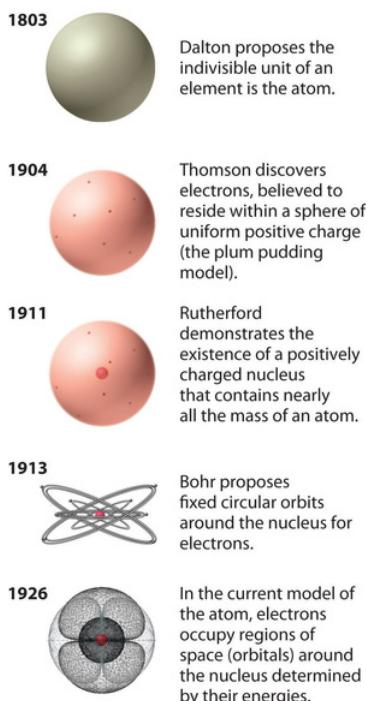


Figure 2.2.9: The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom. Bohr's model and the current model are described in Chapter 6, "The Structure of Atoms." Image used with Permission (CC BY-SA-NC).

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

Rutherford's model of the atom is essentially the same as the modern model, except that it is now known that electrons are not uniformly distributed throughout an atom's volume. Instead, they are distributed according to a set of principles described by Quantum Mechanics. Figure 2.2.9 shows how the model of the atom has evolved over time from the indivisible unit of Dalton to the modern view taught today.

Summary

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

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2.6: Compounds - Introduction to Bonding

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2.7: Compounds - Formulas, Names, and Masses

Learning Objectives

- To describe the composition of a chemical compound.
- To name covalent compounds that contain up to three elements.

As with ionic compounds, the system for naming covalent compounds enables chemists to write the molecular formula from the name and vice versa. This and the following section describe the rules for naming simple covalent compounds, beginning with inorganic compounds and then turning to simple organic compounds that contain only carbon and hydrogen.

When chemists synthesize a new compound, they may not yet know its molecular or structural formula. In such cases, they usually begin by determining its empirical formula, the relative numbers of atoms of the elements in a compound, reduced to the smallest whole numbers. Because the empirical formula is based on experimental measurements of the numbers of atoms in a sample of the compound, it shows only the ratios of the numbers of the elements present. The difference between empirical and molecular formulas can be illustrated with butane, a covalent compound used as the fuel in disposable lighters. The molecular formula for butane is C_4H_{10} . The ratio of carbon atoms to hydrogen atoms in butane is 4:10, which can be reduced to 2:5. The empirical formula for butane is therefore C_2H_5 . The formula unit is the absolute grouping of atoms or ions represented by the empirical formula of a compound, either ionic or covalent. Butane has the empirical formula C_2H_5 , but it contains two C_2H_5 formula units, giving a molecular formula of C_4H_{10} .

Because ionic compounds **do not** contain discrete molecules, empirical formulas are used to indicate their compositions. All compounds, whether ionic or covalent, must be electrically neutral. Consequently, the positive and negative charges in a formula unit must exactly cancel each other. If the cation and the anion have charges of equal magnitude, such as Na^+ and Cl^- , then the compound must have a 1:1 ratio of cations to anions, and the empirical formula must be $NaCl$. If the charges are not the same magnitude, then a cation:anion ratio other than 1:1 is needed to produce a neutral compound. In the case of Mg^{2+} and Cl^- , for example, two Cl^- ions are needed to balance the two positive charges on each Mg^{2+} ion, giving an empirical formula of $MgCl_2$. Similarly, the formula for the ionic compound that contains Na^+ and O^{2-} ions is Na_2O .

Ionic compounds do not contain discrete molecules, so empirical formulas are used to indicate their compositions.

Binary Ionic Compounds

An ionic compound that contains only two elements, one present as a cation and one as an anion, is called a binary ionic compound. One example is $MgCl_2$, a coagulant used in the preparation of tofu from soybeans. For binary ionic compounds, the subscripts in the empirical formula can also be obtained by crossing charges: use the absolute value of the charge on one ion as the subscript for the other ion. This method is shown schematically as follows:



Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

When crossing charges, it is sometimes necessary to reduce the subscripts to their simplest ratio to write the empirical formula. Consider, for example, the compound formed by Mg^{2+} and O^{2-} . Using the absolute values of the charges on the ions as subscripts gives the formula Mg_2O_2 :



This simplifies to its correct empirical formula MgO . The empirical formula has one Mg^{2+} ion and one O^{2-} ion.

Example 2.7.1: Binary Ionic Compounds

Write the empirical formula for the simplest binary ionic compound formed from each ion or element pair.

- Ga^{3+} and As^{3-}
- Eu^{3+} and O^{2-}
- calcium and chlorine

Given: ions or elements

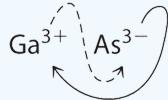
Asked for: empirical formula for binary ionic compound

Strategy:

- If not given, determine the ionic charges based on the location of the elements in the periodic table.
- Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the lowest numbers to write the empirical formula. Check to make sure the empirical formula is electrically neutral.

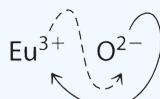
Solution

- Using the absolute values of the charges on the ions as the subscripts gives Ga_3As_3 :



Reducing the subscripts to the smallest whole numbers gives the empirical formula $GaAs$, which is electrically neutral $[+3 + (-3) = 0]$. Alternatively, we could recognize that Ga^{3+} and As^{3-} have charges of equal magnitude but opposite signs. One Ga^{3+} ion balances the charge on one As^{3-} ion, and a 1:1 compound will have no net charge. Because we write subscripts only if the number is greater than 1, the empirical formula is $GaAs$. $GaAs$ is gallium arsenide, which is widely used in the electronics industry in transistors and other devices.

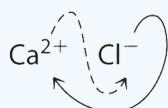
- Because Eu^{3+} has a charge of +3 and O^{2-} has a charge of -2, a 1:1 compound would have a net charge of +1. We must therefore find multiples of the charges that cancel. We cross charges, using the absolute value of the charge on one ion as the subscript for the other ion:



The subscript for Eu^{3+} is 2 (from O^{2-}), and the subscript for O^{2-} is 3 (from Eu^{3+}), giving Eu_2O_3 ; the subscripts cannot be reduced further. The empirical formula contains a positive charge of $2(+3) = +6$ and a negative charge of $3(-2) = -6$, for a net charge of 0. The compound Eu_2O_3 is neutral. Europium oxide is responsible for the red color in television and computer screens.

- Because the charges on the ions are not given, we must first determine the charges expected for the most common ions derived from calcium and chlorine. Calcium lies in group 2, so it should lose two electrons to form Ca^{2+} . Chlorine lies in group 17, so it should gain one electron to form Cl^- .

B Two Cl^- ions are needed to balance the charge on one Ca^{2+} ion, which leads to the empirical formula CaCl_2 . We could also cross charges, using the absolute value of the charge on Ca^{2+} as the subscript for Cl and the absolute value of the charge on Cl^- as the subscript for Ca:



The subscripts in CaCl_2 cannot be reduced further. The empirical formula is electrically neutral $[+2 + 2(-1) = 0]$. This compound is calcium chloride, one of the substances used as “salt” to melt ice on roads and sidewalks in winter.

Exercise 2.7.1

Write the empirical formula for the simplest binary ionic compound formed from each ion or element pair.

- Li^+ and N^{3-}
- Al^{3+} and O^{2-}
- lithium and oxygen

Answer a

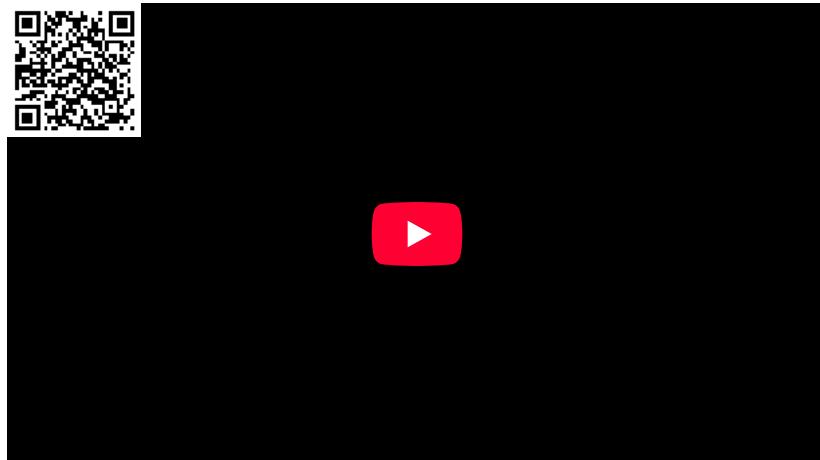
Li_3N

Answer b

Al_2O_3

Answer c

Li_2O



Nomenclature of Metals: [Nomenclature of Metals](#)(opens in new window) [youtu.be]

Polyatomic Ions

Polyatomic ions are groups of atoms that bear net electrical charges, although the atoms in a polyatomic ion are held together by the same covalent bonds that hold atoms together in molecules. Just as there are many more kinds of molecules than simple elements, there are many more kinds of polyatomic ions than monatomic ions. Two examples of polyatomic cations are the ammonium (NH_4^+) and the methylammonium (CH_3NH_3^+) ions. Polyatomic anions are much more numerous than polyatomic cations; some common examples are in Table 2.7.1.

Table 2.7.1: Common Polyatomic Ions and Their Names

Formula	Name of Ion	Formula	Name of Ion
NH_4^+	ammonium	HPO_4^{2-}	hydrogen phosphate
CH_3NH_3^+	methylammonium	H_2PO_4^-	dihydrogen phosphate
OH^-	hydroxide	ClO^-	hypochlorite
O_2^{2-}	peroxide	ClO_2^-	chlorite
CN^-	cyanide	ClO_3^-	chlorate
SCN^-	thiocyanate	ClO_4^-	perchlorate
NO_2^-	nitrite	MnO_4^-	permanganate
NO_3^-	nitrate	CrO_4^{2-}	chromate
CO_3^{2-}	carbonate	$\text{Cr}_2\text{O}_7^{2-}$	dichromate
HCO_3^-	hydrogen carbonate, or bicarbonate	$\text{C}_2\text{O}_4^{2-}$	oxalate
SO_3^{2-}	sulfite	HCO_2^-	formate
SO_4^{2-}	sulfate	CH_3CO_2^-	acetate
HSO_4^-	hydrogen sulfate, or bisulfate	$\text{C}_6\text{H}_5\text{CO}_2^-$	benzoate
PO_4^{3-}	phosphate		

The method used to predict the empirical formulas for ionic compounds that contain monatomic ions can also be used for compounds that contain polyatomic ions. The overall charge on the cations must balance the overall charge on the anions in the formula unit. Thus, K^+ and NO_3^- ions combine in a 1:1 ratio to form KNO_3 (potassium nitrate or saltpeter), a major ingredient in black gunpowder. Similarly, Ca^{2+} and SO_4^{2-} form $CaSO_4$ (calcium sulfate), which combines with varying amounts of water to form gypsum and plaster of Paris. The polyatomic ions NH_4^+ and NO_3^- form NH_4NO_3 (ammonium nitrate), a widely used fertilizer and, in the wrong hands, an explosive. One example of a compound in which the ions have charges of different magnitudes is calcium phosphate, which is composed of Ca^{2+} and PO_4^{3-} ions; it is a major component of bones. The compound is electrically neutral because the ions combine in a ratio of three Ca^{2+} ions [$3(+2) = +6$] for every two ions [$2(-3) = -6$], giving an empirical formula of $Ca_3(PO_4)_2$; the parentheses around PO_4 in the empirical formula indicate that it is a polyatomic ion. Writing the formula for calcium phosphate as $Ca_3P_2O_8$ gives the correct number of each atom in the formula unit, but it obscures the fact that the compound contains readily identifiable PO_4^{3-} ions.

✓ Example 2.7.2

Write the empirical formula for the compound formed from each ion pair.

- Na^+ and HPO_4^{2-}
- potassium cation and cyanide anion
- calcium cation and hypochlorite anion

Given: ions

Asked for: empirical formula for ionic compound

Strategy:

- If it is not given, determine the charge on a monatomic ion from its location in the periodic table. Use Table 2.7.1 to find the charge on a polyatomic ion.
- Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the smallest whole numbers when writing the empirical formula.

Solution:

- B** Because HPO_4^{2-} has a charge of -2 and Na^+ has a charge of $+1$, the empirical formula requires two Na^+ ions to balance the charge of the polyatomic ion, giving Na_2HPO_4 . The subscripts are reduced to the lowest numbers, so the empirical formula is Na_2HPO_4 . This compound is sodium hydrogen phosphate, which is used to provide texture in processed cheese, puddings, and instant breakfasts.
- A** The potassium cation is K^+ , and the cyanide anion is CN^- . **B** Because the magnitude of the charge on each ion is the same, the empirical formula is KCN . Potassium cyanide is highly toxic, and at one time it was used as rat poison. This use has been discontinued, however, because too many people were being poisoned accidentally.
- A** The calcium cation is Ca^{2+} , and the hypochlorite anion is ClO^- . **B** Two ClO^- ions are needed to balance the charge on one Ca^{2+} ion, giving $Ca(ClO)_2$. The subscripts cannot be reduced further, so the empirical formula is $Ca(ClO)_2$. This is calcium hypochlorite, the “chlorine” used to purify water in swimming pools.

? Exercise 2.7.2

Write the empirical formula for the compound formed from each ion pair.

- Ca^{2+} and $H_2PO_4^-$
- sodium cation and bicarbonate anion
- ammonium cation and sulfate anion

Answer a

$Ca(H_2PO_4)_2$: calcium dihydrogen phosphate is one of the ingredients in baking powder.

Answer b

$NaHCO_3$: sodium bicarbonate is found in antacids and baking powder; in pure form, it is sold as baking soda.

Answer c

$(NH_4)_2SO_4$: ammonium sulfate is a common source of nitrogen in fertilizers.



Polyatomics: Polyatomics, YouTube([opens in new window](#)) [[youtu.be](#)] ([opens in new window](#))

Hydrates

Many ionic compounds occur as hydrates, compounds that contain specific ratios of loosely bound water molecules, called waters of hydration. Waters of hydration can often be removed simply by heating. For example, calcium dihydrogen phosphate can form a solid that contains one molecule of water per $Ca(H_2PO_4)_2$ unit and is used as a leavening agent in the food industry to cause baked goods to rise. The empirical formula for the solid is $Ca(H_2PO_4)_2 \cdot H_2O$. In contrast, copper sulfate usually forms a blue solid that contains five waters of hydration per formula unit, with the empirical formula $CuSO_4 \cdot 5 H_2O$. When heated, all five water molecules are lost, giving a white solid with the empirical formula $CuSO_4$.



Figure 2.7.1: Loss of Water from a Hydrate with Heating. (left) When blue $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is heated, two molecules of water are lost at 30°C, two more at 110°C, and the last at 250°C to give white "anhydrous" CuSO_4 (right). Images used with permission from Wikipedia.

Compounds that differ only in the numbers of waters of hydration can have very different properties. For example, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ is *plaster of Paris*, which was often used to make sturdy casts for broken arms or legs, whereas $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the less dense, flakier gypsum, a mineral used in drywall panels for home construction. When a cast would set, a mixture of plaster of Paris and water crystallized to give solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Similar processes are used in the setting of cement and concrete.

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+ , when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a binary acid (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word "acid" is added as a second word

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table 2.7.2.

Table 2.7.2: Names of Some Simple Acids

Name of Gas	Name of Acid
$\text{HF}(g)$, hydrogen fluoride	$\text{HF}(aq)$, hydrofluoric acid
$\text{HCl}(g)$, hydrogen chloride	$\text{HCl}(aq)$, hydrochloric acid
$\text{HBr}(g)$, hydrogen bromide	$\text{HBr}(aq)$, hydrobromic acid
$\text{HI}(g)$, hydrogen iodide	$\text{HI}(aq)$, hydroiodic acid
$\text{H}_2\text{S}(g)$, hydrogen sulfide	$\text{H}_2\text{S}(aq)$, hydrosulfuric acid

Oxyacids

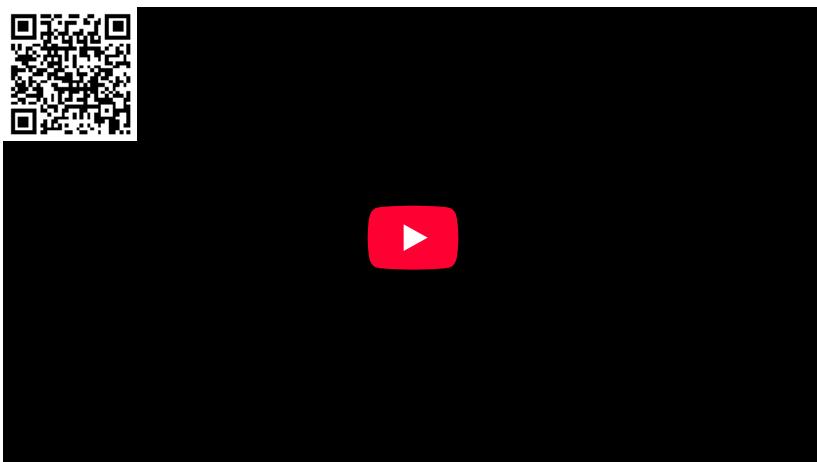
Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as oxyacids, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit "hydrogen"
2. Start with the root name of the anion
3. Replace *-ate* with *-ic*, or *-ite* with *-ous*
4. Add "acid"

For example, consider H_2CO_3 (which you might be tempted to call "hydrogen carbonate"). To name this correctly, "hydrogen" is omitted; the *-ate* of carbonate is replaced with *-ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table 2.7.3. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table 2.7.3: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$\text{HC}_2\text{H}_3\text{O}_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
HClO_4	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid



Nomenclature of Acids: [Nomenclature of Acids, YouTube](#)(opens in new window) [youtu.be]

Bases

We will present more comprehensive definitions of bases in later chapters, but virtually every base you encounter in the meantime will be an ionic compound, such as sodium hydroxide (NaOH) and barium hydroxide ($\text{Ba}(\text{OH})_2$), that contain the hydroxide ion and a metal cation. These have the general formula $\text{M}(\text{OH})_n$. It is important to recognize that alcohols, with the general formula ROH , are covalent compounds, not ionic compounds; consequently, they do *not* dissociate in water to form a basic solution (containing OH^- ions). When a base reacts with any of the acids we have discussed, it accepts a proton (H^+). For example, the hydroxide ion (OH^-) accepts a proton to form H_2O . Thus bases are also referred to as *proton acceptors*.

Concentrated aqueous solutions of ammonia (NH_3) contain significant amounts of the hydroxide ion, even though the dissolved substance is *not* primarily ammonium hydroxide (NH_4OH) as is often stated on the label. Thus aqueous ammonia solution is also a common base. Replacing a hydrogen atom of NH_3 with an alkyl group results in an amine (RNH_2), which is also a base. Amines have pungent odors—for example, methylamine (CH_3NH_2) is one of the compounds responsible for the foul odor associated with spoiled fish. The physiological importance of amines is suggested in the word *vitamin*, which is derived from the phrase *vital amines*. The word was coined to describe dietary substances that were effective at preventing scurvy, rickets, and other diseases because these substances were assumed to be amines. Subsequently, some vitamins have indeed been confirmed to be amines.

Binary Inorganic Compounds

Binary covalent compounds—covalent compounds that contain only two elements—are named using a procedure similar to that used for simple ionic compounds, but prefixes are added as needed to indicate the number of atoms of each kind. The procedure, diagrammed in Figure 2.7.2 consists of the following steps:

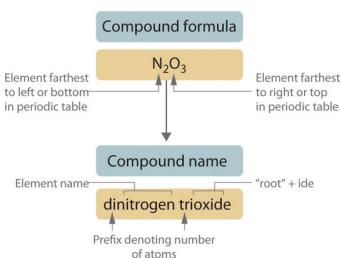


Figure 2.7.2: Naming a Covalent Inorganic Compound

Breakdown of formula names and compound formula. The atom farthest to the left on the periodic table is named first.

- Place the elements in their proper order.
 - The element farthest to the left in the periodic table is usually named first. If both elements are in the same group, the element closer to the bottom of the column is named first.
 - The second element is named as if it were a monatomic anion in an ionic compound (even though it is not), with the suffix *-ide* attached to the root of the element name.
- Identify the number of each type of atom present.
 - Prefixes derived from Greek stems are used to indicate the number of each type of atom in the formula unit (Table 2.7.3). The prefix *mono-* (“one”) is used only when absolutely necessary to avoid confusion, just as the subscript 1 is omitted when writing molecular formulas.

To demonstrate steps 1 and 2a, HCl is named hydrogen chloride (because hydrogen is to the left of chlorine in the periodic table), and PCl_5 is phosphorus pentachloride. The order of the elements in the name of BrF_3 , bromine trifluoride, is determined by the fact that bromine lies below fluorine in Group 17.

Table 2.7.3: Prefixes for Indicating the Number of Atoms in Chemical Names

Prefix	Number
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10

Prefix	Number
undeca-	11
dodeca-	12

2. If a molecule contains more than one atom of both elements, then prefixes are used for both. Thus N_2O_3 is *dinitrogen trioxide*, as shown in Figure 2.13.
3. In some names, the final *a* or *o* of the prefix is dropped to avoid awkward pronunciation. Thus OsO_4 is *osmium tetroxide* rather than *osmium tetraoxide*.
3. Write the name of the compound.
1. Binary compounds of the elements with oxygen are generally named as "element oxide," with prefixes that indicate the number of atoms of each element per formula unit. For example, CO is carbon monoxide. The only exception is binary compounds of oxygen with fluorine, which are named as oxygen fluorides.
 2. Certain compounds are *always* called by the common names that were assigned before formulas were used. For example, H_2O is water (not dihydrogen oxide); NH_3 is ammonia; PH_3 is phosphine; SiH_4 is silane; and B_2H_6 , a *dimer* of BH_3 , is diborane. For many compounds, the systematic name and the common name are both used frequently, requiring familiarity with both. For example, the systematic name for NO is nitrogen monoxide, but it is much more commonly called nitric oxide. Similarly, N_2O is usually called nitrous oxide rather than dinitrogen monoxide. Notice that the suffixes *-ic* and *-ous* are the same ones used for ionic compounds.

Start with the element at the far left in the periodic table and work to the right. If two or more elements are in the same group, start with the bottom element and work up.

✓ Example 2.7.3: Binary Covalent Compounds

Write the name of each binary covalent compound.

- a. SF_6
- b. N_2O_4
- c. ClO_2

Given: molecular formula

Asked for: name of compound

Strategy:

- A. List the elements in order according to their positions in the periodic table. Identify the number of each type of atom in the chemical formula and then use Table 2.7.2 to determine the prefixes needed.
- B. If the compound contains oxygen, follow step 3a. If not, decide whether to use the common name or the systematic name.

Solution:

- a. Because sulfur is to the left of fluorine in the periodic table, sulfur is named first. Because there is only one sulfur atom in the formula, no prefix is needed. **B** There are, however, six fluorine atoms, so we use the prefix for six: *hexa-* (Table 2.7.2). The compound is sulfur hexafluoride.
- b. Because nitrogen is to the left of oxygen in the periodic table, nitrogen is named first. Because more than one atom of each element is present, prefixes are needed to indicate the number of atoms of each. According to Table 2.7.2 "Prefixes for Indicating the Number of Atoms in Chemical Names", the prefix for two is *di-*, and the prefix for four is *tetra-*. **B** The compound is dinitrogen tetroxide (omitting the *a* in *tetra-* according to step 2c) and is used as a component of some rocket fuels.
- c. Although oxygen lies to the left of chlorine in the periodic table, it is not named first because ClO_2 is an oxide of an element other than fluorine (step 3a). Consequently, chlorine is named first, but a prefix is not necessary because each molecule has only one atom of chlorine. **B** Because there are two oxygen atoms, the compound is a dioxide. Thus the compound is chlorine dioxide. It is widely used as a substitute for chlorine in municipal water treatment plants because, unlike chlorine, it does not react with organic compounds in water to produce potentially toxic chlorinated compounds.

? Example 2.7.3

Write the name of each binary covalent compound.

- a. IF_7
- b. N_2O_5
- c. OF_2

Answer a

iodine heptafluoride

Answer b

dinitrogen pentoxide

Answer c

oxygen difluoride

✓ Example 2.7.4

Write the formula for each binary covalent compound.

- a. sulfur trioxide
- b. diiodine pentoxide

Given: name of compound

Asked for: formula

Strategy:

List the elements in the same order as in the formula, use Table 2.7.2 to identify the number of each type of atom present, and then indicate this quantity as a subscript to the right of that element when writing the formula.

Solution:

- a. Sulfur has no prefix, which means that each molecule has only one sulfur atom. The prefix *tri-* indicates that there are three oxygen atoms. The formula is therefore SO_3 . Sulfur trioxide is produced industrially in huge amounts as an intermediate in the synthesis of sulfuric acid.
- b. The prefix *di-* tells you that each molecule has two iodine atoms, and the prefix *penta-* indicates that there are five oxygen atoms. The formula is thus I_2O_5 , a compound used to remove carbon monoxide from air in respirators.

Exercise 2.7.4

Write the formula for each binary covalent compound.

- silicon tetrachloride
- disulfur decafluoride

Answer a

Answer b


The structures of some of the compounds in Examples 2.7.3 and 2.7.4 are shown in Figure 2.7.2 along with the location of the “central atom” of each compound in the periodic table. It may seem that the compositions and structures of such compounds are entirely random, but this is not true. After mastering the material discussed later on this course, one is able to predict the compositions and structures of compounds of this type with a high degree of accuracy.

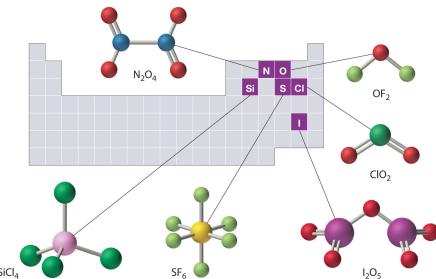
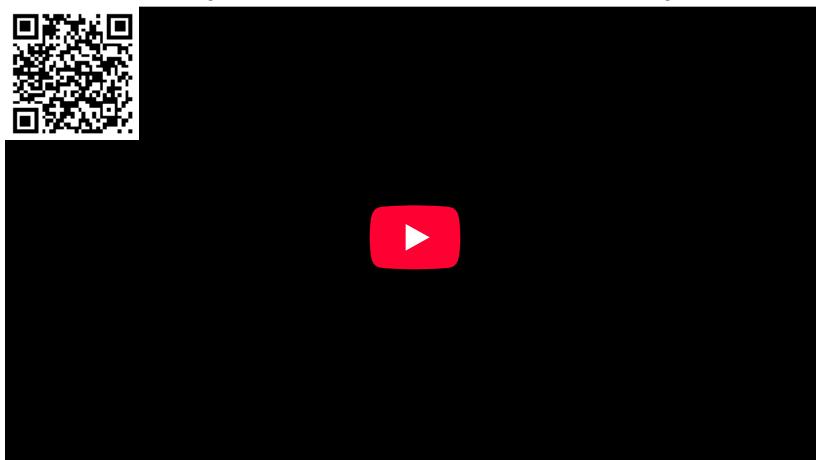


Figure 2.7.2: The Structures of Some Covalent Inorganic Compounds and the Locations of the “Central Atom” in the Periodic Table. The compositions and structures of covalent inorganic compounds are not random and can be predicted from the locations of the component atoms in the periodic table.

Central atoms of compounds N_2O_4 , OF_2 , ClO_2 , I_2O_5 , SF_6 , and SiCl_4 shown on the periodic table.



Nomenclature of Nonmetals: Nomenclature of Nonmetals, YouTube([opens in new window](#)) [[youtu.be](#)] ([opens in new window](#))

Summary

The composition of a compound is represented by an empirical or molecular formula, each consisting of at least one formula unit. Covalent inorganic compounds are named using a procedure similar to that used for ionic compounds, whereas hydrocarbons use a system based on the number of bonds between carbon atoms. Covalent inorganic compounds are named by a procedure similar to that used for ionic compounds, using prefixes to indicate the numbers of atoms in the molecular formula. An empirical formula gives the relative numbers of atoms of the elements in a compound, reduced to the lowest whole numbers. The formula unit is the absolute grouping represented by the empirical formula of a compound, either ionic or covalent. Empirical formulas are particularly useful for describing the composition of ionic compounds, which do not contain readily identifiable molecules. Some ionic compounds occur as hydrates, which contain specific ratios of loosely bound water molecules called waters of hydration.

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CHAPTER OVERVIEW

3: Stoichiometry of Formulas and Equation

Stoichiometry is the calculation of relative quantities of reactants and products in chemical reactions. Stoichiometry is founded on the **law of conservation of mass** where the total mass of the reactants equals the total mass of the products leading to the insight that the relations among quantities of reactants and products typically form a ratio of positive integers. This means that if the amounts of the separate reactants are known, then the amount of the product can be calculated. Conversely, if one reactant has a known quantity and the quantity of product can be empirically determined, then the amount of the other reactants can also be calculated.

We begin this chapter by describing the relationship between the mass of a sample of a substance and its composition. We then develop methods for determining the quantities of compounds produced or consumed in chemical reactions, and we describe some fundamental types of chemical reactions. By applying the concepts and skills introduced in this chapter, you will be able to explain what happens to the sugar in a candy bar you eat, what reaction occurs in a battery when you start your car, what may be causing the “ozone hole” over Antarctica, and how we might prevent the hole’s growth.

[3.1: The Mole](#)

[3.2: Determining the Formula of an Unknown Compound](#)

[3.3: Writing and Balancing Chemical Equations](#)

[3.4: Calculating Quantities of Reactant and Product](#)

[3.E: Stoichiometry of Formulas and Equations \(Exercises\)](#)

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3.1: The Mole

Learning Objectives

- To calculate the molecular mass of a covalent compound and the formula mass of an ionic compound, and to calculate the number of atoms, molecules, or formula units in a sample of a substance.

As discussed previously, the **mass number** is the sum of the numbers of protons and neutrons present in the nucleus of an atom. The mass number is an integer that is approximately equal to the numerical value of the atomic mass. Although the mass number is unitless, it is assigned units called **atomic mass units (amu)**. Because a molecule or a polyatomic ion is an assembly of atoms whose identities are given in its molecular or ionic formula, the average atomic mass of any molecule or polyatomic ion can be calculated from its composition by adding together the masses of the constituent atoms. The average mass of a monatomic ion is the same as the average mass of an atom of the element because the mass of electrons is so small that it is insignificant in most calculations.

Molecular and Formula Masses

The molecular mass of a substance is the sum of the average masses of the atoms in one molecule of a substance. It is calculated by adding together the atomic masses of the elements in the substance, each multiplied by its subscript (written or implied) in the molecular formula. Because the units of atomic mass are atomic mass units, the units of molecular mass are also atomic mass units. The procedure for calculating molecular masses is illustrated in Example 3.1.1.

Example 3.1.1: Molecular Mass of Ethanol

Calculate the molecular mass of ethanol, whose condensed structural formula is $\text{CH}_3\text{CH}_2\text{OH}$. Among its many uses, ethanol is a fuel for internal combustion engines.

Given: molecule

Asked for: molecular mass

Strategy:

- Determine the number of atoms of each element in the molecule.
- Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.
- Add together the masses to give the molecular mass.

Solution:

A The molecular formula of ethanol may be written in three different ways: $\text{CH}_3\text{CH}_2\text{OH}$ (which illustrates the presence of an ethyl group, CH_3CH_2- , and an $-\text{OH}$ group), $\text{C}_2\text{H}_5\text{OH}$, and $\text{C}_2\text{H}_6\text{O}$; all show that ethanol has two carbon atoms, six hydrogen atoms, and one oxygen atom.

B Taking the atomic masses from the periodic table, we obtain

$$2 \times \text{atomic mass of carbon} = 2 \text{ atoms} \left(\frac{12.011 \text{ amu}}{\text{atoms}} \right) \\ = 24.022 \text{ amu}$$

$$6 \times \text{atomic mass of hydrogen} = 2 \text{ atoms} \left(\frac{1.0079 \text{ amu}}{\text{atoms}} \right) \\ = 6.0474 \text{ amu}$$

$$1 \times \text{atomic mass of oxygen} = 1 \text{ atoms} \left(\frac{15.9994 \text{ amu}}{\text{atoms}} \right) \\ = 15.994 \text{ amu}$$

C Adding together the masses gives the molecular mass:

$$24.022 \text{ amu} + 6.0474 \text{ amu} + 15.9994 \text{ amu} = 46.069 \text{ amu}$$

Alternatively, we could have used unit conversions to reach the result in one step:

$$\left[2 \text{ atoms C} \left(\frac{12.011 \text{ amu}}{1 \text{ atom C}} \right) \right] + \left[6 \text{ atoms H} \left(\frac{1.0079 \text{ amu}}{1 \text{ atom H}} \right) \right] + \left[1 \text{ atoms O} \left(\frac{15.9994 \text{ amu}}{1 \text{ atom O}} \right) \right] = 46.069 \text{ amu}$$

The same calculation can also be done in a tabular format, which is especially helpful for more complex molecules:

$$2 \times C \text{ (2 atoms)} (12.011 \text{ amu/atom}) = 24.022 \text{ amu}$$

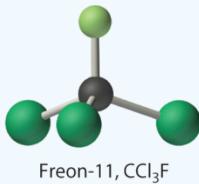
$$6 \times H \text{ (6 atoms)} (1.0079 \text{ amu/atom}) = 6.0474 \text{ amu}$$

$$1 \times O \text{ (1 atoms)} (15.9994 \text{ amu/atom}) = 15.9994 \text{ amu}$$

$$C_2H_6O \text{ molecular mass of ethanol} = 46.069 \text{ amu}$$

? Exercise 3.1.1: Molecular Mass of Freon

Calculate the molecular mass of trichlorofluoromethane, also known as Freon-11, whose condensed structural formula is CCl_3F . Until recently, it was used as a refrigerant. The structure of a molecule of Freon-11 is as follows:



Answer

137.368 amu

Unlike molecules, which form covalent bonds, ionic compounds do not have a readily identifiable molecular unit. Therefore, for ionic compounds, the formula mass (also called the empirical formula mass) of the compound is used instead of the molecular mass. The formula mass is the sum of the atomic masses of all the elements in the empirical formula, each multiplied by its subscript (written or implied). It is directly analogous to the molecular mass of a covalent compound. The units are atomic mass units.

Atomic mass, molecular mass, and formula mass all have the same units: atomic mass units.

✓ Example 3.1.2: Formula Mass of Calcium Phosphate

Calculate the formula mass of $\text{Ca}_3(\text{PO}_4)_2$, commonly called calcium phosphate. This compound is the principal source of calcium found in bovine milk.

Given: ionic compound

Asked for: formula mass

Strategy:

- Determine the number of atoms of each element in the empirical formula.
- Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.
- Add together the masses to give the formula mass.

Solution:

A The empirical formula— $\text{Ca}_3(\text{PO}_4)_2$ —indicates that the simplest electrically neutral unit of calcium phosphate contains three Ca^{2+} ions and two PO_4^{3-} ions. The formula mass of this molecular unit is calculated by adding together the atomic masses of three calcium atoms, two phosphorus atoms, and eight oxygen atoms.

B Taking atomic masses from the periodic table, we obtain

$$3 \times \text{atomic mass of calcium} = 3 \text{ atoms} \left(\frac{40.078 \text{ amu}}{\text{atom}} \right) = 120.234 \text{ amu}$$

$$2 \times \text{atomic mass of phosphorus} = 2 \text{ atoms} \left(\frac{30.973761 \text{ amu}}{\text{atom}} \right) = 61.947522 \text{ amu}$$

$$8 \times \text{atomic mass of oxygen} = 8 \text{ atoms} \left(\frac{15.9994 \text{ amu}}{\text{atom}} \right) = 127.9952 \text{ amu}$$

C Adding together the masses gives the formula mass of $\text{Ca}_3(\text{PO}_4)_2$:

$$120.234 \text{ amu} + 61.947522 \text{ amu} + 127.9952 \text{ amu} = 310.177 \text{ amu}$$

We could also find the formula mass of $\text{Ca}_3(\text{PO}_4)_2$ in one step by using unit conversions or a tabular format:

$$\left[3 \text{ atoms} \text{Ca} \left(\frac{40.078 \text{ amu}}{1 \text{ atom} \text{Ca}} \right) \right] + \left[2 \text{ atoms} \text{P} \left(\frac{30.973761 \text{ amu}}{1 \text{ atom} \text{P}} \right) \right] + \left[8 \text{ atoms} \text{O} \left(\frac{15.9994 \text{ amu}}{1 \text{ atom} \text{O}} \right) \right] = 310.177 \text{ amu}$$

$$3\text{Ca} \quad (3 \text{ atoms})(40.078 \text{ amu}/\text{atom}) = 120.234 \text{ amu}$$

$$2\text{P} \quad (2 \text{ atoms})(30.973761 \text{ amu}/\text{atom}) = 61.947522 \text{ amu}$$

$$+8\text{O} \quad (8 \text{ atoms})(15.9994 \text{ amu}/\text{atom}) = 127.9952 \text{ amu}$$

$$\text{Ca}_3\text{P}_2\text{O}_8 \quad \text{formula mass of } \text{Ca}_3(\text{PO}_4)_2 = 310.177 \text{ amu}$$

Exercise 3.1.2: Formula Mass of Silicon Nitride

Calculate the formula mass of Si_3N_4 , commonly called silicon nitride. It is an extremely hard and inert material that is used to make cutting tools for machining hard metal alloys.

Answer

140.29 amu



Molar Masses of Compounds: [Molar Masses of Compounds, YouTube](#)(opens in new window) [youtu.be]

The Mole

Dalton's theory that each chemical compound has a particular combination of atoms and that the ratios of the numbers of atoms of the elements present are usually small whole numbers. It also describes the law of multiple proportions, which states that the ratios of the masses of elements that form a series of compounds are small whole numbers. The problem for Dalton and other early chemists was to discover the quantitative relationship between the number of atoms in a chemical substance and its mass. Because the masses of individual atoms are so minuscule (on the order of 10^{-23} g/atom), chemists do not measure the mass of individual atoms or molecules. In the laboratory, for example, the masses of compounds and elements used by chemists typically range from milligrams to grams, while in industry, chemicals are bought and sold in kilograms and tons. To analyze the transformations that occur between individual atoms or molecules in a chemical reaction, it is therefore essential for chemists to know how many atoms or molecules are contained in a measurable quantity in the laboratory—a given mass of sample. The unit that provides this link is the mole (mol), from the Latin *moles*, meaning “pile” or “heap.”

Many familiar items are sold in numerical quantities with distinct names. For example, cans of soda come in a six-pack, eggs are sold by the dozen (12), and pencils often come in a gross (12 dozen, or 144). Sheets of printer paper are packaged in reams of 500, a seemingly large number. Atoms are so small, however, that even 500 atoms are too small to see or measure by most common techniques. Any readily measurable mass of an element or compound contains an extraordinarily large number of atoms, molecules, or ions, so an extremely large numerical unit is needed to count them. The mole is used for this purpose.

A mole is defined as the amount of a substance that contains the number of carbon atoms in exactly 12 g of isotopically pure carbon-12. According to the most recent experimental measurements, this mass of carbon-12 contains 6.022142×10^{23} atoms, but for most purposes 6.022×10^{23} provides an adequate number of significant figures. Just as 1 mole of atoms contains 6.022×10^{23} atoms, 1 mole of eggs contains 6.022×10^{23} eggs. This number is called Avogadro's number, after the 19th-century Italian scientist who first proposed a relationship between the volumes of gases and the numbers of particles they contain.

It is not obvious why eggs come in dozens rather than 10s or 14s, or why a ream of paper contains 500 sheets rather than 400 or 600. The definition of a mole—that is, the decision to base it on 12 g of carbon-12—is also arbitrary. The important point is that 1 mole of carbon—or of anything else, whether atoms, compact discs, or houses—always has the same number of objects: 6.022×10^{23} .

One mole always has the same number of objects: 6.022×10^{23} .

To appreciate the magnitude of Avogadro's number, consider a mole of pennies. Stacked vertically, a mole of pennies would be 4.5×10^{17} mi high, or almost six times the diameter of the Milky Way galaxy. If a mole of pennies were distributed equally among the entire population on Earth, each person would have more than one trillion dollars. The mole is so large that it is useful only for measuring very small objects, such as atoms.

The concept of the mole allows scientists to count a specific number of individual atoms and molecules by weighing measurable quantities of elements and compounds. To obtain 1 mol of carbon-12 atoms, one weighs out 12 g of isotopically pure carbon-12. Because each element has a different atomic mass, however, a mole of each element has a different mass, even though it contains the same number of atoms (6.022×10^{23}). This is analogous to the fact that a dozen extra large eggs weighs more than a dozen small eggs, or that the total weight of 50 adult humans is greater than the total weight of 50 children. Because of the way the mole is defined, for every element the number of grams in a mole is the same as the number of atomic mass units in the atomic mass of the element. For example, the mass of 1 mol of magnesium (atomic mass = 24.305 amu) is 24.305 g. Because the atomic mass of magnesium (24.305 amu) is slightly more than twice that of a carbon-12 atom (12 amu), the mass of 1 mol of magnesium atoms (24.305 g) is slightly more than twice that of 1 mol of carbon-12 (12 g). Similarly, the mass of 1 mol of helium (atomic mass = 4.002602 amu) is 4.002602 g, which is about one-third that of 1 mol of carbon-12. Using the concept of the mole, Dalton's theory can be restated: 1 mol of a compound is formed by combining elements in amounts whose mole ratios are small whole numbers. For example, 1 mol of water (H_2O) has 2 mol of hydrogen atoms and 1 mol of oxygen atoms.

Molar Mass

The molar mass of a substance is defined as the mass in grams of 1 mole of that substance. One mole of isotopically pure carbon-12 has a mass of 12 g. For an element, the molar mass is the mass of 1 mol of atoms of that element; for a covalent molecular compound, it is the mass of 1 mol of molecules of that compound; for an ionic compound, it is the mass of 1 mol of formula units. That is, the molar mass of a substance is the mass (in grams per mole) of 6.022×10^{23} atoms, molecules, or formula units of that

substance. In each case, the number of grams in 1 mol is the same as the number of atomic mass units that describe the atomic mass, the molecular mass, or the formula mass, respectively.

The molar mass of any substance is its atomic mass, molecular mass, or formula mass in grams per mole.

The periodic table lists the atomic mass of carbon as 12.011 amu; the average molar mass of carbon—the mass of 6.022×10^{23} carbon atoms—is therefore 12.011 g/mol:

Atomic mass of carbon as 12.011 amu; the average molar mass of carbon

Substance (formula)	Atomic, Molecular, or Formula Mass (amu)	Molar Mass (g/mol)
carbon (C)	12.011 (atomic mass)	12.011
ethanol (C_2H_5OH)	46.069 (molecular mass)	46.069
calcium phosphate [$Ca_3(PO_4)_2$]	310.177 (formula mass)	310.177



Determining the Molar Mass of a Molecule, YouTube: [Determining the Molar Mass of a Molecule](#)(opens in new window) [youtu.be]

The molar mass of naturally-occurring carbon is different from that of carbon-12, and is not an integer because carbon occurs as a mixture of carbon-12, carbon-13, and carbon-14. One mole of carbon still has 6.022×10^{23} carbon atoms, but 98.89% of those atoms are carbon-12, 1.11% are carbon-13, and a trace (about 1 atom in 10¹²) are carbon-14. (For more information, see Section 1.6.) Similarly, the molar mass of uranium is 238.03 g/mol, and the molar mass of iodine is 126.90 g/mol. When dealing with elements such as iodine and sulfur, which occur as a diatomic molecule (I_2) and a polyatomic molecule (S_8), respectively, molar mass usually refers to the mass of 1 mol of atoms of the element—in this case I and S, not to the mass of 1 mol of molecules of the element (I_2 and S_8).

The molar mass of ethanol is the mass of ethanol (C_2H_5OH) that contains 6.022×10^{23} ethanol molecules. As in Example 3.1.1, the molecular mass of ethanol is 46.069 amu. Because 1 mol of ethanol contains 2 mol of carbon atoms (2×12.011 g), 6 mol of hydrogen atoms (6×1.0079 g), and 1 mol of oxygen atoms (1×15.9994 g), its molar mass is 46.069 g/mol. Similarly, the formula mass of calcium phosphate [$Ca_3(PO_4)_2$] is 310.177 amu, so its molar mass is 310.177 g/mol. This is the mass of calcium phosphate that contains 6.022×10^{23} formula units.

The mole is the basis of quantitative chemistry. It provides chemists with a way to convert easily between the mass of a substance and the number of individual atoms, molecules, or formula units of that substance. Conversely, it enables chemists to calculate the mass of a substance needed to obtain a desired number of atoms, molecules, or formula units. For example, to convert moles of a substance to mass, the following relationship is used:

$$(moles) \times (molar mass) \rightarrow \text{mass} \quad (3.1.1)$$

or, more specifically,

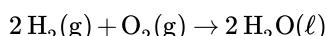
$$\cancel{\text{moles}} \times \left(\frac{\text{grams}}{\text{mole}} \right) = \text{grams}$$

Conversely, to convert the mass of a substance to moles:

$$\left(\frac{\text{grams}}{\text{molar mass}} \right) \rightarrow \text{moles} \quad (3.1.2)$$

$$\left(\frac{\text{grams}}{\text{grams/mole}} \right) = \cancel{\text{grams}} \left(\frac{\text{mole}}{\cancel{\text{grams}}} \right) = \text{moles} \quad (3.1.3)$$

The coefficients in a balanced chemical equation can be interpreted both as the relative numbers of molecules involved in the reaction and as the relative number of moles. For example, in the *balanced* equation:



the production of two moles of water would require the consumption of 2 moles of H₂ and one mole of O₂. Therefore, when considering **this** particular reaction

- 2 moles of H₂
- 1 mole of O₂ and
- 2 moles of H₂O

would be considered to be **stoichiometrically equivalent quantities**.

These stoichiometric relationships, derived from balanced equations, can be used to determine expected amounts of products given amounts of reactants. For example, how many moles of H₂O would be produced from 1.57 moles of O₂?

$$(1.57 \text{ mol O}_2) \left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2} \right) = 3.14 \text{ mol H}_2\text{O}$$

The ratio $\left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2} \right)$ is the stoichiometric relationship between H₂O and O₂ from the balanced equation for this reaction.

Be sure to pay attention to the units when converting between mass and moles. Figure 3.1.1 is a flowchart for converting between mass; the number of moles; and the number of atoms, molecules, or formula units. The use of these conversions is illustrated in Examples 3.1.3 and 3.1.4.

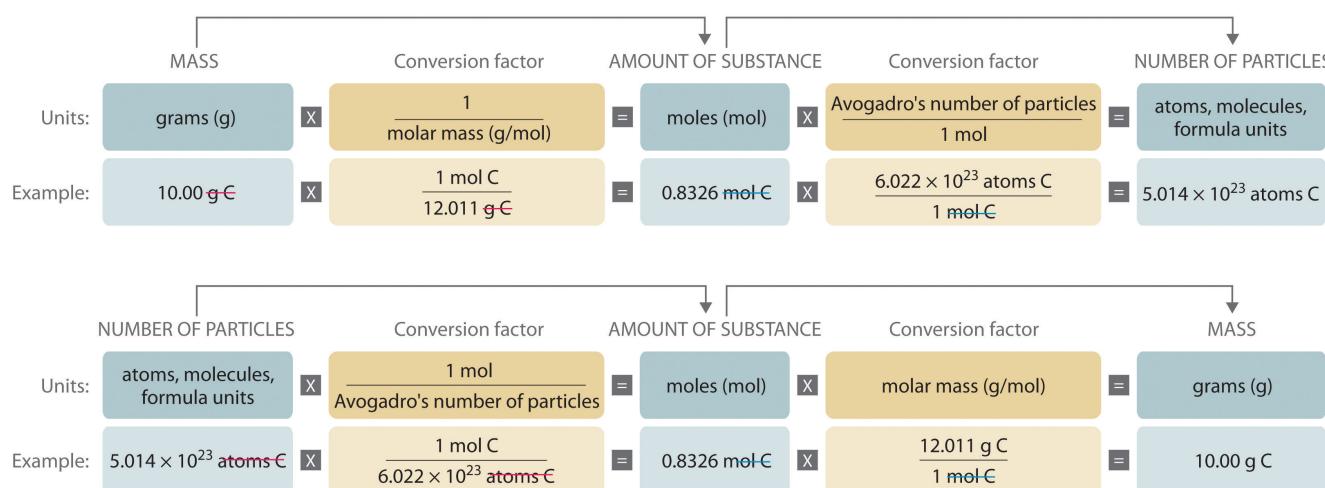
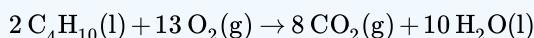


Figure 3.1.1: A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units

Flowchart of conversions between mass, amount of substance, and number of particles using conversion factors of molar mass and Avogadro's number.

✓ Example 3.1.3: Combustion of Butane

For the combustion of butane (C_4H_{10}) the balanced equation is:



Calculate the mass of CO_2 that is produced in burning 1.00 gram of C_4H_{10} .

Solution

Thus, the overall sequence of steps to solve this problem is:



First of all we need to calculate how many moles of butane we have in a 1.00 gram sample:

$$(1.00 \text{ g C}_4\text{H}_{10}) \left(\frac{1 \text{ mol C}_4\text{H}_{10}}{58.0 \text{ g C}_4\text{H}_{10}} \right) = 1.72 \times 10^{-2} \text{ mol C}_4\text{H}_{10}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8 \text{ mol CO}_2}{2 \text{ mol C}_4\text{H}_{10}} \right)$$

Therefore:

$$\left(\frac{8 \text{ mol CO}_2}{2 \text{ mol C}_4\text{H}_{10}} \right) \times 1.72 \times 10^{-2} \text{ mol C}_4\text{H}_{10} = 6.88 \times 10^{-2} \text{ mol CO}_2$$

The question called for the determination of the mass of CO_2 produced, thus we have to convert moles of CO_2 into grams (by using the **molecular weight** of CO_2):

$$6.88 \times 10^{-2} \text{ mol CO}_2 \left(\frac{44.0 \text{ g CO}_2}{1 \text{ mol CO}_2} \right) = 3.03 \text{ g CO}_2$$

✓ Example 3.1.4: Ethylene Glycol

For 35.00 g of ethylene glycol (HOCH2CH2OH), which is used in inks for ballpoint pens, calculate the number of

- moles.
- molecules.

Given: mass and molecular formula

Asked for: number of moles and number of molecules

Strategy:

- Use the molecular formula of the compound to calculate its molecular mass in grams per mole.
- Convert from mass to moles by dividing the mass given by the compound's molar mass.
- Convert from moles to molecules by multiplying the number of moles by Avogadro's number.

Solution:

A The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 3.1.1:

$$2\text{C}(2 \text{ atoms})(12.011 \text{ amu/atom}) = 24.022 \text{ amu}$$

$$6\text{H}(6 \text{ atoms})(1.0079 \text{ amu/atom}) = 6.0474 \text{ amu}$$

$$2\text{O}(2 \text{ atoms})(15.9994 \text{ amu/atom}) = 31.9988 \text{ amu}$$

$$\text{C}_2\text{H}_6\text{O}_2 \text{molecular mass of ethylene glycol} = 62.068 \text{ amu}$$

The molar mass of ethylene glycol is 62.068 g/mol.

B The number of moles of ethylene glycol present in 35.00 g can be calculated by dividing the mass (in grams) by the molar mass (in grams per mole):

$$\frac{\text{mass of ethylene glycol (g)}}{\text{molar mass (g/mol)}} = \text{moles ethylene glycol (mol)}$$

So

$$35.00 \text{ g ethylene glycol} \left(\frac{1 \text{ mole ethylene glycol}}{62.068 \text{ g ethylene glycol}} \right) = 0.5639 \text{ mole ethylene glycol}$$

It is always a good idea to estimate the answer before you do the actual calculation. In this case, the mass given (35.00 g) is less than the molar mass, so the answer should be less than 1 mol. The calculated answer (0.5639 mol) is indeed less than 1 mol, so we have probably not made a major error in the calculations.

C To calculate the number of molecules in the sample, we multiply the number of moles by Avogadro's number:

$$\begin{aligned} \text{molecules of ethylene glycol} &= 0.5639 \text{ mol} \left(\frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \right) \\ &= 3.396 \times 10^{23} \text{ molecules} \end{aligned}$$

Because we are dealing with slightly more than 0.5 mol of ethylene glycol, we expect the number of molecules present to be slightly more than one-half of Avogadro's number, or slightly more than 3×10^{23} molecules, which is indeed the case.

?

Exercise 3.1.4: Freon-11

For 75.0 g of CCl_3F (Freon-11), calculate the number of

- moles.
- molecules.

Answer a

0.546 mol

Answer b

3.29×10^{23} molecules

✓ Example 3.1.5

Calculate the mass of 1.75 mol of each compound.

- S_2Cl_2 (common name: sulfur monochloride; systematic name: disulfur dichloride)
- $\text{Ca}(\text{ClO})_2$ (calcium hypochlorite)

Given: number of moles and molecular or empirical formula

Asked for: mass

Strategy:

A Calculate the molecular mass of the compound in grams from its molecular formula (if covalent) or empirical formula (if ionic).

B Convert from moles to mass by multiplying the moles of the compound given by its molar mass.

Solution:

We begin by calculating the molecular mass of S_2Cl_2 and the formula mass of $\text{Ca}(\text{ClO})_2$.

A The molar mass of S_2Cl_2 is obtained from its molecular mass as follows:

$$2S(2 \text{ atoms})(32.065 \text{ amu/atom}) = 64.130 \text{ amu}$$

$$+2Cl(2 \text{ atoms})(35.453 \text{ amu/atom}) = 70.906 \text{ amu}$$

$$S_2Cl_2 \text{ molecular mass of } S_2Cl_2 = 135.036 \text{ amu}$$

The molar mass of S_2Cl_2 is 135.036 g/mol.

B The mass of 1.75 mol of S_2Cl_2 is calculated as follows:

$$\text{moles } S_2Cl_2 \left[\text{molar mass} \left(\frac{g}{\text{mol}} \right) \right] \rightarrow \text{mass of } S_2Cl_2 (g)$$

$$1.75 \text{ mol } S_2Cl_2 \left(\frac{135.036 \text{ g } S_2Cl_2}{1 \text{ mol } S_2Cl_2} \right) = 236 \text{ g } S_2Cl_2$$

A The formula mass of $Ca(ClO)_2$ is obtained as follows:

$$1Ca(1 \text{ atom})(40.078 \text{ amu/atom}) = 40.078 \text{ amu}$$

$$2Cl(2 \text{ atoms})(35.453 \text{ amu/atom}) = 70.906 \text{ amu}$$

$$+2O(2 \text{ atoms})(15.9994 \text{ amu/atom}) = 31.9988 \text{ amu}$$

$$Ca(ClO)_2 \text{ formula mass of } Ca(ClO)_2 = 142.983 \text{ amu}$$

The molar mass of $Ca(ClO)_2$ is 142.983 g/mol.

B The mass of 1.75 mol of $Ca(ClO)_2$ is calculated as follows:

$$\text{moles } Ca(ClO)_2 \left[\frac{\text{molar mass } Ca(ClO)_2}{1 \text{ mol } Ca(ClO)_2} \right] = \text{mass } Ca(ClO)_2$$

$$1.75 \text{ mol } Ca(ClO)_2 \left[\frac{142.983 \text{ g } Ca(ClO)_2}{1 \text{ mol } Ca(ClO)_2} \right] = 250 \text{ g } Ca(ClO)_2$$

Because 1.75 mol is less than 2 mol, the final quantity in grams in both cases should be less than twice the molar mass, which it is.

Exercise 3.1.5

Calculate the mass of 0.0122 mol of each compound.

- a. Si_3N_4 (silicon nitride), used as bearings and rollers
- b. $(CH_3)_3N$ (trimethylamine), a corrosion inhibitor

Answer a

1.71 g

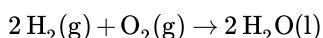
Answer b

0.721 g



Conversions Between Grams, Mol, & Atoms: [Conversions Between Grams, Mol & Atoms, YouTube](#)(opens in new window)
[youtu.be]

The coefficients in a balanced chemical equation can be interpreted both as the relative numbers of molecules involved in the reaction and as the relative number of moles. For example, in the *balanced* equation:



the production of two moles of water would require the consumption of 2 moles of H_2 and one mole of O_2 . Therefore, when considering *this* particular reaction

- 2 moles of H_2
- 1 mole of O_2 and
- 2 moles of H_2O

would be considered to be ***stoichiometrically equivalent quantities***.

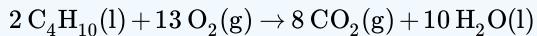
These stoichiometric relationships, derived from balanced equations, can be used to determine expected amounts of products given amounts of reactants. For example, how many moles of H_2O would be produced from 1.57 moles of O_2 ?

$$(1.57 \text{ mol O}_2) \left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2} \right) = 3.14 \text{ mol H}_2\text{O}$$

The ratio $\left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2} \right)$ is the stoichiometric relationship between H_2O and O_2 from the balanced equation for this reaction.

✓ Example 3.1.6

For the combustion of butane (C_4H_{10}) the balanced equation is:



Calculate the mass of CO_2 that is produced in burning 1.00 gram of C_4H_{10} .

Solution

First of all we need to calculate how many moles of butane we have in a 1.00 gram sample:

$$(1.00 \text{ g C}_4\text{H}_{10}) \left(\frac{1 \text{ mol C}_4\text{H}_{10}}{58.0 \text{ g C}_4\text{H}_{10}} \right) = 1.72 \times 10^{-2} \text{ mol C}_4\text{H}_{10}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8 \text{ mol CO}_2}{2 \text{ mol C}_4\text{H}_{10}} \right)$$

Therefore:

$$\left(\frac{8 \text{ mol } CO_2}{2 \text{ mol } C_4H_{10}} \right) \times 1.72 \times 10^{-2} \text{ mol } C_4H_{10} = 6.88 \times 10^{-2} \text{ mol } CO_2$$

The question called for the determination of the mass of CO_2 produced, thus we have to convert moles of CO_2 into grams (by using the **molecular weight** of CO_2):

$$6.88 \times 10^{-2} \text{ mol } CO_2 \left(\frac{44.0 \text{ g } CO_2}{1 \text{ mol } CO_2} \right) = 3.03 \text{ g } CO_2$$

Thus, the overall sequence of steps to solve this problem were:



In a similar way we could determine the mass of water produced, or oxygen consumed, etc.



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

Summary

To analyze chemical transformations, it is essential to use a standardized unit of measure called the mole. The molecular mass and the formula mass of a compound are obtained by adding together the atomic masses of the atoms present in the molecular formula or empirical formula, respectively; the units of both are atomic mass units (amu). The mole is a unit used to measure the number of atoms, molecules, or (in the case of ionic compounds) formula units in a given mass of a substance. The mole is defined as the amount of substance that contains the number of carbon atoms in exactly 12 g of carbon-12, Avogadro's number (6.022×10^{23}) of atoms of carbon-12. The molar mass of a substance is defined as the mass of 1 mol of that substance, expressed in grams per mole, and is equal to the mass of 6.022×10^{23} atoms, molecules, or formula units of that substance.

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3.E: Stoichiometry of Formulas and Equations (Exercises)

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CHAPTER OVERVIEW

4: Three Major Classes of Chemical Reactions

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII
XVIII XIX XX XXI XXII XXIII XXIV

Template:HideTOC

- 4.1: Solution Concentration and the Role of Water as a Solvent
- 4.2: Writing Equations for Aqueous Ionic Reactions
- 4.3: Precipitation Reactions
- 4.4: Acid-Base Reactions
- 4.5: Oxidation-Reduction (Redox) Reactions
- 4.6: Elements in Redox Reactions
- 4.7: The Reversibility of Reactions and the Equilibrium State

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4.1: Solution Concentration and the Role of Water as a Solvent

Learning Objectives

- To describe the concentrations of solutions quantitatively

Many people have a qualitative idea of what is meant by *concentration*. Anyone who has made instant coffee or lemonade knows that too much powder gives a strongly flavored, highly concentrated drink, whereas too little results in a dilute solution that may be hard to distinguish from water. In chemistry, the concentration of a solution is the quantity of a **solute** that is contained in a particular quantity of **solvent** or solution. Knowing the concentration of solutes is important in controlling the stoichiometry of reactants for solution reactions. Chemists use many different methods to define concentrations, some of which are described in this section.

Molarity

The most common unit of concentration is *molarity*, which is also the most useful for calculations involving the stoichiometry of reactions in solution. The molarity (M) is defined as the number of moles of solute present in exactly 1 L of solution. It is, equivalently, the number of millimoles of solute present in exactly 1 mL of solution:

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{mmoles of solute}}{\text{milliliters of solution}} \quad (4.1.1)$$

The units of molarity are therefore moles per liter of solution (mol/L), abbreviated as M. An aqueous solution that contains 1 mol (342 g) of sucrose in enough water to give a final volume of 1.00 L has a sucrose concentration of 1.00 mol/L or 1.00 M. In chemical notation, square brackets around the name or formula of the solute represent the molar concentration of a solute. Therefore,

$$[\text{sucrose}] = 1.00 \text{ M}$$

is read as “the concentration of sucrose is 1.00 molar.” The relationships between volume, molarity, and moles may be expressed as either

$$V_L M_{\text{mol/L}} = \cancel{V} \left(\frac{\text{mol}}{\cancel{V}} \right) = \text{moles} \quad (4.1.2)$$

or

$$V_{\text{mL}} M_{\text{mmol/mL}} = \cancel{mL} \left(\frac{\text{mmol}}{\cancel{mL}} \right) = \text{mmoles} \quad (4.1.3)$$

Figure 4.1.1 illustrates the use of Equations 4.1.2 and 4.1.3.

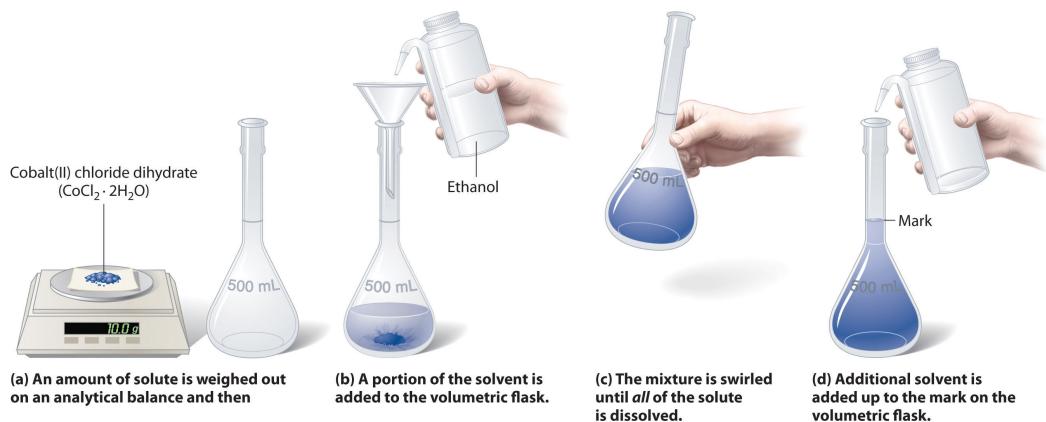


Figure 4.1.1: Preparation of a Solution of Known Concentration Using a Solid Solute

✓ Example 4.1.1: Calculating Moles from Concentration of NaOH

Calculate the number of moles of sodium hydroxide (NaOH) in 2.50 L of 0.100 M NaOH.

Given: identity of solute and volume and molarity of solution

Asked for: amount of solute in moles

Strategy:

Use either Equation 4.1.2 or Equation 4.1.3, depending on the units given in the problem.

Solution:

Because we are given the volume of the solution in liters and are asked for the number of moles of substance, Equation 4.1.2 is more useful:

$$\text{moles NaOH} = V_L M_{\text{mol/L}} = (2.50 \text{ L}) \left(\frac{0.100 \text{ mol}}{\text{L}} \right) = 0.250 \text{ mol NaOH}$$

? Exercise 4.1.1: Calculating Moles from Concentration of Alanine

Calculate the number of millimoles of alanine, a biologically important molecule, in 27.2 mL of 1.53 M alanine.

Answer

41.6 mmol



Calculations Involving Molarity (M): [Calculations Involving Molarity \(M\), YouTube](#)(opens in new window) [youtu.be]

Concentrations are also often reported on a mass-to-mass (m/m) basis or on a mass-to-volume (m/v) basis, particularly in clinical laboratories and engineering applications. A concentration expressed on an m/m basis is equal to the number of grams of solute per gram of solution; a concentration on an m/v basis is the number of grams of solute per milliliter of solution. Each measurement can be expressed as a percentage by multiplying the ratio by 100; the result is reported as percent m/m or percent m/v. The concentrations of very dilute solutions are often expressed in *parts per million (ppm)*, which is grams of solute per 10^6 g of solution, or in *parts per billion (ppb)*, which is grams of solute per 10^9 g of solution. For aqueous solutions at 20°C, 1 ppm corresponds to 1 µg per milliliter, and 1 ppb corresponds to 1 ng per milliliter. These concentrations and their units are summarized in Table 4.1.1.

Table 4.1.1: Common Units of Concentration

Concentration	Units
m/m	g of solute/g of solution
m/v	g of solute/mL of solution

Concentration	Units
ppm	g of solute/ 10^6 g of solution
	$\mu\text{g}/\text{mL}$
ppb	g of solute/ 10^9 g of solution
	ng/mL

The Preparation of Solutions

To prepare a solution that contains a specified concentration of a substance, it is necessary to dissolve the desired number of moles of solute in enough solvent to give the desired final volume of solution. Figure 4.1.1 illustrates this procedure for a solution of cobalt(II) chloride dihydrate in ethanol. Note that the volume of the *solvent* is not specified. Because the solute occupies space in the solution, the volume of the solvent needed is almost always *less* than the desired volume of solution. For example, if the desired volume were 1.00 L, it would be incorrect to add 1.00 L of water to 342 g of sucrose because that would produce more than 1.00 L of solution. As shown in Figure 4.1.2, for some substances this effect can be significant, especially for concentrated solutions.

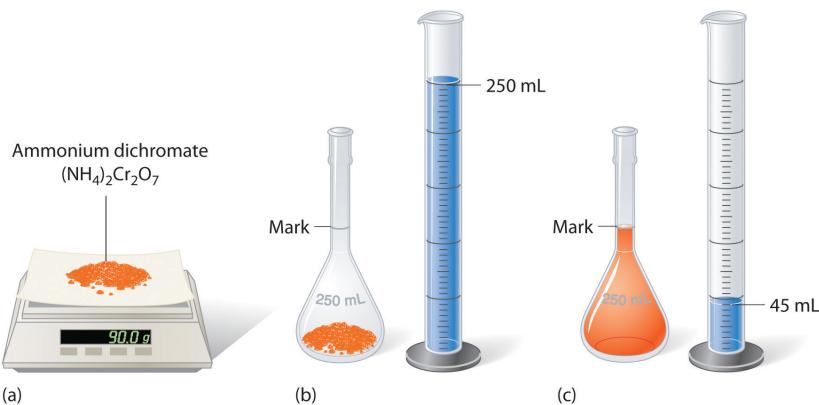


Figure 4.1.2: Preparation of 250 mL of a Solution of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in Water. The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.

45 milliliters of water remain in the graduated cylinder even after addition to the mark of the volumetric flask.

✓ Example 4.1.2

The solution contains 10.0 g of cobalt(II) chloride dihydrate, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$?

Given: mass of solute and volume of solution

Asked for: concentration (M)

Strategy:

To find the number of moles of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, divide the mass of the compound by its molar mass. Calculate the molarity of the solution by dividing the number of moles of solute by the volume of the solution in liters.

Solution:

The molar mass of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ is 165.87 g/mol. Therefore,

$$\text{moles } \text{CoCl}_2 \cdot 2\text{H}_2\text{O} = \left(\frac{10.0 \text{ g}}{165.87 \text{ g/mol}} \right) = 0.0603 \text{ mol}$$

The volume of the solution in liters is

$$\text{volume} = 500 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.500 \text{ L}$$

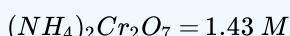
Molarity is the number of moles of solute per liter of solution, so the molarity of the solution is

$$\text{molarity} = \frac{0.0603 \text{ mol}}{0.500 \text{ L}} = 0.121 \text{ M} = \text{CoCl}_2 \cdot \text{H}_2\text{O}$$

? Exercise 4.1.2

The solution shown in Figure 4.1.2 contains 90.0 g of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in enough water to give a final volume of exactly 250 mL. What is the molar concentration of ammonium dichromate?

Answer



To prepare a particular volume of a solution that contains a specified concentration of a solute, we first need to calculate the number of moles of solute in the desired volume of solution using the relationship shown in Equation 4.1.2. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example 4.1.3.

✓ Example 4.1.3: D5W Solution

The so-called D5W solution used for the intravenous replacement of body fluids contains 0.310 M glucose. (D5W is an approximately 5% solution of dextrose [the medical name for glucose] in water.) Calculate the mass of glucose necessary to prepare a 500 mL pouch of D5W. Glucose has a molar mass of 180.16 g/mol.

Given: molarity, volume, and molar mass of solute

Asked for: mass of solute

Strategy:

- Calculate the number of moles of glucose contained in the specified volume of solution by multiplying the volume of the solution by its molarity.
- Obtain the mass of glucose needed by multiplying the number of moles of the compound by its molar mass.

Solution:

A We must first calculate the number of moles of glucose contained in 500 mL of a 0.310 M solution:

$$V_L M_{\text{mol/L}} = \text{moles}$$

$$500 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{0.310 \text{ mol glucose}}{1 \text{ L}} \right) = 0.155 \text{ mol glucose}$$

B We then convert the number of moles of glucose to the required mass of glucose:

$$\text{mass of glucose} = 0.155 \text{ mol glucose} \left(\frac{180.16 \text{ g glucose}}{1 \text{ mol glucose}} \right) = 27.9 \text{ g glucose}$$

? Exercise 4.1.3

Another solution commonly used for intravenous injections is normal saline, a 0.16 M solution of sodium chloride in water. Calculate the mass of sodium chloride needed to prepare 250 mL of normal saline solution.

Answer

2.3 g NaCl

A solution of a desired concentration can also be prepared by diluting a small volume of a more concentrated solution with additional solvent. A stock solution is a commercially prepared solution of known concentration and is often used for this purpose. Diluting a stock solution is preferred because the alternative method, weighing out tiny amounts of solute, is difficult to carry out

with a high degree of accuracy. Dilution is also used to prepare solutions from substances that are sold as concentrated aqueous solutions, such as strong acids.

The procedure for preparing a solution of known concentration from a stock solution is shown in Figure 4.1.3. It requires calculating the number of moles of solute desired in the final volume of the more dilute solution and then calculating the volume of the stock solution that contains this amount of solute. Remember that diluting a given quantity of stock solution with solvent does *not* change the number of moles of solute present. The relationship between the volume and concentration of the stock solution and the volume and concentration of the desired diluted solution is therefore

$$(V_s)(M_s) = \text{moles of solute} = (V_d)(M_d) \quad (4.1.4)$$

where the subscripts *s* and *d* indicate the stock and dilute solutions, respectively. Example 4.1.4 demonstrates the calculations involved in diluting a concentrated stock solution.

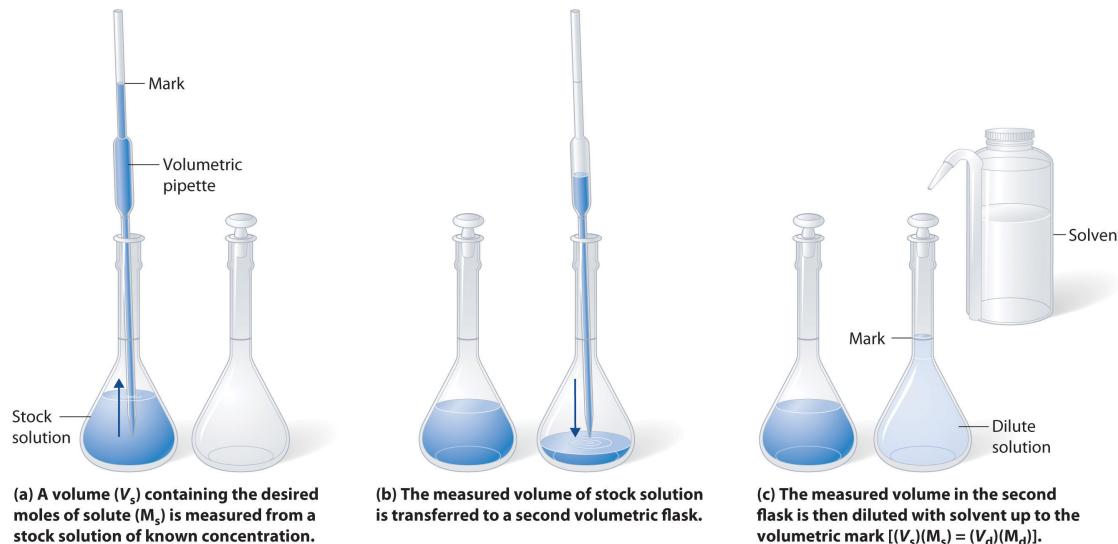


Figure 4.1.3: Preparation of a Solution of Known Concentration by Diluting a Stock Solution. (a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration. (b) The measured volume of stock solution is transferred to a second volumetric flask. (c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].

✓ Example 4.1.4

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example 4.1.3?

Given: volume and molarity of dilute solution

Asked for: volume of stock solution

Strategy:

- Calculate the number of moles of glucose contained in the indicated volume of dilute solution by multiplying the volume of the solution by its molarity.
- To determine the volume of stock solution needed, divide the number of moles of glucose by the molarity of the stock solution.

Solution:

A The D5W solution in Example 4.5.3 was 0.310 M glucose. We begin by using Equation 4.5.4 to calculate the number of moles of glucose contained in 2500 mL of the solution:

$$\text{moles glucose} = 2500 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{0.310 \text{ mol glucose}}{1 \text{ L}} \right) = 0.775 \text{ mol glucose}$$

B We must now determine the volume of the 3.00 M stock solution that contains this amount of glucose:

$$\text{volume of stock soln} = 0.775 \text{ mol glucose} \left(\frac{1 \text{ L}}{3.00 \text{ mol glucose}} \right) = 0.258 \text{ L or } 258 \text{ mL}$$

In determining the volume of stock solution that was needed, we had to divide the desired number of moles of glucose by the concentration of the stock solution to obtain the appropriate units. Also, the number of moles of solute in 258 mL of the stock solution is the same as the number of moles in 2500 mL of the more dilute solution; *only the amount of solvent has changed*. The answer we obtained makes sense: diluting the stock solution about tenfold increases its volume by about a factor of 10 (258 mL → 2500 mL). Consequently, the concentration of the solute must decrease by about a factor of 10, as it does (3.00 M → 0.310 M).

We could also have solved this problem in a single step by solving Equation 4.5.4 for V_s and substituting the appropriate values:

$$V_s = \frac{(V_d)(M_d)}{M_s} = \frac{(2.500 \text{ L})(0.310 \text{ M})}{3.00 \text{ M}} = 0.258 \text{ L}$$

As we have noted, there is often more than one correct way to solve a problem.

Exercise 4.1.4

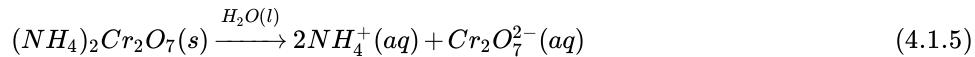
What volume of a 5.0 M NaCl stock solution is necessary to prepare 500 mL of normal saline solution (0.16 M NaCl)?

Answer

16 mL

Ion Concentrations in Solution

In Example 4.1.2, the concentration of a solution containing 90.00 g of ammonium dichromate in a final volume of 250 mL were calculated to be 1.43 M. Let's consider in more detail exactly what that means. Ammonium dichromate is an ionic compound that contains two NH_4^+ ions and one $\text{Cr}_2\text{O}_7^{2-}$ ion per formula unit. Like other ionic compounds, it is a strong electrolyte that dissociates in aqueous solution to give hydrated NH_4^+ and $\text{Cr}_2\text{O}_7^{2-}$ ions:



Thus 1 mol of ammonium dichromate formula units dissolves in water to produce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ anions and 2 mol of NH_4^+ cations (see Figure 4.1.4).

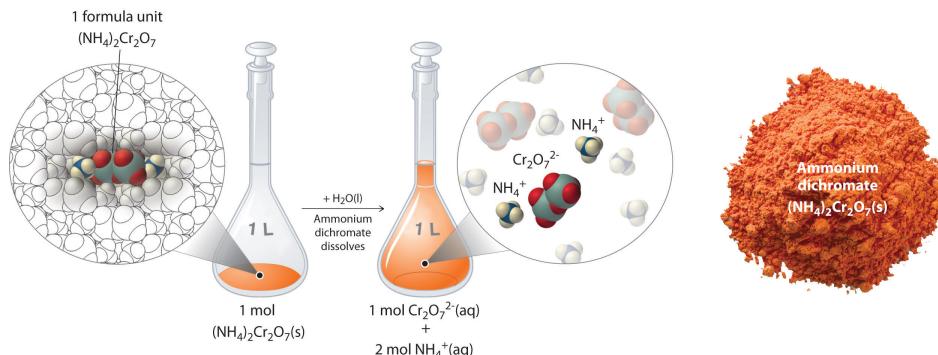
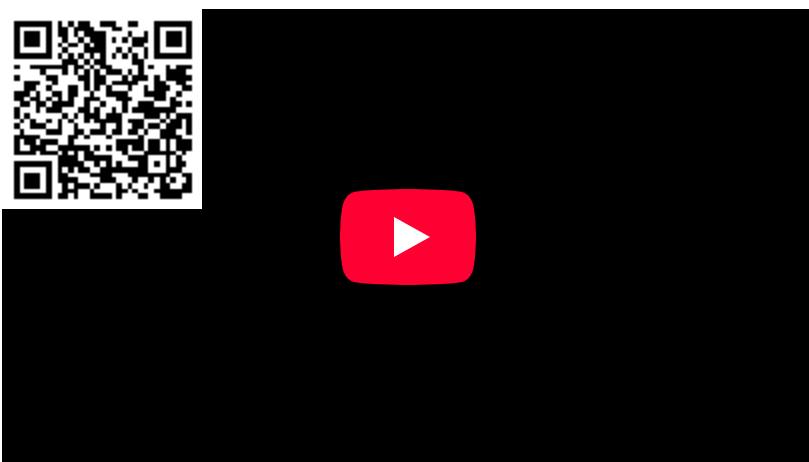


Figure 4.1.4: Dissolution of 1 mol of an Ionic Compound. In this case, dissolving 1 mol of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ produces a solution that contains 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)

1 mol of ammonium dichromate is shown in a 1 liter volumetric flask. The resulting volumetric flask on the right contains 1 liter of solution after being dissolved with water. Powdered form of ammonium dichromate is also included in diagram.

When carrying out a chemical reaction using a solution of a salt such as ammonium dichromate, it is important to know the concentration of each ion present in the solution. If a solution contains 1.43 M $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, then the concentration of $\text{Cr}_2\text{O}_7^{2-}$

must also be 1.43 M because there is one $\text{Cr}_2\text{O}_7^{2-}$ ion per formula unit. However, there are two NH_4^+ ions per formula unit, so the concentration of NH_4^+ ions is $2 \times 1.43 \text{ M} = 2.86 \text{ M}$. Because each formula unit of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ produces *three* ions when dissolved in water ($2\text{NH}_4^+ + 1\text{Cr}_2\text{O}_7^{2-}$), the *total* concentration of ions in the solution is $3 \times 1.43 \text{ M} = 4.29 \text{ M}$.



Concentration of Ions in Solution from a Soluble Salt: [Concentration of Ions in Solution from a Soluble Salt, YouTube](#)(opens in new window) [youtu.be]

✓ Example 4.1.5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

- 0.21 M NaOH
- 3.7 M $(\text{CH}_3)_2\text{CHOH}$
- 0.032 M In(NO₃)₃

Given: molarity

Asked for: concentrations

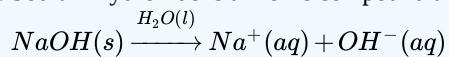
Strategy:

A Classify each compound as either a strong electrolyte or a nonelectrolyte.

B If the compound is a nonelectrolyte, its concentration is the same as the molarity of the solution. If the compound is a strong electrolyte, determine the number of each ion contained in one formula unit. Find the concentration of each species by multiplying the number of each ion by the molarity of the solution.

Solution:

- Sodium hydroxide is an ionic compound that is a strong electrolyte (and a strong base) in aqueous solution:

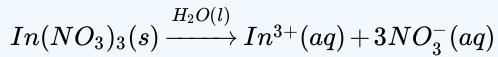


B Because each formula unit of NaOH produces one Na^+ ion and one OH^- ion, the concentration of each ion is the same as the concentration of NaOH: $[\text{Na}^+] = 0.21 \text{ M}$ and $[\text{OH}^-] = 0.21 \text{ M}$.

- The formula $(\text{CH}_3)_2\text{CHOH}$ represents 2-propanol (isopropyl alcohol) and contains the $-\text{OH}$ group, so it is an alcohol. Recall from Section 4.1 that alcohols are covalent compounds that dissolve in water to give solutions of neutral molecules. Thus alcohols are nonelectrolytes.

B The only solute species in solution is therefore $(\text{CH}_3)_2\text{CHOH}$ molecules, so $[(\text{CH}_3)_2\text{CHOH}] = 3.7 \text{ M}$.

- Indium nitrate is an ionic compound that contains In^{3+} ions and NO_3^- ions, so we expect it to behave like a strong electrolyte in aqueous solution:



B One formula unit of $\text{In}(\text{NO}_3)_3$ produces one In^{3+} ion and three NO_3^- ions, so a 0.032 M $\text{In}(\text{NO}_3)_3$ solution contains 0.032 M In^{3+} and $3 \times 0.032 \text{ M} = 0.096 \text{ M } \text{NO}_3^-$ —that is, $[\text{In}^{3+}] = 0.032 \text{ M}$ and $[\text{NO}_3^-] = 0.096 \text{ M}$.

? Exercise 4.1.5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

- a. 0.0012 M Ba(OH)₂
- b. 0.17 M Na₂SO₄
- c. 0.50 M (CH₃)₂CO, commonly known as acetone



Answer a

$$[Ba^{2+}] = 0.0012 \text{ M}; [OH^-] = 0.0024 \text{ M}$$

Answer b

$$[Na^+] = 0.34 \text{ M}; [SO_4^{2-}] = 0.17 \text{ M}$$

Answer c

$$[(CH_3)_2CO] = 0.50 \text{ M}$$

Summary

Solution concentrations are typically expressed as molarities and can be prepared by dissolving a known mass of solute in a solvent or diluting a stock solution.

- **definition of molarity:**

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{mmoles of solute}}{\text{milliliters of solution}}$$

- **relationship among volume, molarity, and moles:**

$$V_L M_{mol/L} = L \left(\frac{\text{mol}}{L} \right) = \text{moles}$$

- **relationship between volume and concentration of stock and dilute solutions:**

$$(V_s)(M_s) = \text{moles of solute} = (V_d)(M_d)$$

The **concentration** of a substance is the quantity of solute present in a given quantity of solution. Concentrations are usually expressed in terms of **molarity**, defined as the number of moles of solute in 1 L of solution. Solutions of known concentration can be prepared either by dissolving a known mass of solute in a solvent and diluting to a desired final volume or by diluting the appropriate volume of a more concentrated solution (a **stock solution**) to the desired final volume.

Contributors and Attributions

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4.2: Writing Equations for Aqueous Ionic Reactions

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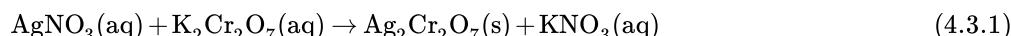
4.3: Precipitation Reactions

Learning Objectives

- To identify a precipitation reaction and predict solubilities.

Exchange (Double-Displacement) Reactions

A precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. We described a precipitation reaction in which a colorless solution of silver nitrate was mixed with a yellow-orange solution of potassium dichromate to give a reddish precipitate of silver dichromate:



This unbalanced equation has the general form of an exchange reaction:



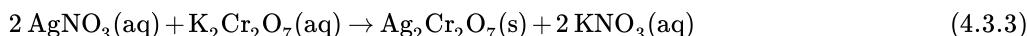
The solubility and insoluble annotations are specific to the reaction in Equation 4.3.1 and not characteristic of all exchange reactions (e.g., both products can be soluble or insoluble). *Precipitation reactions* are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. Because both components of each compound change partners, such reactions are sometimes called *double-displacement reactions*. Two important uses of precipitation reactions are to isolate metals that have been extracted from their ores and to recover precious metals for recycling.



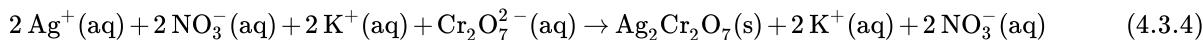
Video 4.3.1: Mixing Potassium Chromate and Silver Nitrate together to initiate a precipitation reaction (Equation 4.3.1).

While full chemical equations show the identities of the reactants and the products and give the stoichiometries of the reactions, they are less effective at describing what is actually occurring in solution. In contrast, equations that show only the hydrated species focus our attention on the chemistry that is taking place and allow us to see similarities between reactions that might not otherwise be apparent.

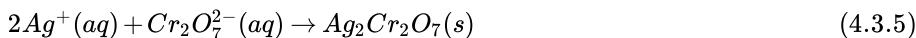
Let's consider the reaction of silver nitrate with potassium dichromate above. When aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall balanced chemical equation for the reaction shows each reactant and product as undissociated, electrically neutral compounds:



Although Equation 4.3.3 gives the identity of the reactants and the products, it does not show the identities of the actual species in solution. Because ionic substances such as AgNO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ are *strong electrolytes* (i.e., they dissociate completely in aqueous solution to form ions). In contrast, because $\text{Ag}_2\text{Cr}_2\text{O}_7$ is not very soluble, it separates from the solution as a solid. To find out what is actually occurring in solution, it is more informative to write the reaction as a complete ionic equation showing which ions and molecules are hydrated and which are present in other forms and phases:

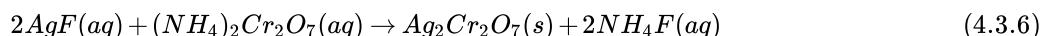


Note that $\text{K}^+(\text{aq})$ and $\text{NO}_3^-(\text{aq})$ ions are present on both sides of Equation 4.3.4 and their coefficients are the same on both sides. These ions are called *spectator ions* because they do not participate in the actual reaction. Canceling the spectator ions gives the net ionic equation, which shows only those species that participate in the chemical reaction:

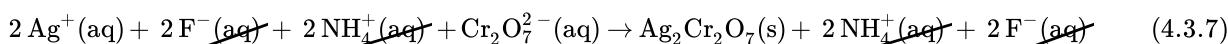


Both mass and charge must be conserved in chemical reactions because the numbers of electrons and protons do not change. For charge to be conserved, the sum of the charges of the ions multiplied by their coefficients must be the same on both sides of the equation. In Equation 4.3.5, the charge on the left side is $2(+1) + 1(-2) = 0$, which is the same as the charge of a neutral $\text{Ag}_2\text{Cr}_2\text{O}_7$ formula unit on the right side.

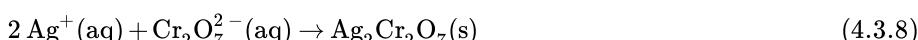
By eliminating the spectator ions, we can focus on the chemistry that takes place in a solution. For example, the overall chemical equation for the reaction between silver fluoride and ammonium dichromate is as follows:



The complete ionic equation for this reaction is as follows:



Because two $\text{NH}_4^+(\text{aq})$ and two $\text{F}^-(\text{aq})$ ions appear on both sides of Equation 4.3.7, they are spectator ions. They can therefore be canceled to give the **net ionic equation** (Equation 4.3.8), which is identical to Equation 4.3.5:



If we look at net ionic equations, it becomes apparent that many different combinations of reactants can result in the same net chemical reaction. For example, we can predict that silver fluoride could be replaced by silver nitrate in the preceding reaction without affecting the outcome of the reaction.



Determining the Products for Precipitation Reactions: [Determining the Products for Precipitation Reactions, YouTube](#)(opens in new window) [youtu.be]

✓ Example 4.3.1: Balancing Precipitation Equations

Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous barium nitrate with aqueous sodium phosphate to give solid barium phosphate and a solution of sodium nitrate.

Given: reactants and products

Asked for: overall, complete ionic, and net ionic equations

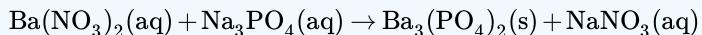
Strategy:

Write and balance the overall chemical equation. Write all the soluble reactants and products in their dissociated form to give the complete ionic equation; then cancel species that appear on both sides of the complete ionic equation to give the net ionic

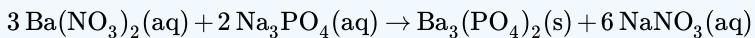
equation.

Solution:

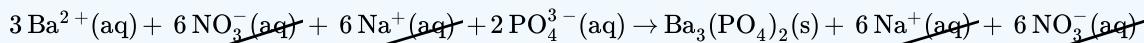
From the information given, we can write the unbalanced chemical equation for the reaction:



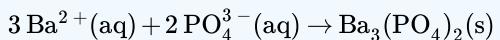
Because the product is $\text{Ba}_3(\text{PO}_4)_2$, which contains three Ba^{2+} ions and two PO_4^{3-} ions per formula unit, we can balance the equation by inspection:



This is the overall balanced chemical equation for the reaction, showing the reactants and products in their undissociated form. To obtain the complete ionic equation, we write each soluble reactant and product in dissociated form:



The six NO_3^- (aq) ions and the six Na^+ (aq) ions that appear on both sides of the equation are spectator ions that can be canceled to give the net ionic equation:

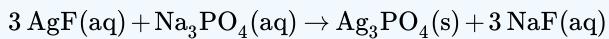


Exercise 4.3.1: Mixing Silver Fluoride with Sodium Phosphate

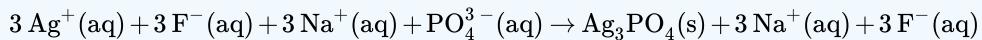
Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous silver fluoride with aqueous sodium phosphate to give solid silver phosphate and a solution of sodium fluoride.

Answer

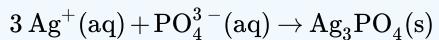
overall chemical equation:



complete ionic equation:



net ionic equation:



So far, we have always indicated whether a reaction will occur when solutions are mixed and, if so, what products will form. As you advance in chemistry, however, you will need to predict the results of mixing solutions of compounds, anticipate what kind of reaction (if any) will occur, and predict the identities of the products. Students tend to think that this means they are supposed to “just know” what will happen when two substances are mixed. Nothing could be further from the truth: an infinite number of chemical reactions is possible, and neither you nor anyone else could possibly memorize them all. Instead, you must begin by identifying the various reactions that *could* occur and then assessing which is the most probable (or least improbable) outcome.

The most important step in analyzing an unknown reaction is to *write down all the species—whether molecules or dissociated ions—that are actually present in the solution* (not forgetting the solvent itself) so that you can assess which species are most likely to react with one another. The easiest way to make that kind of prediction is to attempt to place the reaction into one of several familiar classifications, refinements of the five general kinds of reactions (acid–base, exchange, condensation, cleavage, and oxidation–reduction reactions). In the sections that follow, we discuss three of the most important kinds of reactions that occur in aqueous solutions: precipitation reactions (also known as exchange reactions), acid–base reactions, and oxidation–reduction reactions.

Predicting Solubilities

Table 4.3.1 gives guidelines for predicting the solubility of a wide variety of ionic compounds. To determine whether a precipitation reaction will occur, we identify each species in the solution and then refer to Table 4.3.1 to see which, if any,

combination(s) of cation and anion are likely to produce an insoluble salt. In doing so, it is important to recognize that *soluble* and *insoluble* are relative terms that span a wide range of actual solubilities. We will discuss solubilities in more detail later, where you will learn that very small amounts of the constituent ions remain in solution even after precipitation of an “insoluble” salt. For our purposes, however, we will assume that precipitation of an insoluble salt is complete.

Table 4.3.1: Guidelines for Predicting the Solubility of Ionic Compounds in Water

	Soluble	Exceptions	
Rule 1	most salts that contain an alkali metal (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+) and ammonium (NH_4^+)		
Rule 2	most salts that contain the nitrate (NO_3^-) anion		
Rule 3	most salts of anions derived from monocarboxylic acids (e.g., CH_3CO_2^-)	but not	silver acetate and salts of long-chain carboxylates
Rule 4	most chloride, bromide, and iodide salts	but not	salts of metal ions located on the lower right side of the periodic table (e.g., Cu^+ , Ag^+ , Pb^{2+} , and Hg_2^{2+}).
	Insoluble	Exceptions	
Rule 5	most salts that contain the hydroxide (OH^-) and sulfide (S^{2-}) anions	but not	salts of the alkali metals (group 1), the heavier alkaline earths (Ca^{2+} , Sr^{2+} , and Ba^{2+} in group 2), and the NH_4^+ ion.
Rule 6	most carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) salts	but not	salts of the alkali metals or the NH_4^+ ion.
Rule 7	most sulfate (SO_4^{2-}) salts that contain main group cations with a charge $\geq +2$	but not	salts of +1 cations, Mg^{2+} , and dipoles transition metal cations (e.g., Ni^{2+})

Just as important as predicting the product of a reaction is knowing when a chemical reaction will *not* occur. Simply mixing solutions of two different chemical substances does *not* guarantee that a reaction will take place. For example, if 500 mL of a 1.0 M aqueous NaCl solution is mixed with 500 mL of a 1.0 M aqueous KBr solution, the final solution has a volume of 1.00 L and contains 0.50 M $\text{Na}^+(\text{aq})$, 0.50 M $\text{Cl}^-(\text{aq})$, 0.50 M $\text{K}^+(\text{aq})$, and 0.50 M $\text{Br}^-(\text{aq})$. As you will see in the following sections, none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other (Figure 4.3.1).

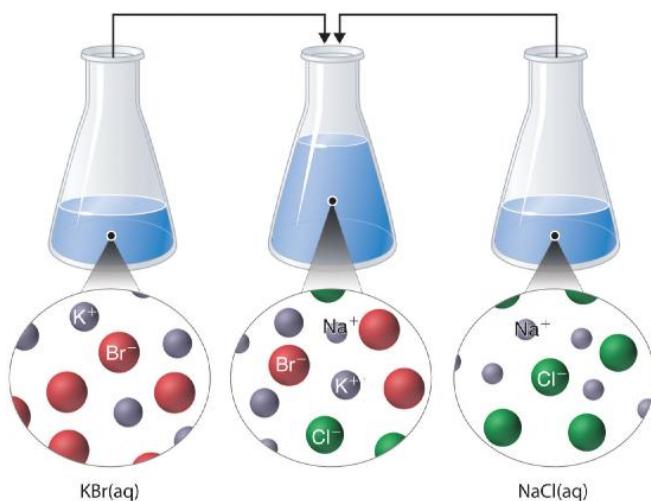


Figure 4.3.1: The Effect of Mixing Aqueous KBr and NaCl Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

✓ Example 4.3.2

Using the information in Table 4.3.1, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

- Aqueous solutions of barium chloride and lithium sulfate are mixed.
- Aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.
- Aqueous solutions of strontium bromide and aluminum nitrate are mixed.
- Solid lead(II) acetate is added to an aqueous solution of ammonium iodide.

Given: reactants

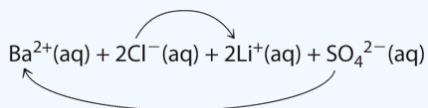
Asked for: reaction and net ionic equation

Strategy:

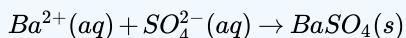
- Identify the ions present in solution and write the products of each possible exchange reaction.
- Refer to Table 4.3.1 to determine which, if any, of the products is insoluble and will therefore form a precipitate. If a precipitate forms, write the net ionic equation for the reaction.

Solution:

A Because barium chloride and lithium sulfate are strong electrolytes, each dissociates completely in water to give a solution that contains the constituent anions and cations. Mixing the two solutions *initially* gives an aqueous solution that contains Ba^{2+} , Cl^- , Li^+ , and SO_4^{2-} ions. The only possible exchange reaction is to form LiCl and BaSO_4 :



B We now need to decide whether either of these products is insoluble. Table 4.3.1 shows that LiCl is soluble in water (rules 1 and 4), but BaSO_4 is not soluble in water (rule 5). Thus BaSO_4 will precipitate according to the net ionic equation

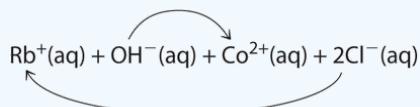


Although soluble barium salts are toxic, BaSO_4 is so insoluble that it can be used to diagnose stomach and intestinal problems without being absorbed into tissues. An outline of the digestive organs appears on x-rays of patients who have been given a “barium milkshake” or a “barium enema”—a suspension of very fine BaSO_4 particles in water.

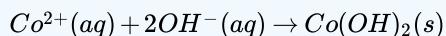


An x-ray of the digestive organs of a patient who has swallowed a “barium milkshake.” A barium milkshake is a suspension of very fine BaSO_4 particles in water; the high atomic mass of barium makes it opaque to x-rays. from Wikipedia.

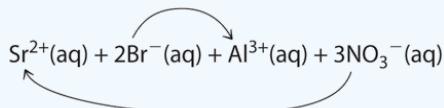
- A** Rubidium hydroxide and cobalt(II) chloride are strong electrolytes, so when aqueous solutions of these compounds are mixed, the resulting solution initially contains Rb^+ , OH^- , Co^{2+} , and Cl^- ions. The possible products of an exchange reaction are rubidium chloride and cobalt(II) hydroxide:



- B** According to Table 4.3.1, RbCl is soluble (rules 1 and 4), but Co(OH)_2 is not soluble (rule 5). Hence Co(OH)_2 will precipitate according to the following net ionic equation:

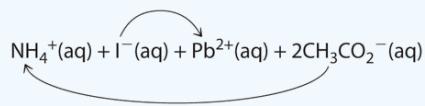


- A** When aqueous solutions of strontium bromide and aluminum nitrate are mixed, we initially obtain a solution that contains Sr^{2+} , Br^- , Al^{3+} , and NO_3^- ions. The two possible products from an exchange reaction are aluminum bromide and strontium nitrate:

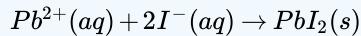


- B** According to Table 4.3.1, both AlBr_3 (rule 4) and $\text{Sr}(\text{NO}_3)_2$ (rule 2) are soluble. Thus no net reaction will occur.

- A** According to Table 4.3.1, lead acetate is soluble (rule 3). Thus solid lead acetate dissolves in water to give Pb^{2+} and CH_3CO_2^- ions. Because the solution also contains NH_4^+ and I^- ions, the possible products of an exchange reaction are ammonium acetate and lead(II) iodide:



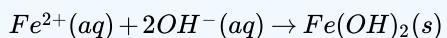
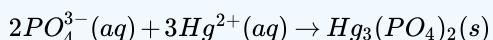
- B** According to Table 4.3.1, ammonium acetate is soluble (rules 1 and 3), but PbI_2 is insoluble (rule 4). Thus $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ will dissolve, and PbI_2 will precipitate. The net ionic equation is as follows:



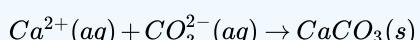
Exercise 4.3.2

Using the information in Table 4.3.1, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

- An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
- Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
- Solid sodium fluoride is added to an aqueous solution of ammonium formate.
- Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Answer a**Answer b****Answer c**

$NaF(s)$ dissolves; no net reaction

Answer d

Predicting the Solubility of Ionic Compounds: [Predicting the Solubility of Ionic Compounds, YouTube](#)([opens in new window](#))
[youtu.be] ([opens in new window](#))

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4.4: Acid-Base Reactions

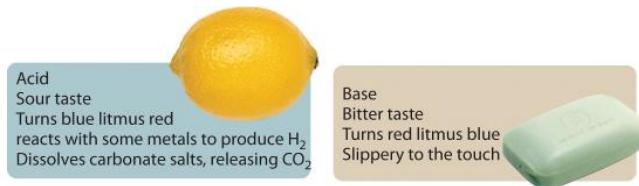
Learning Objectives

- To know the characteristic properties of acids and bases.

Acid-base reactions are essential in both biochemistry and industrial chemistry. Moreover, many of the substances we encounter in our homes, the supermarket, and the pharmacy are acids or bases. For example, aspirin is an acid (acetylsalicylic acid), and antacids are bases. In fact, every amateur chef who has prepared mayonnaise or squeezed a wedge of lemon to marinate a piece of fish has carried out an acid–base reaction. Before we discuss the characteristics of such reactions, let's first describe some of the properties of acids and bases.

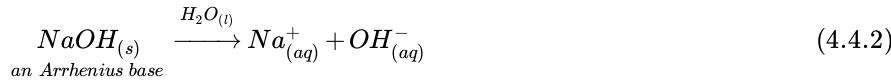
Definitions of Acids and Bases

We can define **acids** as substances that dissolve in water to produce H^+ ions, whereas **bases** are defined as substances that dissolve in water to produce OH^- ions. In fact, this is only one possible set of definitions. Although the general properties of acids and bases have been known for more than a thousand years, the definitions of *acid* and *base* have changed dramatically as scientists have learned more about them. In ancient times, an acid was any substance that had a sour taste (e.g., vinegar or lemon juice), caused consistent color changes in dyes derived from plants (e.g., turning blue litmus paper red), reacted with certain metals to produce hydrogen gas and a solution of a salt containing a metal cation, and dissolved carbonate salts such as limestone ($CaCO_3$) with the evolution of carbon dioxide. In contrast, a base was any substance that had a bitter taste, felt slippery to the touch, and caused color changes in plant dyes that differed diametrically from the changes caused by acids (e.g., turning red litmus paper blue). Although these definitions were useful, they were entirely descriptive.



The Arrhenius Definition of Acids and Bases

The first person to define acids and bases in detail was the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry, 1903). According to the *Arrhenius definition*, an acid is a substance like hydrochloric acid that dissolves in water to produce H^+ ions (protons; Equation 4.4.1), and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide (OH^-) ions (Equation 4.4.2):



According to Arrhenius, the characteristic properties of acids and bases are due exclusively to the presence of H^+ and OH^- ions, respectively, in solution. Although Arrhenius's ideas were widely accepted, his definition of acids and bases had two major limitations:

- First, because acids and bases were defined in terms of ions obtained from water, the Arrhenius concept applied only to substances in aqueous solution.
- Second, and more important, the Arrhenius definition predicted that *only* substances that dissolve in water to produce H^+ and OH^- ions should exhibit the properties of acids and bases, respectively. For example, according to the Arrhenius definition, the reaction of ammonia (a base) with gaseous HCl (an acid) to give ammonium chloride (Equation 4.4.3) is not an acid–base reaction because it does not involve H^+ and OH^- :



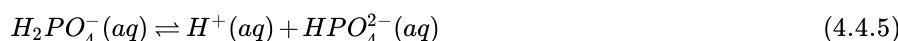
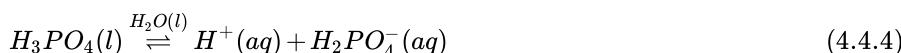
The Brønsted–Lowry Definition of Acids and Bases

Because of the limitations of the Arrhenius definition, a more general definition of acids and bases was needed. One was proposed independently in 1923 by the Danish chemist J. N. Brønsted (1879–1947) and the British chemist T. M. Lowry (1874–1936), who defined acid–base reactions in terms of the transfer of a proton (H^+ ion) from one substance to another.

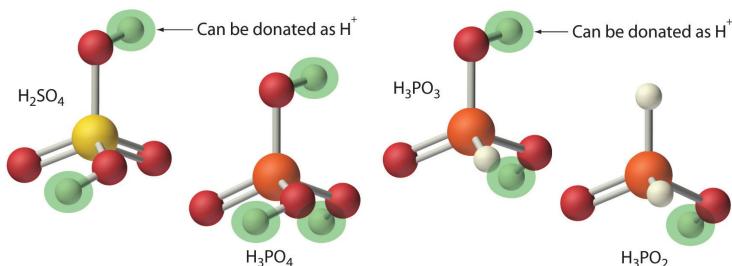
According to Brønsted and Lowry, an acid (A substance with at least one hydrogen atom that can dissociate to form an anion and an H^+ ion (a proton) in aqueous solution, thereby forming an acidic solution) is any substance that can donate a proton, and a base (a substance that produces one or more hydroxide ions (OH^-) and a cation when dissolved in aqueous solution, thereby forming a basic solution) is any substance that can accept a proton. The Brønsted–Lowry definition of an acid is essentially the same as the Arrhenius definition, except that it is not restricted to aqueous solutions. The Brønsted–Lowry definition of a base, however, is far more general because the hydroxide ion is just one of many substances that can accept a proton. Ammonia, for example, reacts with a proton to form NH_4^+ , so in Equation 4.4.3, NH_3 is a Brønsted–Lowry base and HCl is a Brønsted–Lowry acid. Because of its more general nature, the Brønsted–Lowry definition is used throughout this text unless otherwise specified.

Polyprotic Acids

Acids differ in the number of protons they can donate. For example, monoprotic acids (a compound that is capable of donating one proton per molecule) are compounds that are capable of donating a single proton per molecule. Monoprotic acids include HF, HCl, HBr, HI, HNO_3 , and HNO_2 . All carboxylic acids that contain a single $-CO_2H$ group, such as acetic acid (CH_3CO_2H), are monoprotic acids, dissociating to form RCO_2^- and H^+ . A compound that can donate more than one proton per molecule is known as a **polyprotic acid**. For example, H_2SO_4 can donate two H^+ ions in separate steps, so it is a diprotic acid (a compound that can donate two protons per molecule in separate steps) and H_3PO_4 , which is capable of donating three protons in successive steps, is a triprotic acid (a compound that can donate three protons per molecule in separate steps), (Equation 4.4.4, Equation 4.4.5, and Equation 4.4.6):



In chemical equations such as these, a double arrow is used to indicate that both the forward and reverse reactions occur simultaneously, so the forward reaction does not go to completion. Instead, the solution contains significant amounts of both reactants and products. Over time, the reaction reaches a state in which the concentration of each species in solution remains constant. The reaction is then said to be in **equilibrium** (the point at which the rates of the forward and reverse reactions become the same, so that the net composition of the system no longer changes with time).

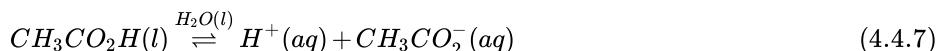


Ball and stick diagram of sulfuric acid, phosphoric acid, phosphorous acid, and hypophosphorous acid with all of the hydrogen atoms highlighted to show availability to be donated as H^+ positive ion.

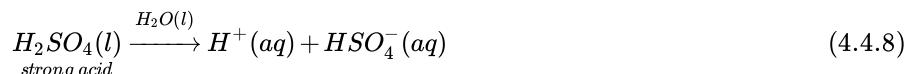
Strengths of Acids and Bases

We will not discuss the strengths of acids and bases quantitatively until next semester. Qualitatively, however, we can state that **strong acids** react essentially completely with water to give H^+ and the corresponding anion. Similarly, **strong bases** dissociate essentially completely in water to give OH^- and the corresponding cation. Strong acids and strong bases are both strong electrolytes. In contrast, only a fraction of the molecules of weak acids and weak bases react with water to produce ions, so weak acids and weak bases are also weak electrolytes. Typically less than 5% of a weak electrolyte dissociates into ions in solution, whereas more than 95% is present in undissociated form.

In practice, only a few strong acids are commonly encountered: HCl, HBr, HI, HNO₃, HClO₄, and H₂SO₄ (H₃PO₄ is only moderately strong). The most common strong bases are ionic compounds that contain the hydroxide ion as the anion; three examples are NaOH, KOH, and Ca(OH)₂. Common weak acids include HCN, H₂S, HF, oxoacids such as HNO₂ and HClO, and carboxylic acids such as acetic acid. The ionization reaction of acetic acid is as follows:

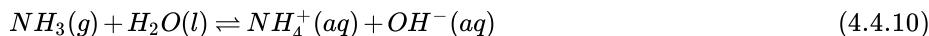


Although acetic acid is *very* soluble in water, almost all of the acetic acid in solution exists in the form of neutral molecules (less than 1% dissociates). Sulfuric acid is unusual in that it is a strong acid when it donates its first proton (Equation 4.4.8) but a weak acid when it donates its second proton (Equation 4.4.9) as indicated by the single and double arrows, respectively:



Consequently, an aqueous solution of sulfuric acid contains $H_{(aq)}^+$ ions and a mixture of $HSO_4^-_{(aq)}$ and $SO_4^{2-}_{(aq)}$ ions, but no H_2SO_4 molecules. All other polyprotic acids, such as H₃PO₄, are weak acids.

The most common weak base is ammonia, which reacts with water to form small amounts of hydroxide ion:



Most of the ammonia (>99%) is present in the form of NH₃(g). Amines, which are organic analogues of ammonia, are also weak bases, as are ionic compounds that contain anions derived from weak acids (such as S²⁻).

There is no correlation between the solubility of a substance and whether it is a strong electrolyte, a weak electrolyte, or a nonelectrolyte.



Definition of Strong/Weak Acids & Bases: [Definition of Strong/Weak Acids & Bases, YouTube \(opens in new window\)](#) [Definition of Strong] [Definition of Strong] [youtu.be] ([opens in new window](#))

Table 4.4.1 lists some common strong acids and bases. Acids other than the six common strong acids are almost invariably weak acids. The only common strong bases are the hydroxides of the alkali metals and the heavier alkaline earths (Ca, Sr, and Ba); any other bases you encounter are most likely weak. Remember that *there is no correlation between solubility and whether a substance is a strong or a weak electrolyte!* Many weak acids and bases are extremely soluble in water.

Table 4.4.1: Common Strong Acids and Bases

Strong Acids	Strong Bases
Hydrogen Halides	Oxoacids

Strong Acids		Strong Bases	
Hydrogen Halides	Oxoacids	Group 1 Hydroxides	Hydroxides of Heavy Group 2 Elements
HCl	HNO ₃	LiOH	Ca(OH) ₂
HBr	H ₂ SO ₄	NaOH	Sr(OH) ₂
HI	HClO ₄	KOH	Ba(OH) ₂
		RbOH	
		CsOH	

✓ Example 4.4.1: Acid Strength

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

- a. CH₃CH₂CO₂H
- b. CH₃OH
- c. Sr(OH)₂
- d. CH₃CH₂NH₂
- e. HBrO₄

Given: compound

Asked for: acid or base strength

Strategy:

A Determine whether the compound is organic or inorganic.

B If inorganic, determine whether the compound is acidic or basic by the presence of dissociable H⁺ or OH⁻ ions, respectively. If organic, identify the compound as a weak base or a weak acid by the presence of an amine or a carboxylic acid group, respectively. Recall that all polyprotic acids except H₂SO₄ are weak acids.

Solution:

- a. A This compound is propionic acid, which is organic. B It contains a carboxylic acid group analogous to that in acetic acid, so it must be a weak acid.
- b. A CH₃OH is methanol, an organic compound that contains the -OH group. B As a covalent compound, it does not dissociate to form the OH⁻ ion. Because it does not contain a carboxylic acid (-CO₂H) group, methanol also cannot dissociate to form H⁺(aq) ions. Thus we predict that in aqueous solution methanol is neither an acid nor a base.
- c. A Sr(OH)₂ is an inorganic compound that contains one Sr²⁺ and two OH⁻ ions per formula unit. B We therefore expect it to be a strong base, similar to Ca(OH)₂.
- d. A CH₃CH₂NH₂ is an amine (ethylamine), an organic compound in which one hydrogen of ammonia has been replaced by an R group. B Consequently, we expect it to behave similarly to ammonia (Equation 4.4.7), reacting with water to produce small amounts of the OH⁻ ion. Ethylamine is therefore a weak base.
- e. A HBrO₄ is perbromic acid, an inorganic compound. B It is not listed in Table 4.4.1 as one of the common strong acids, but that does not necessarily mean that it is a weak acid. If you examine the periodic table, you can see that Br lies directly below Cl in group 17. We might therefore expect that HBrO₄ is chemically similar to HClO₄, a strong acid—and, in fact, it is.

? Exercise 4.4.1: Acid Strength

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

- a. Ba(OH)₂
- b. HIO₄
- c. CH₃CH₂CH₂CO₂H

- d. $(\text{CH}_3)_2\text{NH}$
- e. CH_2O

Answer a

strong base

Answer b

strong acid

Answer c

weak acid

Answer d

weak base

Answer e

none of these; formaldehyde is a neutral molecule

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4.5: Oxidation-Reduction (Redox) Reactions

Learning Objectives

- To identify oxidation–reduction reactions in solution.

The term oxidation was first used to describe reactions in which metals react with oxygen in air to produce metal oxides. When iron is exposed to air in the presence of water, for example, the iron turns to rust—an iron oxide. When exposed to air, aluminum metal develops a continuous, transparent layer of aluminum oxide on its surface. In both cases, the metal acquires a positive charge by transferring electrons to the neutral oxygen atoms of an oxygen molecule. As a result, the oxygen atoms acquire a negative charge and form oxide ions (O^{2-}). Because the metals have lost electrons to oxygen, they have been oxidized; oxidation is therefore the loss of electrons. Conversely, because the oxygen atoms have gained electrons, they have been reduced, so reduction is the gain of electrons. For every oxidation, there must be an associated reduction. Therefore, these reactions are known as oxidation-reduction reactions, or "redox" reactions for short.

Any oxidation must ALWAYS be accompanied by a reduction and vice versa.

Originally, the term reduction referred to the decrease in mass observed when a metal oxide was heated with carbon monoxide, a reaction that was widely used to extract metals from their ores. When solid copper(I) oxide is heated with hydrogen, for example, its mass decreases because the formation of pure copper is accompanied by the loss of oxygen atoms as a volatile product (water vapor). The reaction is as follows:



Oxidation-reduction reactions are now defined as reactions that exhibit a change in the oxidation states of one or more elements in the reactants by a transfer of electrons, which follows the mnemonic "oxidation is loss, reduction is gain", or "**oil rig**". The **oxidation state** of each atom in a compound is the charge an atom would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons. Atoms in their elemental form, such as O_2 or H_2 , are assigned an oxidation state of zero. For example, the reaction of aluminum with oxygen to produce aluminum oxide is



Each neutral oxygen atom gains two electrons and becomes negatively charged, forming an oxide ion; thus, oxygen has an oxidation state of -2 in the product and has been reduced. Each neutral aluminum atom loses three electrons to produce an aluminum ion with an oxidation state of $+3$ in the product, so aluminum has been oxidized. In the formation of Al_2O_3 , electrons are transferred as follows (the small overset number emphasizes the oxidation state of the elements):



Equation 4.5.1 and Equation 4.5.2 are examples of oxidation–reduction (redox) reactions. In redox reactions, there is a net transfer of electrons from one reactant to another. In any redox reaction, the total number of electrons lost must equal the total of electrons gained to preserve electrical neutrality. In Equation 4.5.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$\begin{aligned} \text{electrons lost} &= 4 \text{ Al atoms} \times \frac{3 e^- \text{ lost}}{\text{Al atom}} \\ &= 12 e^- \text{ lost} \\ \text{electrons gained} &= 6 \text{ O atoms} \times \frac{2 e^- \text{ gained}}{\text{O atom}} \\ &= 12 e^- \text{ gained} \end{aligned}$$

The same pattern is seen in all oxidation–reduction reactions: the number of electrons lost must equal the number of electrons gained. An additional example of a redox reaction, the reaction of sodium metal with chlorine is illustrated in Figure 4.5.1.

In all oxidation–reduction (redox) reactions, the number of electrons lost equals the number of electrons gained.

Assigning Oxidation States

Assigning oxidation states to the elements in binary ionic compounds is straightforward: the oxidation states of the elements are identical to the charges on the monatomic ions. Previously, you learned how to predict the formulas of simple ionic compounds based on the sign and magnitude of the charge on monatomic ions formed by the neutral elements. Examples of such compounds are sodium chloride (NaCl ; Figure 4.5.1), magnesium oxide (MgO), and calcium chloride (CaCl_2). In covalent compounds, in contrast, atoms share electrons. However, we can still assign oxidation states to the elements involved by treating them as if they were ionic (that is, as if all the bonding electrons were transferred to the more attractive element). Oxidation states in covalent compounds are somewhat arbitrary, but they are useful bookkeeping devices to help you understand and predict many reactions.

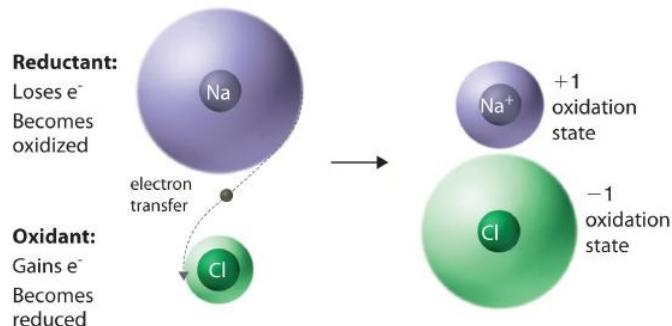


Figure 4.5.1: The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom. The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl .

Sodium atom acts as the reductant and chlorine as the oxidant. The result is an oxidation state of positive 1 and negative 1 for sodium and chloride ion respectively.

A set of rules for assigning oxidation states to atoms in chemical compounds follows.

Rules for Assigning Oxidation States

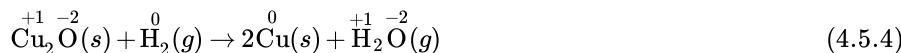
1. The oxidation state of an atom in any pure element, whether monatomic, diatomic, or polyatomic, is zero.
2. The oxidation state of a monatomic ion is the same as its charge—for example, $\text{Na}^+ = +1$, $\text{Cl}^- = -1$.
3. The oxidation state of fluorine in chemical compounds is always -1 . Other halogens usually have oxidation states of -1 as well, except when combined with oxygen or other halogens.
4. Hydrogen is assigned an oxidation state of $+1$ in its compounds with nonmetals and -1 in its compounds with metals.
5. Oxygen is normally assigned an oxidation state of -2 in compounds, with two exceptions: in compounds that contain oxygen–fluorine or oxygen–oxygen bonds, the oxidation state of oxygen is determined by the oxidation states of the other elements present.
6. The sum of the oxidation states of all the atoms in a neutral molecule or ion must equal the charge on the molecule or ion.

Nonintegral (fractional) oxidation states are encountered occasionally. They are usually due to the presence of two or more atoms of the same element with different oxidation states.

In any chemical reaction, the net charge must be conserved; that is, in a chemical reaction, the total number of electrons is constant, just like the total number of atoms. Consistent with this, rule 1 states that the sum of the individual oxidation states of the atoms in a molecule or ion must equal the net charge on that molecule or ion. In NaCl , for example, Na has an oxidation state of $+1$ and Cl is -1 . The net charge is zero, as it must be for any compound.

Rule 3 is required because fluorine attracts electrons more strongly than any other element, for reasons you will discover in Chapter 6. Hence fluorine provides a reference for calculating the oxidation states of other atoms in chemical compounds. Rule 4 reflects the difference in chemistry observed for compounds of hydrogen with nonmetals (such as chlorine) as opposed to compounds of hydrogen with metals (such as sodium). For example, NaH contains the H^- ion, whereas HCl forms H^+ and Cl^- ions when dissolved in water. Rule 5 is necessary because fluorine has a greater attraction for electrons than oxygen does; this rule also prevents violations of rule 2. So the oxidation state of oxygen is $+2$ in OF_2 but $-\frac{1}{2}$ in KO_2 . Note that an oxidation state of $-\frac{1}{2}$ for O in KO_2 is perfectly acceptable.

The reduction of copper(I) oxide shown in Equation 4.5.4 demonstrates how to apply these rules. Rule 1 states that atoms in their elemental form have an oxidation state of zero, which applies to H₂ and Cu. From rule 4, hydrogen in H₂O has an oxidation state of +1, and from rule 5, oxygen in both Cu₂O and H₂O has an oxidation state of -2. Rule 6 states that the sum of the oxidation states in a molecule or formula unit must equal the net charge on that compound. This means that each Cu atom in Cu₂O must have a charge of +1: 2(+1) + (-2) = 0. So the oxidation states are as follows:



Assigning oxidation states allows us to see that there has been a net transfer of electrons from hydrogen (0 → +1) to copper (+1 → 0). Thus, this is a redox reaction. Once again, the number of electrons lost equals the number of electrons gained, and there is a net conservation of charge:

$$\text{electrons lost} = 2 \text{ H atoms} \times \frac{1 e^- \text{ lost}}{\text{H atom}} = 2 e^- \text{ lost} \quad (4.5.5)$$

$$\text{electrons gained} = 2 \text{ Cu atoms} \times \frac{1 e^- \text{ gained}}{\text{Cu atom}} = 2 e^- \text{ gained} \quad (4.5.6)$$

Remember that oxidation states are useful for visualizing the transfer of electrons in oxidation-reduction reactions, but the oxidation state of an atom and its actual charge are the same only for simple ionic compounds. Oxidation states are a convenient way of assigning electrons to atoms, and they are useful for predicting the types of reactions that substances undergo.

✓ Example 4.5.1: Oxidation States

Assign oxidation states to all atoms in each compound.

- sulfur hexafluoride (SF₆)
- methanol (CH₃OH)
- ammonium sulfate [(NH₄)₂SO₄]
- magnetite (Fe₃O₄)
- ethanoic (acetic) acid (CH₃CO₂H)

Given: molecular or empirical formula

Asked for: oxidation states

Strategy:

Begin with atoms whose oxidation states can be determined unambiguously from the rules presented (such as fluorine, other halogens, oxygen, and monatomic ions). Then determine the oxidation states of other atoms present according to rule 1.

Solution:

a. We know from rule 3 that fluorine always has an oxidation state of -1 in its compounds. The six fluorine atoms in sulfur hexafluoride give a total negative charge of -6. Because rule 1 requires that the sum of the oxidation states of all atoms be zero in a neutral molecule (here SF₆), the oxidation state of sulfur must be +6:

$$[(6 \text{ F atoms})(-1)] + [(1 \text{ S atom})(+6)] = 0$$

b. According to rules 4 and 5, hydrogen and oxygen have oxidation states of +1 and -2, respectively. Because methanol has no net charge, carbon must have an oxidation state of -2:

$$[(4 \text{ H atoms})(+1)] + [(1 \text{ O atom})(-2)] + [(1 \text{ C atom})(-2)] = 0$$

c. Note that (NH₄)₂SO₄ is an ionic compound that consists of both a polyatomic cation (NH₄⁺) and a polyatomic anion (SO₄²⁻) (see Table 2.4). We assign oxidation states to the atoms in each polyatomic ion separately. For NH₄⁺, hydrogen has an oxidation state of +1 (rule 4), so nitrogen must have an oxidation state of -3:

$$[(4 \text{ H atoms})(+1)] + [(1 \text{ N atom})(-3)] = +1, \text{ the charge on the NH}_4^+ \text{ ion}$$

For SO₄²⁻, oxygen has an oxidation state of -2 (rule 5), so sulfur must have an oxidation state of +6:

$$[(4 \text{ O atoms})(-2)] + [(1 \text{ S atom})(+6)] = -2, \text{ the charge on the sulfate ion}$$

- d. Oxygen has an oxidation state of -2 (rule 5), giving an overall charge of -8 per formula unit. This must be balanced by the positive charge on three iron atoms, giving an oxidation state of $+8/3$ for iron:

$$[(4 \text{ O atoms})(-2)] + [(3 \text{ Fe atoms})\left(+\frac{8}{3}\right)] = 0$$

Fractional oxidation states are allowed because oxidation states are a somewhat arbitrary way of keeping track of electrons. In fact, Fe_3O_4 can be viewed as having two Fe^{3+} ions and one Fe^{2+} ion per formula unit, giving a net positive charge of $+8$ per formula unit. Fe_3O_4 is a magnetic iron ore commonly called magnetite. In ancient times, magnetite was known as lodestone because it could be used to make primitive compasses that pointed toward Polaris (the North Star), which was called the “lodestar.”

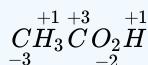
- e. Initially, we assign oxidation states to the components of $\text{CH}_3\text{CO}_2\text{H}$ in the same way as any other compound. Hydrogen and oxygen have oxidation states of $+1$ and -2 (rules 4 and 5, respectively), resulting in a total charge for hydrogen and oxygen of

$$[(4 \text{ H atoms})(+1)] + [(2 \text{ O atoms})(-2)] = 0$$

So the oxidation state of carbon must also be zero (rule 6). This is, however, an average oxidation state for the two carbon atoms present. Because each carbon atom has a different set of atoms bonded to it, they are likely to have different oxidation states. To determine the oxidation states of the individual carbon atoms, we use the same rules as before but with the additional assumption that bonds between atoms of the same element do not affect the oxidation states of those atoms. The carbon atom of the methyl group ($-\text{CH}_3$) is bonded to three hydrogen atoms and one carbon atom. We know from rule 4 that hydrogen has an oxidation state of $+1$, and we have just said that the carbon–carbon bond can be ignored in calculating the oxidation state of the carbon atom. For the methyl group to be electrically neutral, its carbon atom must have an oxidation state of -3 . Similarly, the carbon atom of the carboxylic acid group ($-\text{CO}_2\text{H}$) is bonded to one carbon atom and two oxygen atoms. Again ignoring the bonded carbon atom, we assign oxidation states of -2 and $+1$ to the oxygen and hydrogen atoms, respectively, leading to a net charge of

$$[(2 \text{ O atoms})(-2)] + [(1 \text{ H atom})(+1)] = -3$$

To obtain an electrically neutral carboxylic acid group, the charge on this carbon must be $+3$. The oxidation states of the individual atoms in acetic acid are thus



Thus the sum of the oxidation states of the two carbon atoms is indeed zero.

? Exercise 4.5.1: Oxidation States

Assign oxidation states to all atoms in each compound.

- barium fluoride (BaF_2)
- formaldehyde (CH_2O)
- potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)
- cesium oxide (CsO_2)
- ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)

Answer a

$\text{Ba}, +2; \text{F}, -1$

Answer b

$\text{C}, 0; \text{H}, +1; \text{O}, -2$

Answer c

$\text{K}, +1; \text{Cr}, +6; \text{O}, -2$

Answer d

$\text{Cs}, +1; \text{O}, -\frac{1}{2}$

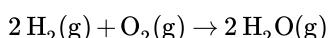
Answer e

C, -3; H, +1; C, -1; H, +1; O, -2; H, +1

Types of Redox Reactions

Many types of chemical reactions are classified as redox reactions, and it would be impossible to memorize all of them. However, there are a few important types of redox reactions that you are likely to encounter and should be familiar with. These include:

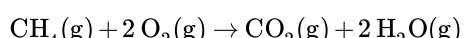
- **Synthesis** reactions: The formation of any compound directly from the elements is a redox reaction, for example, the formation of water from hydrogen and oxygen:



- **Decomposition** reactions: Conversely, the decomposition of a compound to its elements is also a redox reaction, as in the electrolysis of water:



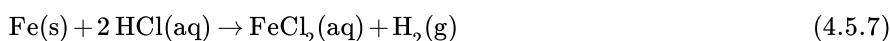
- **Combustion** reactions: Many chemicals combust (burn) with oxygen. In particular, organic chemicals such as hydrocarbons burn in the presence of oxygen to produce carbon dioxide and water as the products:



The following sections describe another important class of redox reactions: single-displacement reactions of metals in solution.

Redox Reactions of Solid Metals in Aqueous Solution

- A widely encountered class of oxidation-reduction reactions is the reaction of aqueous solutions of acids or metal salts with solid metals. An example is the corrosion of metal objects, such as the rusting of an automobile (Figure 4.5.2). Rust is formed from a complex oxidation-reduction reaction involving dilute acid solutions that contain Cl^- ions (effectively, dilute HCl), iron metal, and oxygen. When an object rusts, iron metal reacts with $\text{HCl}(\text{aq})$ to produce iron(II) chloride and hydrogen gas:



In subsequent steps, FeCl_2 undergoes oxidation to form a reddish-brown precipitate of Fe(OH)_3 .



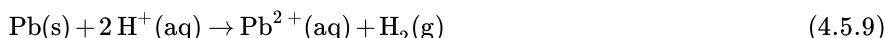
Figure 4.5.2: Rust Formation. The corrosion process involves an oxidation-reduction reaction in which metallic iron is converted to Fe(OH)_3 , a reddish-brown solid.

Many metals dissolve through reactions of this type, which have the general form



Some of these reactions have important consequences. For example, it has been proposed that one factor that contributed to the fall of the Roman Empire was the widespread use of lead in cooking utensils and pipes that carried water. Rainwater, as we

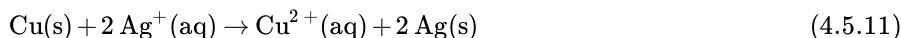
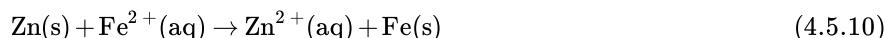
have seen, is slightly acidic, and foods such as fruits, wine, and vinegar contain organic acids. In the presence of these acids, lead dissolves:



Consequently, it has been speculated that both the water and the food consumed by Romans contained toxic levels of lead, which resulted in widespread lead poisoning and eventual madness. Perhaps this explains why the Roman Emperor Caligula appointed his favorite horse as consul!

- **Single-Displacement Reactions**

Certain metals are oxidized by aqueous acid, whereas others are oxidized by aqueous solutions of various metal salts. Both types of reactions are called single-displacement reactions, in which the ion in solution is displaced through oxidation of the metal. Two examples of single-displacement reactions are the reduction of iron salts by zinc (Equation 4.5.10) and the reduction of silver salts by copper (Equation 4.5.11 and Figure 4.5.3):



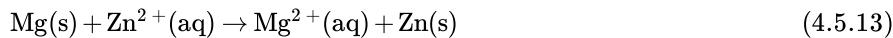
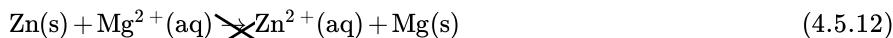
The reaction in Equation 4.5.10 is widely used to prevent (or at least postpone) the corrosion of iron or steel objects, such as nails and sheet metal. The process of “galvanizing” consists of applying a thin coating of zinc to the iron or steel, thus protecting it from oxidation as long as zinc remains on the object.



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- **The Activity Series**

By observing what happens when samples of various metals are placed in contact with solutions of other metals, chemists have arranged the metals according to the relative ease or difficulty with which they can be oxidized in a single-displacement reaction. For example, metallic zinc reacts with iron salts, and metallic copper reacts with silver salts. Experimentally, it is found that zinc reacts with both copper salts and silver salts, producing Zn_2^+ . Zinc therefore has a greater tendency to be oxidized than does iron, copper, or silver. Although zinc will not react with magnesium salts to give magnesium metal, magnesium metal will react with zinc salts to give zinc metal:



Magnesium has a greater tendency to be oxidized than zinc does.

Pairwise reactions of this sort are the basis of the activity series (Figure 4.5.4), which lists metals and hydrogen in order of their relative tendency to be oxidized. The metals at the top of the series, which have the greatest tendency to lose electrons, are the alkali metals (group 1), the alkaline earth metals (group 2), and Al (group 13). In contrast, the metals at the bottom of the series, which have the lowest tendency to be oxidized, are the precious metals or coinage metals—platinum, gold, silver, and copper, and mercury, which are located in the lower right portion of the metals in the periodic table. You should be generally familiar with which kinds of metals are active metals, which have the greatest tendency to be oxidized. (located at the top of the series) and which are inert metals, which have the least tendency to be oxidized. (at the bottom of the series).

Element	Oxidation Reaction
Lithium	$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$
Potassium	$\text{K} \rightarrow \text{K}^+ + \text{e}^-$
Barium	$\text{Ba} \rightarrow \text{Ba}^{2+} + 2\text{e}^-$
Calcium	$\text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{e}^-$
Sodium	$\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$
Magnesium	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$
Aluminum	$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$
Manganese	$\text{Mn} \rightarrow \text{Mn}^{2+} + 2\text{e}^-$
Zinc	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
Chromium	$\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-$
Iron	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$
Cadmium	$\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$
Cobalt	$\text{Co} \rightarrow \text{Co}^{2+} + 2\text{e}^-$
Nickel	$\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$
Tin	$\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^-$
Lead	$\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$
Hydrogen	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$
Copper	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
Silver	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$
Mercury	$\text{Hg} \rightarrow \text{Hg}^{2+} + 2\text{e}^-$
Platinum	$\text{Pt} \rightarrow \text{Pt}^{2+} + 2\text{e}^-$
Gold	$\text{Au} \rightarrow \text{Au}^+ + \text{e}^-$

Figure 4.5.4: The Activity Series

When using the activity series to predict the outcome of a reaction, keep in mind that *any element will reduce compounds of the elements below it in the series*. Because magnesium is above zinc in Figure 4.5.4, magnesium metal will reduce zinc salts but not vice versa. Similarly, the precious metals are at the bottom of the activity series, so virtually any other metal will reduce precious metal salts to the pure precious metals. Hydrogen is included in the series, and the tendency of a metal to react with an acid is indicated by its position relative to hydrogen in the activity series. *Only those metals that lie above hydrogen in the activity series dissolve in acids to produce H₂*. Because the precious metals lie below hydrogen, they do not dissolve in dilute acid and therefore do not corrode readily. Example 4.5.2 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions.

✓ Example 4.5.2: Activity

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

- A strip of aluminum foil is placed in an aqueous solution of silver nitrate.
- A few drops of liquid mercury are added to an aqueous solution of lead(II) acetate.
- Some sulfuric acid from a car battery is accidentally spilled on the lead cable terminals.

Given: reactants

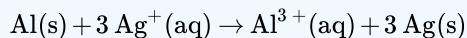
Asked for: overall reaction and net ionic equation

Strategy:

- Locate the reactants in the activity series in Figure 4.5.4 and from their relative positions, predict whether a reaction will occur. If a reaction does occur, identify which metal is oxidized and which is reduced.
- Write the net ionic equation for the redox reaction.

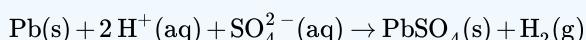
Solution:

- Aluminum is an active metal that lies above silver in the activity series, so we expect a reaction to occur. According to their relative positions, aluminum will be oxidized and dissolve, and silver ions will be reduced to silver metal. **B** The net ionic equation is as follows:



Recall from our discussion of solubilities that most nitrate salts are soluble. In this case, the nitrate ions are spectator ions and are not involved in the reaction.

2. A Mercury lies below lead in the activity series, so no reaction will occur.
3. A Lead is above hydrogen in the activity series, so the lead terminals will be oxidized, and the acid will be reduced to form H₂. B From our discussion of solubilities, recall that Pb²⁺ and SO₄²⁻ form insoluble lead(II) sulfate. In this case, the sulfate ions are *not* spectator ions, and the reaction is as follows:



Lead(II) sulfate is the white solid that forms on corroded battery terminals.



Corroded battery terminals. The white solid is lead(II) sulfate, formed from the reaction of solid lead with a solution of sulfuric acid.

? Exercise 4.5.2

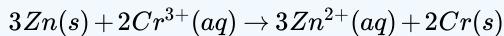
Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

- A strip of chromium metal is placed in an aqueous solution of aluminum chloride.
- A strip of zinc is placed in an aqueous solution of chromium(III) nitrate.
- A piece of aluminum foil is dropped into a glass that contains vinegar (the active ingredient is acetic acid).

Answer a

no reaction

Answer b



Answer c



Summary

Oxidation-reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation. In oxidation-reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation-reduction reactions in solution using the **oxidation state method** (Table 4.5.1), in which the overall reaction is separated into an oxidation equation and a reduction equation. There are many types of redox reactions. **Single-displacement reactions** are reactions of metals with either acids or another metal salt that result in dissolution of the first metal and precipitation of a second (or evolution of hydrogen gas). The outcome of these reactions can be predicted using the **activity series** (Figure 4.5.4), which arranges metals and H₂ in decreasing order of their tendency to be oxidized. Any metal will reduce metal ions below it in the activity series. **Active metals** lie at the top of the activity series, whereas **inert metals** are at the bottom of the activity series.

4.6: Elements in Redox Reactions

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4.7: The Reversibility of Reactions and the Equilibrium State

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CHAPTER OVERVIEW

5: Gases and the Kinetic-Molecular Theory

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII
XVIII XIX XX XXI XXII XXIII XXIV

Template:HideTOC

- 5.1: An Overview of the Physical States of Matter
- 5.2: Gas Pressure and Its Measurement
- 5.3: The Gas Laws and Their Experimental Foundations
- 5.4: Rearrangements of the Ideal Gas Law
- 5.5: The Kinetic-Molecular Theory - A Model for Gas Behavior
- 5.6: Real Gases - Deviations from Ideal Behavior
- 5.E: Gases and the Kinetic-Molecular Theory (Exercises)

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5.1: An Overview of the Physical States of Matter

Learning Objectives

- To describe the characteristics of a gas.

The three common phases (or states) of matter are gases, liquids, and solids. Gases have the lowest density of the three, are highly compressible, and completely fill any container in which they are placed. Gases behave this way because their intermolecular forces are relatively weak, so their molecules are constantly moving independently of the other molecules present. Solids, in contrast, are relatively dense, rigid, and incompressible because their intermolecular forces are so strong that the molecules are essentially locked in place. Liquids are relatively dense and incompressible, like solids, but they flow readily to adapt to the shape of their containers, like gases. We can therefore conclude that the sum of the intermolecular forces in liquids are between those of gases and solids. Figure 5.1.1 compares the three states of matter and illustrates the differences at the molecular level.

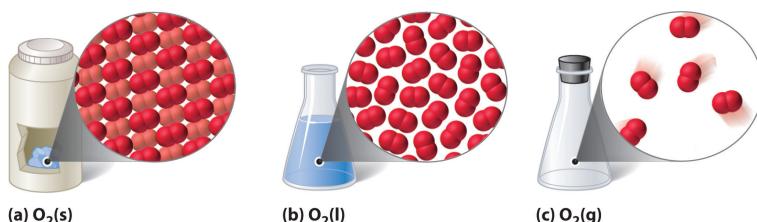


Figure 5.1.1: A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States: (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

The state of a given substance depends strongly on conditions. For example, H_2O is commonly found in all three states: solid ice, liquid water, and water vapor (its gaseous form). Under most conditions, we encounter water as the liquid that is essential for life; we drink it, cook with it, and bathe in it. When the temperature is cold enough to transform the liquid to ice, we can ski or skate on it, pack it into a snowball or snow cone, and even build dwellings with it. Water vapor (the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions so nitrogen (N_2) and oxygen (O_2) are referred to as gases, but gaseous water in the atmosphere is called water vapor) is a component of the air we breathe, and it is produced whenever we heat water for cooking food or making coffee or tea. Water vapor at temperatures greater than $100^\circ C$ 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.

Table 5.1.1: Properties of Water at 1.0 atm

Temperature	State	Density (g/cm ³)
$\leq 0^\circ C$	solid (ice)	0.9167 (at $0.0^\circ C$)
$0^\circ C - 100^\circ C$	liquid (water)	0.9997 (at $4.0^\circ C$)
$\geq 100^\circ C$	vapor (steam)	0.005476 (at $127^\circ C$)

The geometric structure and the physical and chemical properties of atoms, ions, and molecules usually do *not* depend on their physical state; the individual water molecules in ice, liquid water, and steam, for example, are all identical. In contrast, the macroscopic properties of a substance depend strongly on its physical state, which is determined by intermolecular forces and conditions such as temperature and pressure.

Figure 5.1.2 shows the locations in the periodic table of those elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble gases (group 18) are monatomic gases, whereas the other gaseous elements are diatomic molecules (H_2 , N_2 , O_2 , F_2 , and Cl_2). Oxygen can also form a second allotrope, the highly reactive triatomic molecule ozone (O_3), which is also a gas. In contrast, bromine (as Br_2) and mercury (Hg) are liquids under normal conditions ($25^\circ C$ and 1.0 atm, commonly referred to as “room temperature and pressure”). Gallium (Ga), which melts at only $29.76^\circ C$, can be converted to a liquid simply by holding a container

of it in your hand or keeping it in a non-air-conditioned room on a hot summer day. The rest of the elements are all solids under normal conditions.

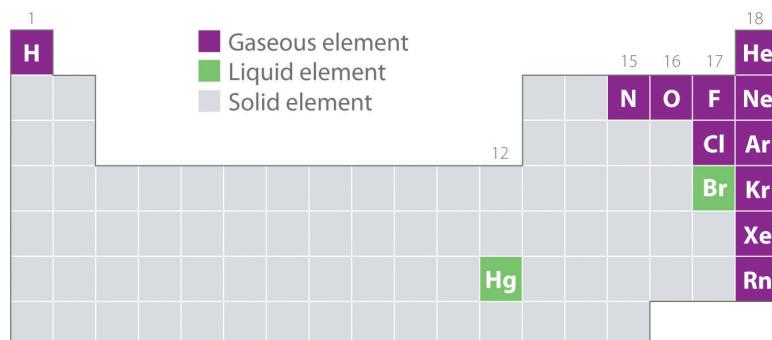


Figure 5.1.2: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

Purple elements are gaseous elements, green are liquid, and gray and solid. H, N, O, F, Cl, He, Ne, Ar, Kr, Xe, and Rn are all purple. Br and Hg are green. The rest are gray.

All of the gaseous elements (other than the monatomic noble gases) are molecules. Within the same group (1, 15, 16 and 17), the lightest elements are gases. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms.

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, N₂, O₂).



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5.2: Gas Pressure and Its Measurement

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 demonstrated below, these variables are *not* independent (i.e., they cannot be arbitrarily be varied). 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) of the gas, the force (F) per unit area (A) of surface:

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \quad (5.2.1)$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 5.2.1 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. 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)**, after the French mathematician Blaise Pascal (1623–1662):

$$1 \text{ Pa} = 1 \text{ N/m}^2 \quad (5.2.2)$$

Example 5.2.1

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

- lying flat?
- standing on edge in a bookcase?

Given: mass and dimensions of object

Asked for: pressure

Strategy:

- Calculate the force exerted by the book and then compute the area that is in contact with a surface.
- Substitute these two values into Equation 5.2.1 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 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

$$F = ma = 2.00 \text{ kg} \times 9.8067 \frac{\text{m}}{\text{s}^2} = 19.6 \frac{\text{kg} \cdot \text{m}}{\text{s}^2} = 19.6 \text{ N}$$

A We calculated the force as 19.6 N. When the book is lying flat, the area is

$$A = 0.270 \text{ m} \times 0.210 \text{ m} = 0.0567 \text{ m}^2.$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{F}{A} = \frac{19.6 \text{ N}}{0.0567 \text{ m}^2} = 3.46 \times 10^2 \text{ Pa}$$

A If the book is standing on its end, the force remains the same, but the area decreases:

$$A = 21.0 \text{ cm} \times 4.5 \text{ cm} = 0.210 \text{ m} \times 0.045 \text{ m} = 9.5 \times 10^{-3} \text{ m}^2$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{19.6 \text{ N}}{9.5 \times 10^{-3} \text{ m}^2} = 2.06 \times 10^3 \text{ Pa}$$

? Exercise 5.2.1

What pressure does a 60.0 kg student exert on the floor

- when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?
- as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answer a

$$3.27 \times 10^4 \text{ Pa}$$

Answer b

$$5.9 \times 10^6 \text{ Pa}$$

Barometric 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 (Figure 5.2.1). Every point on Earth's surface experiences a net pressure called **barometric pressure**. The pressure exerted by the atmosphere is considerable: a 1 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 101 kPa:

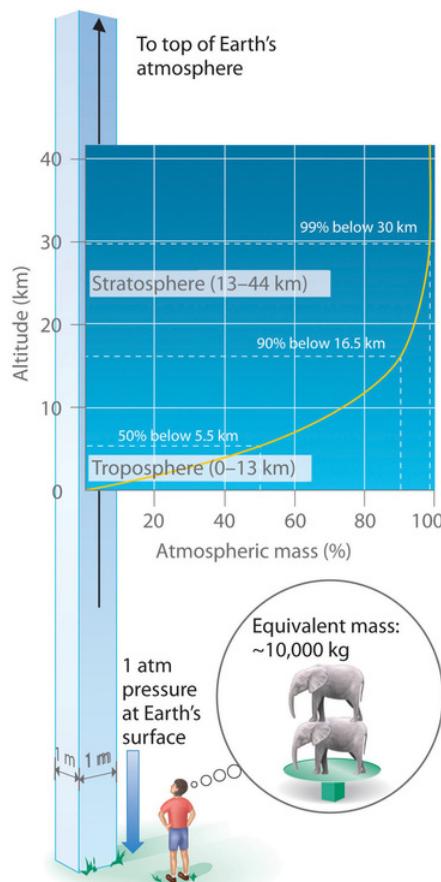


Figure 5.2.1: Barometric Pressure. Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface.

Barometric pressure can be measured using a barometer, a device 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 5.2.2). 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. The pressure exerted by the mercury column can be expressed as:

$$P = \frac{F}{A} \quad (5.2.3)$$

$$= \frac{mg}{A} \quad (5.2.4)$$

$$= \frac{\rho V \cdot g}{A} \quad (5.2.5)$$

$$= \frac{\rho \cdot Ah \cdot g}{A} \quad (5.2.6)$$

$$= \rho gh \quad (5.2.7)$$

with

- g is the gravitational acceleration,
- m is the mass,
- ρ is the density,

- V is the volume,
- A is the bottom area, and
- h is height of the mercury column.

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 5.2.2. 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.

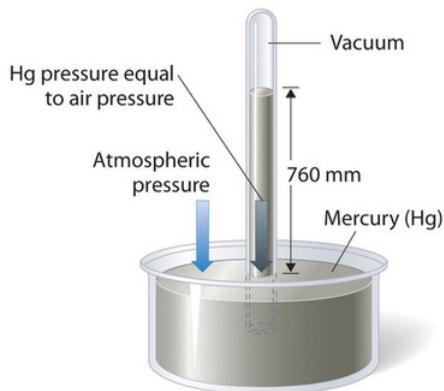


Figure 5.2.2: A Mercury Barometer. The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the mercury column.

Mercury barometers have been used to measure barometric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg), often called the torr, after Torricelli. Standard barometric pressure is the barometric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm). These units are also related to the pascal:

$$1 \text{ atm} = 760 \text{ mmHg} \quad (5.2.8)$$

$$= 760 \text{ torr} \quad (5.2.9)$$

$$= 1.01325 \times 10^5 \text{ Pa} \quad (5.2.10)$$

$$= 101.325 \text{ kPa} \quad (5.2.11)$$

Thus a pressure of 1 atm equals 760 mmHg exactly.

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 barometric 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 barometric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

✓ Example 5.2.2: Barometric Pressure

One of the authors visited Rocky Mountain National Park several years ago. After departing from an airport at sea level in the eastern United States, he arrived in Denver (altitude 5280 ft), rented a car, and drove to the top of the highway outside Estes Park (elevation 14,000 ft). He noticed that even slight exertion was very difficult at this altitude, where the barometric pressure is only 454 mmHg. Convert this pressure to

- atmospheres (atm).
- bar.

Given: pressure in millimeters of mercury

Asked for: pressure in atmospheres and bar

Strategy:

Use the conversion factors in Equation 5.2.11 to convert from millimeters of mercury to atmospheres and kilopascals.

Solution:

From Equation 5.2.11, we have $1 \text{ atm} = 760 \text{ mmHg} = 101.325 \text{ kPa}$. The pressure at 14,000 ft in atm is thus

$$P = 454 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \quad (5.2.12)$$

$$= 0.597 \text{ atm}$$

The pressure in bar is given by

$$P = 0.597 \text{ atm} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} \quad (5.2.13)$$

$$= 0.605 \text{ bar}$$

Exercise 5.2.2: Barometric Pressure

Mt. Everest, at 29,028 ft above sea level, is the world's tallest mountain. The normal barometric pressure at this altitude is about 0.308 atm. Convert this pressure to

- millimeters of mercury.
- bar.

Answer a

234 mmHg;

Answer b

0.312 bar

Manometers

Barometers measure barometric 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 5.2.3. 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.

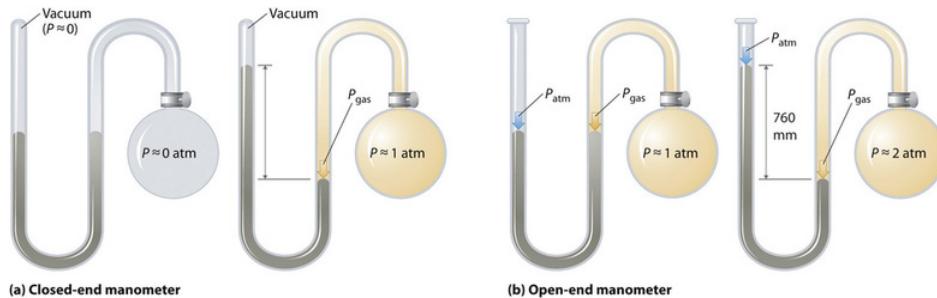


Figure 5.2.3: The Two Types of Manometer. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere ($P \approx 1 \text{ atm}$), and the difference in the heights of the two columns gives the *difference* between barometric 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 5.2.3, then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the barometric 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 barometric 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 barometric pressure minus the difference in the heights of the two columns.

✓ Example 5.2.3

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? (The density of water is 1.00 g/cm³; the density of mercury is 13.53 g/cm³.)

Given: pressure range and densities of water and mercury

Asked for: column height

Strategy:

- 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.
- 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

$$P = 0.200 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 152 \text{ mmHg}$$

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 to the density of water

$$\begin{aligned} P &= d_{\text{wat}}gh_{\text{wat}} = d_{\text{Hg}}gh_{\text{Hg}} \\ h_{\text{wat}} &= h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} = 152 \text{ mm} \times \frac{13.53 \text{ g/cm}^3}{1.00 \text{ g/cm}^3} = 2070 \text{ mm} \end{aligned}$$

The answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

? Exercise 5.2.3

Suppose you want to design a barometer to measure barometric 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/cm³. How tall a column of gallium do you need if $P = 1.00 \text{ atm}$?

Answer

1.68 m

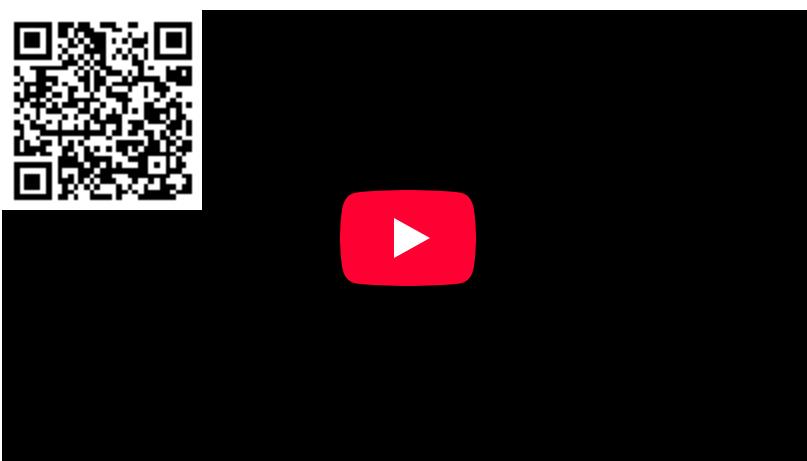
The answer to Example 5.2.3 also tells us the maximum depth of a farmer's well if a simple suction pump will be used to get the water out. The 1.00 atm corresponds to a column height of

$$\begin{aligned} h_{\text{wat}} &= h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} \\ &= 760 \text{ mm} \times \frac{13.53 \text{ g/cm}^3}{1.00 \text{ g/cm}^3} \\ &= 1.03 \times 10^4 \text{ mm} \\ &= 10.3 \text{ m} \end{aligned}$$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on barometric 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 barometric 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

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. 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 *barometric pressure*, is about 101 kPa or 14.7 lb/in.² at sea level. Barometric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to barometric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard barometric 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.



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5.3: The Gas Laws and Their Experimental Foundations

Learning Objectives

- To understand the relationships among pressure, temperature, volume, and the amount of a gas.

Early scientists explored the relationships among the pressure of a gas (P) and its temperature (T), volume (V), and amount (n) by holding two of the four variables constant (amount and temperature, for example), varying a third (such as pressure), and measuring the effect of the change on the fourth (in this case, volume). The history of their discoveries provides several excellent examples of the [scientific method](#).

The Relationship between Pressure and Volume: Boyle's Law

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

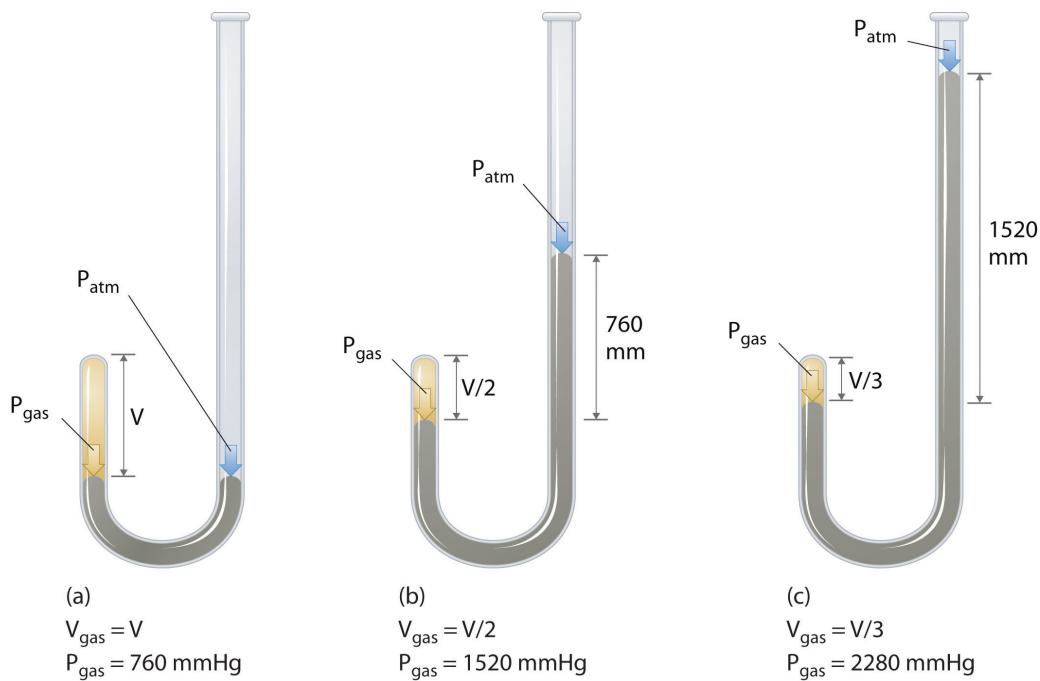


Figure 5.3.1: Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is V . (b) If enough mercury is added to the right side to give a difference in height of 760 mmHg between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is $V/2$. (c) If an additional 760 mmHg is added to the column on the right, the total pressure on the gas increases to 2280 mmHg, and the volume of the gas decreases to $V/3$ (CC BY-SA-NC; anonymous).

The Irish chemist Robert Boyle (1627–1691) carried out some of the earliest experiments that determined the quantitative relationship between the pressure and the volume of a gas. Boyle used a J-shaped tube partially filled with mercury, as shown in Figure 5.3.1. In these experiments, a small amount of a gas or air is trapped above the mercury column, and its volume is measured at atmospheric pressure and constant temperature. More mercury is then poured into the open arm to increase the pressure on the gas sample. The pressure on the gas is atmospheric pressure plus the difference in the heights of the mercury columns, and the resulting volume is measured. This process is repeated until either there is no more room in the open arm or the volume of the gas is too small to be measured accurately. Data such as those from one of Boyle's own experiments may be plotted in several ways (Figure 5.3.2). A simple plot of V versus P gives a curve called a hyperbola and reveals an inverse relationship between pressure and volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the two quantities is described as follows:

$$PV = \text{constant} \quad (5.3.1)$$

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V :

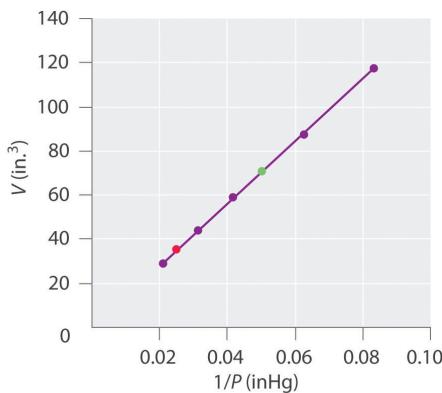
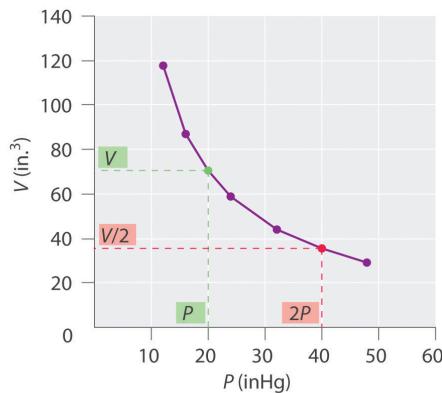
$$V = \frac{\text{const.}}{P} = \text{const.} \left(\frac{1}{P} \right) \quad (5.3.2)$$

or

$$V \propto \frac{1}{P} \quad (5.3.3)$$

where the \propto symbol is read “is proportional to.” A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equations 5.3.1 and 5.3.3. Dividing both sides of Equation 5.3.1 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of the constant depends on the amount of gas used in the experiment and on the temperature at which the experiments are carried out. This relationship between pressure and volume is known as Boyle’s law, after its discoverer, and can be stated as follows: *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.* This law in practice is shown in Figure 5.3.2.

P (inHg)	V (in. ³)	PV
12.0	117.5	1410
16.0	87.2	1400
20.0	70.7	1410
24.0	58.8	1410
32.0	44.2	1410
40.0	35.3	1410
48.0	29.1	1400



(a) Data from Boyle’s experiment

(b) Volume vs. pressure

(c) Volume vs. 1/pressure

Figure 5.3.2: Plots of Boyle’s Data. (a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.³ rather than cm³) and the pressure (in. Hg rather than mmHg). (b) This plot of pressure versus volume is a hyperbola. Because PV is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) A plot of volume versus $1/\text{pressure}$ for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation $V = \text{constant}/P$ (CC BY-SA-NC; anonymous).

At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure

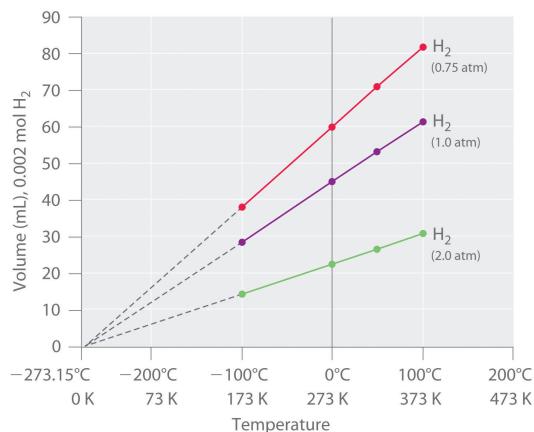


The Relationship between Temperature and Volume: Charles's Law

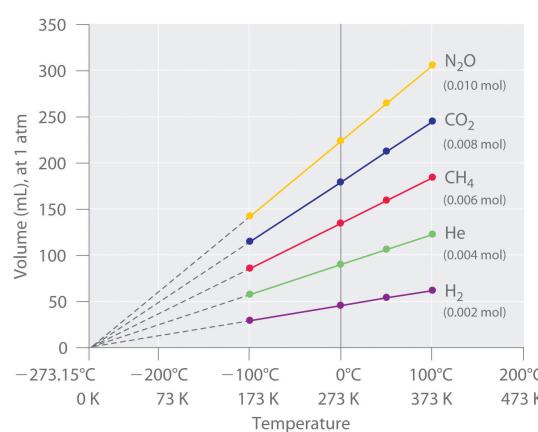
Hot air rises, which is why hot-air balloons ascend through the atmosphere and why warm air collects near the ceiling and cooler air collects at ground level. Because of this behavior, heating registers are placed on or near the floor, and vents for air-conditioning

are placed on or near the ceiling. The fundamental reason for this behavior is that gases expand when they are heated. Because the same amount of substance now occupies a greater volume, hot air is less dense than cold air. The substance with the lower density—in this case hot air—rises through the substance with the higher density, the cooler air.

The first experiments to quantify the relationship between the temperature and the volume of a gas were carried out in 1783 by an avid balloonist, the French chemist Jacques Alexandre César Charles (1746–1823). Charles's initial experiments showed that a plot of the volume of a given sample of gas versus temperature (in degrees Celsius) at constant pressure is a straight line. Similar but more precise studies were carried out by another balloon enthusiast, the Frenchman Joseph-Louis Gay-Lussac (1778–1850), who showed that a plot of V versus T was a straight line that could be extrapolated to a point at zero volume, a theoretical condition now known to correspond to -273.15°C (Figure 5.3.3). A sample of gas cannot really have a volume of zero because any sample of matter must have some volume. Furthermore, at 1 atm pressure all gases liquefy at temperatures well above -273.15°C . Note from part (a) in Figure 5.3.3 that the slope of the plot of V versus T varies for the same gas at different pressures but that the intercept remains constant at -273.15°C . Similarly, as shown in part (b) in Figure 5.3.3, plots of V versus T for different amounts of varied gases are straight lines with different slopes but the same intercept on the T axis.



(a)



(b)

Figure 5.3.3: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to -100°C , and the broken lines show the extrapolation of the data to $V = 0$. The temperature scale is given in both degrees Celsius and kelvins. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at $V = 0$ ($-273.15^{\circ}\text{C} = 0\text{ K}$). (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 (CC BY-SA-NC; anonymous).

The significance of the invariant T intercept in plots of V versus T was recognized in 1848 by the British physicist William Thomson (1824–1907), later named Lord Kelvin. He postulated that -273.15°C was the lowest possible temperature that could theoretically be achieved, for which he coined the term absolute zero (0 K).

We can state Charles's and Gay-Lussac's findings in simple terms: At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in kelvins). This relationship, illustrated in part (b) in Figure 5.3.3 is often referred to as Charles's law and is stated mathematically as

$$V = \text{const. } T \quad (5.3.4)$$

or

$$V \propto T \quad (5.3.5)$$

with *temperature expressed in kelvins, not in degrees Celsius*. Charles's law is valid for virtually all gases at temperatures well above their boiling points.



The Relationship between Amount and Volume: Avogadro's Law

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac's work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles (Figure 5.3.4). This is the historic "Avogadro's hypothesis."

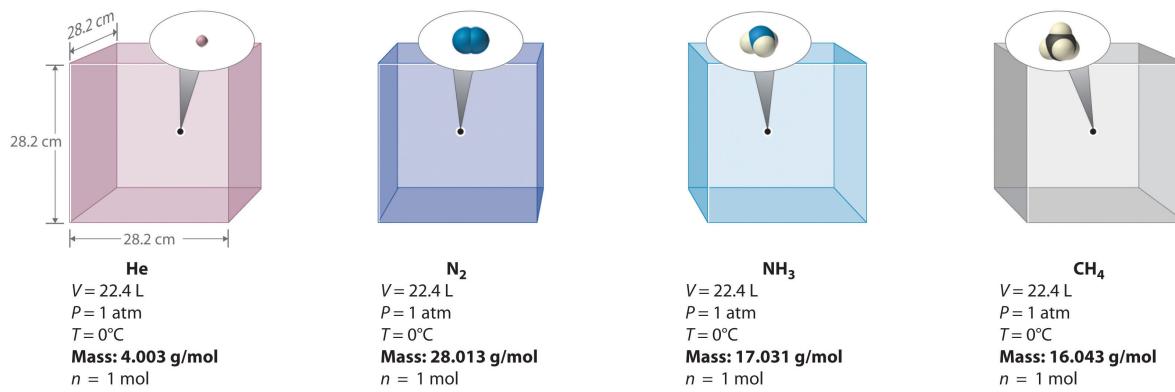


Figure 5.3.4: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous).

A logical corollary to Avogadro's hypothesis (sometimes called Avogadro's law) describes the relationship between the volume and the amount of a gas: *At constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.* Stated mathematically,

$$V = \text{const. } (n) \quad (5.3.6)$$

or

$$V \propto n @ \text{constant T and P} \quad (5.3.7)$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.



For a sample of gas,

- V increases as P decreases (and vice versa)
- V increases as T increases (and vice versa)
- V increases as n increases (and vice versa)

The relationships among the volume of a gas and its pressure, temperature, and amount are summarized in Figure 5.3.5. Volume *increases* with increasing temperature or amount, but *decreases* with increasing pressure.

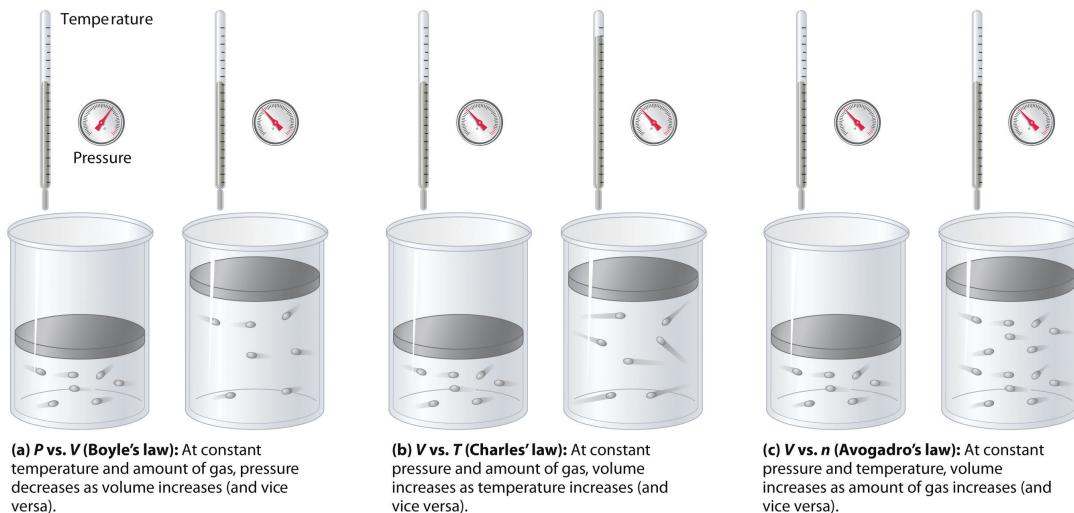


Figure 5.3.5: The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas. The thermometer and pressure gauge indicate the temperature and the pressure qualitatively, the level in the flask indicates the volume, and the number of particles in each flask indicates relative amounts (CC BY-SA-NC; anonymous).

Summary

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to its pressure (**Boyle's law**), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature (in kelvins) at constant pressure (**Charles's law**), and Avogadro postulated that the volume of a gas is directly proportional to the number of moles of gas present (**Avogadro's law**). Plots of the volume of gases versus temperature extrapolate to zero volume at -273.15°C , which is **absolute zero (0 K)**, the lowest temperature possible. Charles's law implies that the volume of a gas is directly proportional to its absolute temperature.

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5.4: Rearrangements of the Ideal Gas Law

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5.5: The Kinetic-Molecular Theory - A Model for Gas Behavior

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

A Molecular Description

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

five postulates of Kinetic Molecular Theory

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In the following sections, we explain how this theory must be modified to account for the behavior of real gases.

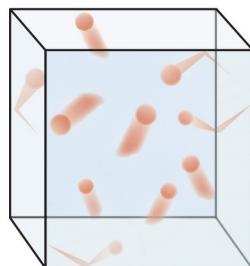


Figure 5.5.1: Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 5.5.2).

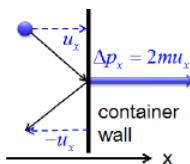


Figure 5.5.2: Momentum transfer (impulse) from a molecule to the container wall as it bounces off the wall. u_x and Δp_x are the x component of the molecular velocity and the momentum transferred to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity u_x in x direction hits is expressed as:

$$\Delta p_x = 2mu_x \quad (5.5.1)$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (u_x) \times \left(\frac{N}{V} \right) \quad (5.5.2)$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V} \right) \propto \left(\frac{N}{V} \right) mu_x^2 \quad (5.5.3)$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace u_x^2 in the expression above with the average value of u_x^2 , which is denoted by $\overline{u_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m \overline{u_x^2} \quad (5.5.4)$$

Finally, we must consider that there is nothing special about x direction. We should expect that

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3} \overline{u^2}.$$

Here the quantity $\overline{u^2}$ is called the **mean-square speed** defined as the average value of square-speed (u^2) over all molecules. Since

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

for each molecule, then

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}.$$

By substituting $\frac{1}{3} \overline{u^2}$ for $\overline{u_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3} \frac{N}{V} m \overline{u^2} \quad (5.5.5)$$

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Postulate 5 refers to the *average translational kinetic energy* of the molecules of a gas ($\overline{e_K}$), which can be represented as *and states that at a given Kelvin temperature (T), all gases have the same value of*

$$\overline{e_K} = \frac{1}{2} mu^2 = \frac{3}{2} \frac{R}{N_A} T \quad (5.5.6)$$

where N_A is the Avogadro's constant. The total translational kinetic energy of 1 mole of molecules can be obtained by multiplying the equation by N_A :

$$N_A \overline{e_K} = \frac{1}{2} M \overline{u^2} = \frac{3}{2} RT \quad (5.5.7)$$

where M is the molar mass of the gas molecules and is related to the molecular mass by $M = N_A m$. By rearranging the equation, we can get the relationship between the root-mean square speed (u_{rms}) and the temperature. The rms speed (u_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \dots + u_N^2}{N}} \quad (5.5.8)$$

where N is the number of particles and u_i is the speed of particle i .

The relationship between u_{rms} and the temperature is given by:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (5.5.9)$$

In Equation 5.5.9, u_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol). Equation 5.5.9 shows that u_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however, because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, not the same average speed. In contrast, the most probable speed (v_p) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then Equation 5.5.8 tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and v_p increases.

At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.

✓ Example 5.5.1

The speeds of eight particles were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{av}), root mean square speed (v_{rms}), and most probable speed (v_m).

Given: particle speeds

Asked for: average speed (v_{av}), root mean square speed (v_{rms}), and most probable speed (v_m)

Strategy:

Use Equation 5.5.6 to calculate the average speed and Equation 5.5.8 to calculate the rms speed. Find the most probable speed by determining the speed at which the greatest number of particles is moving.

Solution:

The average speed is the sum of the speeds divided by the number of particles:

$$v_{\text{av}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0) \text{ m/s}}{8} = 5.6 \text{ m/s}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\text{rms}} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2) \text{ m}^2/\text{s}^2}{8}} = 6.2 \text{ m/s}$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence $v_m = 6.0$ m/s. The v_{rms} of the particles, which is related to the average kinetic energy, is greater than their average speed.

Boltzmann Distributions

At any given time, what fraction of the molecules in a particular sample has a given speed? Some of the molecules will be moving more slowly than average, and some will be moving faster than average, but how many in each situation? Answers to questions such as these can have a substantial effect on the amount of product formed during a chemical reaction. This problem was solved mathematically by Maxwell in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature. Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in Figure 5.5.3. Increasing the temperature has two effects. First, the peak of the curve moves to the right because the most probable speed increases. Second, the curve becomes broader because of the increased spread of the speeds. Thus increased temperature increases the *value* of the most probable speed but decreases the relative number of molecules that have that speed. Although the mathematics behind curves such as those in Figure 5.5.3 were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributions, after one of the other major figures responsible for the kinetic molecular theory of gases.

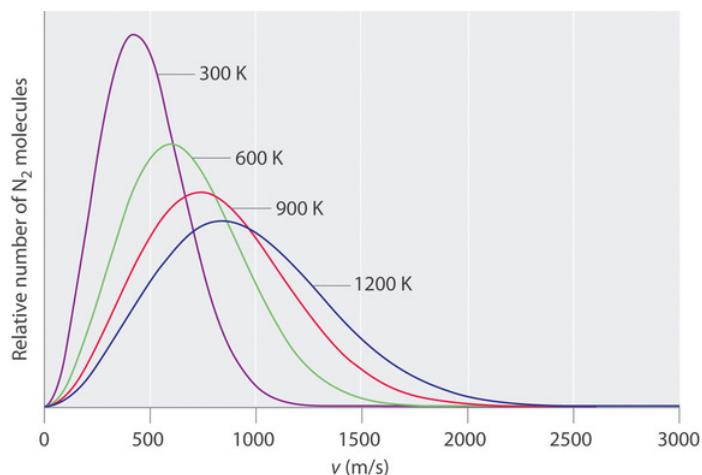


Figure 5.5.3: The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

The Relationships among Pressure, Volume, and Temperature

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

- **Pressure versus Volume:** At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.
- **Volume versus Temperature:** Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the pressure, as we have just seen. Thus an increase in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.
- **Pressure of Gas Mixtures:** Postulate 3 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton's law of partial pressures holds.

✓ Example 5.5.2

The temperature of a 4.75 L container of N₂ gas is increased from 0°C to 117°C. What is the qualitative effect of this change on the

- average kinetic energy of the N₂ molecules?
- rms speed of the N₂ molecules?
- average speed of the N₂ molecules?
- impact of each N₂ molecule on the wall of the container during a collision with the wall?
- total number of collisions per second of N₂ molecules with the walls of the entire container?
- number of collisions per second of N₂ molecules with each square centimeter of the container wall?
- pressure of the N₂ gas?

Given: temperatures and volume

Asked for: effect of increase in temperature

Strategy:

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

Solution:

- Increasing the temperature increases the average kinetic energy of the N₂ molecules.
- An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
- If the rms speed of the N₂ molecules increases, the average speed also increases.
- If, on average, the particles are moving faster, then they strike the container walls with more energy.
- Because the particles are moving faster, they collide with the walls of the container more often per unit time.
- The number of collisions per second of N₂ molecules with each square centimeter of container wall increases because the total number of collisions has increased, but the volume occupied by the gas and hence the total area of the walls are unchanged.
- The pressure exerted by the N₂ gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law.

? Exercise 5.5.2

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at constant temperature. What is the qualitative effect of this change on the

- average kinetic energy of the He atoms?
- rms speed of the He atoms?
- average speed of the He atoms?
- impact of each He atom on the wall of the container during a collision with the wall?
- total number of collisions per second of He atoms with the walls of the entire container?
- number of collisions per second of He atoms with each square centimeter of the container wall?
- pressure of the He gas?

Answer a

no change

Answer b

no change

Answer c

no change

Answer d

no change

Answer e

decreases

Answer f

decreases

Answer g

decreases



Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m u_{\text{rms}}^2 = \frac{3}{2} \frac{R}{N_A} T n$$

- Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \dots + u_N^2}{N}}$$

- Kinetic molecular theory of gases:**

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

The behavior of ideal gases is explained by the **kinetic molecular theory of gases**. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same **root mean square (rms) speed** (v_{rms}). The actual values of speed and kinetic energy are not the same for all particles of a gas but are given by a **Boltzmann distribution**, in which some molecules have higher or lower speeds (and kinetic energies) than average.

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5.6: Real Gases - Deviations from Ideal Behavior

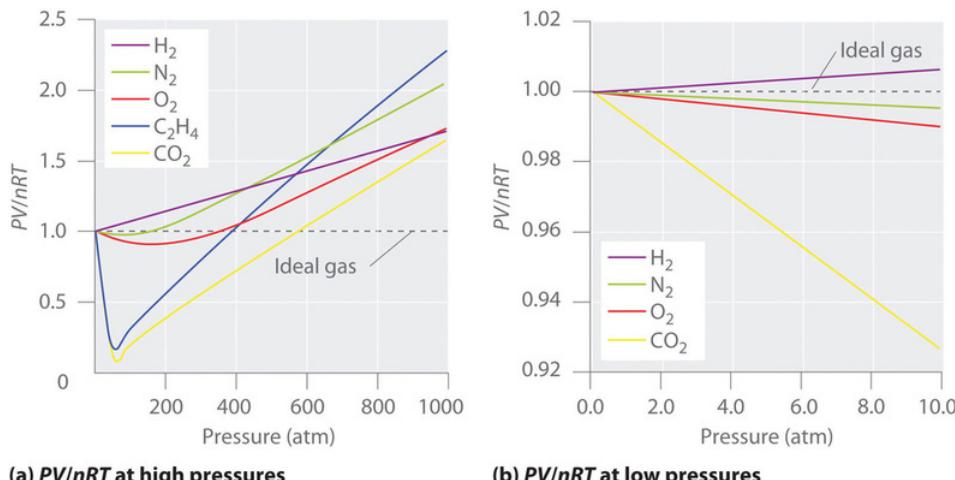
Learning Objectives

- To recognize the differences between the behavior of an ideal gas and a real gas
- To understand how molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (Figure 5.6.1a). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (Figure 5.6.1b).



(a) PV/nRT at high pressures

(b) PV/nRT at low pressures

Figure 5.6.1: Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures. (a) In these plots of PV/nRT versus P at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.

Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure 5.6.2 for N_2 . Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

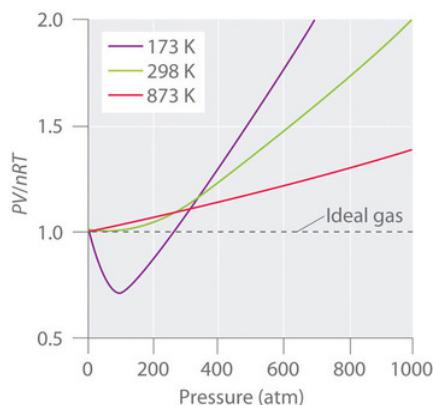


Figure 5.6.2: The Effect of Temperature on the Behavior of Real Gases. A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure 5.6.3). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of PV/nRT is greater than the value predicted by the ideal gas law.

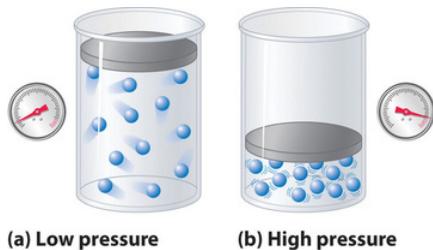


Figure 5.6.3: The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the 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 5.6.4). Thus as shown in Figure 5.6.2, at low temperatures, the ratio of (PV/nRT) is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

Nonzero molecular volume makes the actual volume greater than predicted at high pressures; intermolecular attractions make the pressure less than predicted.

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas behavior, the so-called *van der Waals* equation,

$$\underbrace{\left(P + \frac{an^2}{V^2} \right)}_{\text{Pressure Term}} \overbrace{(V - nb)}^{\text{Pressure Term}} = nRT \quad (5.6.1)$$

a and b are empirical constants that are different for each gas. The values of a and b are listed in Table 5.6.1 for several common gases.

Table 5.6.1:: van der Waals Constants for Some Common Gases (see [Table A8](#) for more complete list)

Gas	a ((L ² ·atm)/mol ²)	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H ₂	0.2420	0.0265
N ₂	1.352	0.0387
O ₂	1.364	0.0319
Cl ₂	6.260	0.0542
NH ₃	4.170	0.0371
CH ₄	2.273	0.0430
CO ₂	3.610	0.0429

The pressure term in Equation 5.6.1 corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure 5.6.4. The volume term corrects for the volume occupied by the gaseous molecules.

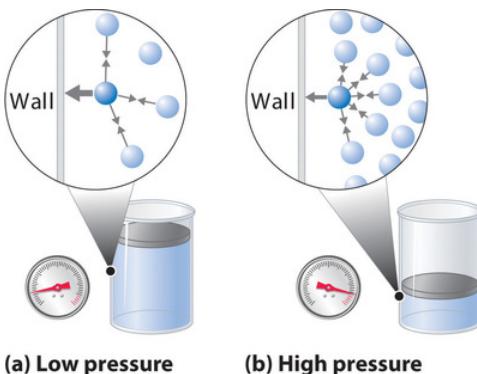


Figure 5.6.4: The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on V and P , respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the an^2/V^2 term must be added to the measured pressure to correct for these effects.

✓ Example 5.6.1

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.00 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain a and b values for Cl_2 from Table 5.6.1. Use the van der Waals equation (5.6.1) to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$n = \frac{m}{M} \quad (5.6.2)$$

$$= \frac{500 \text{ g}}{70.906 \text{ g/mol}} \quad (5.6.3)$$

$$= 7.052 \text{ mol}$$

Using the ideal gas law and the temperature in kelvin (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} \quad (5.6.4)$$

$$= \frac{7.052 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}}{4.00 \text{ L}} \quad (5.6.5)$$

$$= 43.1 \text{ atm} \quad (5.6.6)$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the a and b values for Cl_2 from Table 5.6.1. Solving for P gives

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad (5.6.7)$$

$$= \frac{7.052 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}}{4.00 \text{ L} - 7.052 \text{ mol} \times 0.0542 \frac{\text{L}}{\text{mol}}} - \frac{6.260 \frac{\text{L}^2 \cdot \text{atm}}{\text{mol}^2} \times (7.052 \text{ mol})^2}{(4.00 \text{ L})^2} \quad (5.6.8)$$

$$= 28.2 \text{ atm} \quad (5.6.9)$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

? Exercise 5.6.1

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

- a. ideal gas law.
- b. van der Waals equation.

Answer a

77 atm

Answer b

67 atm

Liquefaction of Gases

Liquefaction of gases is the condensation of gases into a liquid form, which is neither anticipated nor explained by the kinetic molecular theory of gases. Both the theory and the ideal gas law predict that gases compressed to very high pressures and cooled to very low temperatures should still behave like gases, albeit cold, dense ones. As gases are compressed and cooled, however, they invariably condense to form liquids, although very low temperatures are needed to liquefy light elements such as helium (for He, 4.2 K at 1 atm pressure).

Liquefaction can be viewed as an extreme deviation from ideal gas behavior. It occurs when the molecules of a gas are cooled to the point where they no longer possess sufficient kinetic energy to overcome intermolecular attractive forces. The precise combination of temperature and pressure needed to liquefy a gas depends strongly on its molar mass and structure, with heavier and more complex molecules usually liquefying at higher temperatures. In general, substances with large van der Waals a coefficients are relatively easy to liquefy because large a coefficients indicate relatively strong intermolecular attractive interactions. Conversely, small molecules with only light elements have small a coefficients, indicating weak intermolecular interactions, and they are relatively difficult to liquefy. Gas liquefaction is used on a massive scale to separate O₂, N₂, Ar, Ne, Kr, and Xe. After a sample of air is liquefied, the mixture is warmed, and the gases are separated according to their boiling points.

A large value of a in the van der Waals equation indicates the presence of relatively strong intermolecular attractive interactions.

The ultracold liquids formed from the liquefaction of gases are called cryogenic liquids, from the Greek *kryo*, meaning “cold,” and *genes*, meaning “producing.” They have applications as refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.



Figure 5.6.5: A Liquid Natural Gas Transport Ship.

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure 5.6.5). Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are liquefied forms of hydrocarbons produced from natural gas or petroleum reserves. LNG consists mostly of methane, with small amounts of heavier hydrocarbons; it is prepared by cooling natural gas to below about -162°C. It can be stored in double-walled, vacuum-insulated containers at or slightly above atmospheric pressure. Because LNG occupies only about 1/600 the volume of natural gas, it is easier and more economical to transport. LPG is typically a mixture of propane, propene, butane, and butenes and is primarily used as a fuel for home heating. It is also used as a feedstock for chemical plants and as an inexpensive and relatively nonpolluting fuel for some automobiles.

Summary

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Deviations from ideal gas behavior can be seen in plots of PV/nRT versus P at a given temperature; for an ideal gas, PV/nRT versus $P = 1$ under all

conditions. At high pressures, most real gases exhibit larger PV/nRT values than predicted by the ideal gas law, whereas at low pressures, most real gases exhibit PV/nRT values close to those predicted by the ideal gas law. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the **van der Waals equation**, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces. If the temperature of a gas is decreased sufficiently, **liquefaction** occurs, in which the gas condenses into a liquid form. Liquefied gases have many commercial applications, including the transport of large amounts of gases in small volumes and the uses of ultracold **cryogenic liquids**.

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Chemistry: The Molecular Nature of Matter and Change

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CHAPTER OVERVIEW

7: Quantum Theory and Atomic Structure

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- 7.1: The Nature of Light
- 7.2: Atomic Spectra
- 7.3: The Wave-Particle Duality of Matter and Energy
- 7.4: The Quantum-Mechanical Model of the Atom
- 7.E: Quantum Theory and Atomic Structure (Exercises)

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7.1: The Nature of Light

Learning Objectives

- To learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves are 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 7.1.1: 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 7.1.1). 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.

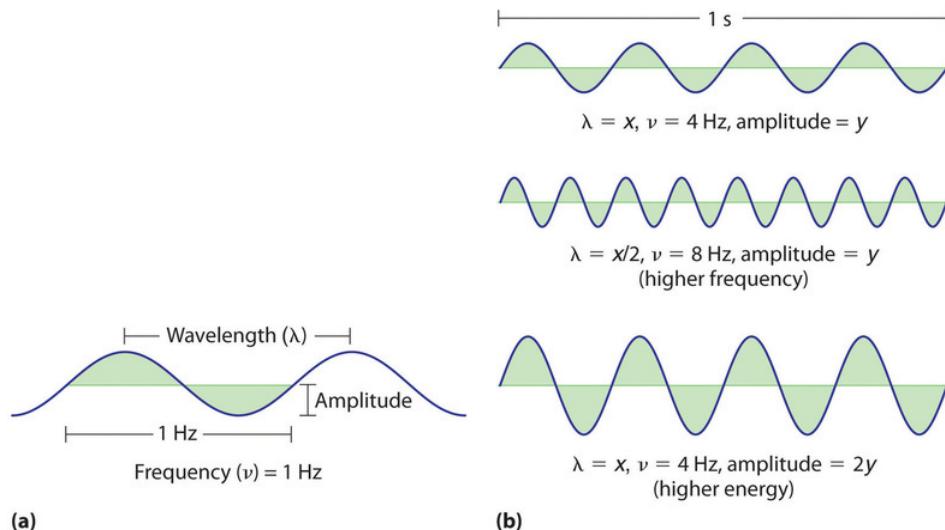


Figure 7.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν , in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 7.1.2). As you may have noticed in Figure 7.1.1, 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 , lowercase Greek lambda). Wavelengths are described by a unit of distance, typically meters. The **frequency** (u , lowercase Greek nu) of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations per second ($1/\text{s} = \text{s}^{-1}$), 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**, 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 7.1.2, 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), 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:

$$\begin{aligned} (\text{wavelength})(\text{frequency}) &= \text{speed} \\ \lambda u &= v \end{aligned} \quad (7.1.1)$$

$$\left(\frac{\text{meters}}{\text{wave}} \right) \left(\frac{\text{wave}}{\text{second}} \right) = \frac{\text{meters}}{\text{second}} \quad (7.1.2)$$

Be careful not to confuse the symbols for the speed, v , with the frequency, u .

Different types of waves may have vastly different possible speeds and frequencies. 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**. (Figure 7.1.3). Some forms of electromagnetic radiation are shown in Figure 7.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which turns out to be a fundamental physical constant with a value of 2.99792458×10^8 m/s (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.

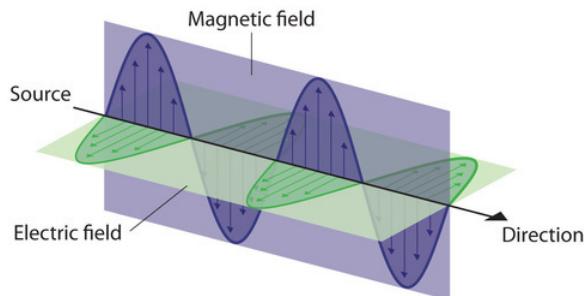


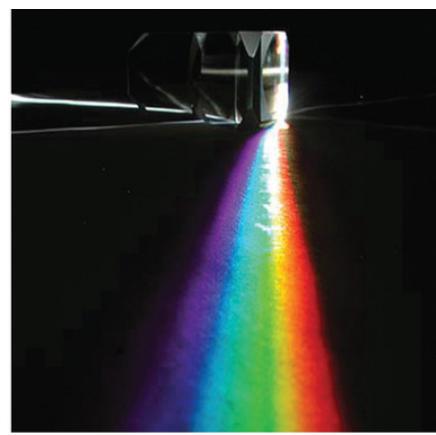
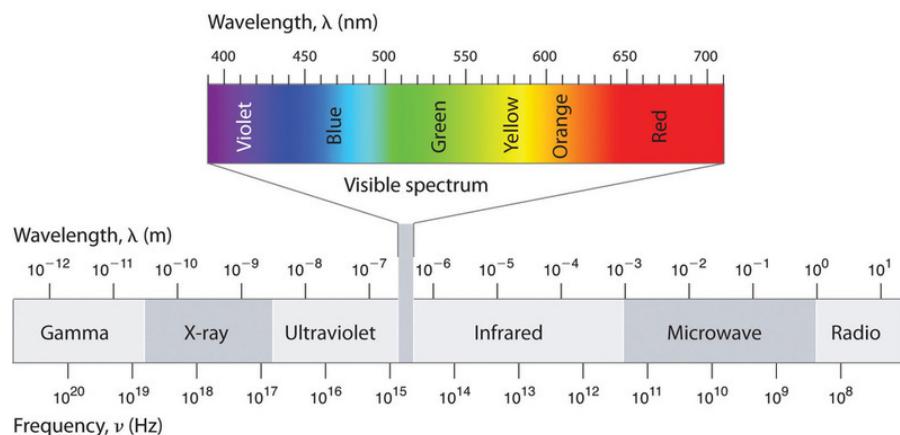
Figure 7.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 7.1.4 and Table 7.1.1, 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 7.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda u \quad (7.1.3)$$

$$u = \frac{c}{\lambda} \quad (7.1.4)$$

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.



(a)

Figure 7.1.4: 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.

Within the 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 7.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 7.1.1: Common Wavelength Units for Electromagnetic Radiation

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

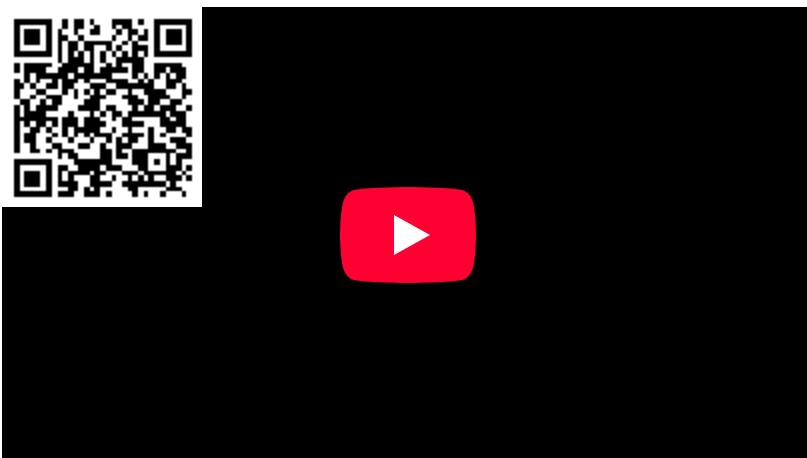
As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto u \quad (7.1.5)$$

$$\propto \frac{1}{\lambda} \quad (7.1.6)$$

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 of the atmosphere 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.



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

✓ Example 7.1.1: Wavelength of Radiowaves

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 7.1.4 to calculate the wavelength in meters.

Solution:

From Equation 7.1.4, 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:

$$\begin{aligned}\lambda\nu &= c \\ &= 2.998 \times 10^8 \text{ m/s}\end{aligned}$$

Thus the wavelength λ is given by

$$\begin{aligned}\lambda &= \frac{c}{\nu} \\ &= \left(\frac{2.998 \times 10^8 \text{ m/s}}{101.1 \text{ MHz}} \right) \left(\frac{1 \text{ MHz}}{10^6 \text{ s}^{-1}} \right) \\ &= 2.965 \text{ m}\end{aligned}$$

? Exercise 7.1.1

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

Summary

Understanding 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.

Contributors and Attributions

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7.2: Atomic Spectra

Learning Objectives

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

The concept of the photon emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. However, more direct evidence was needed to verify the quantized nature of energy in all matter. In this section, we describe how observation of the interaction of atoms 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 H₂ 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 of particular wavelengths, called a **line spectrum**, are observed rather than a continuous range of wavelengths (Figure 7.2.1). 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.

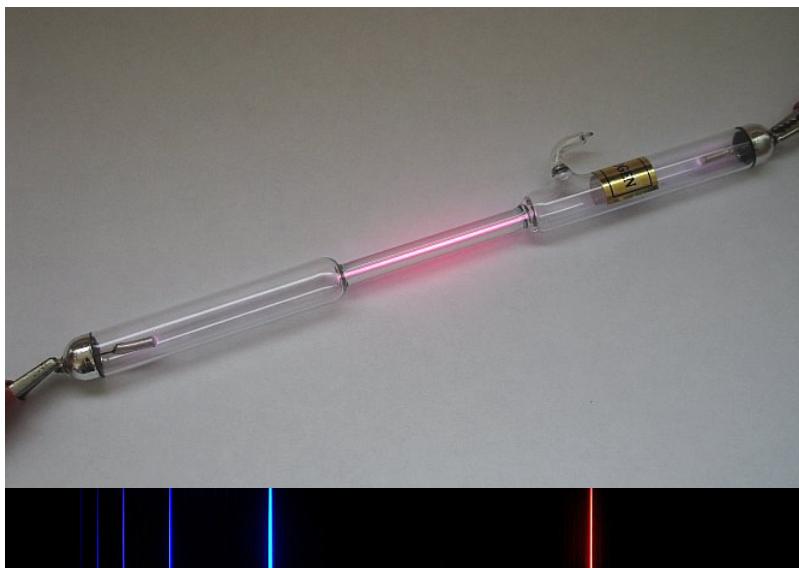


Figure 7.2.1: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (CC BY-SA 3.0 Unported; [Science Made Alive](#) via [Wikipedia](#)) (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm. (CC BY-SA 3.0; [Jan Homann](#) via [Wikipedia](#))

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 Planck's equation: the observation of only a few values of λ (or u) 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:

$$u = \text{constant} \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad (7.2.1)$$

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*:

$$\frac{1}{\lambda} = \mathfrak{R} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (7.2.2)$$

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

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 $n_1 = 2, n_2 = 3, 4, 5, \dots$). More important, Rydberg's equation also predicted the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet ($n_1 = 1, n_2 = 2, 3, 4, \dots$) 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.

Bohr's Model

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

$$E_n = \frac{-\mathfrak{R}hc}{n^2} \quad (7.2.3)$$

where \mathfrak{R} 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.

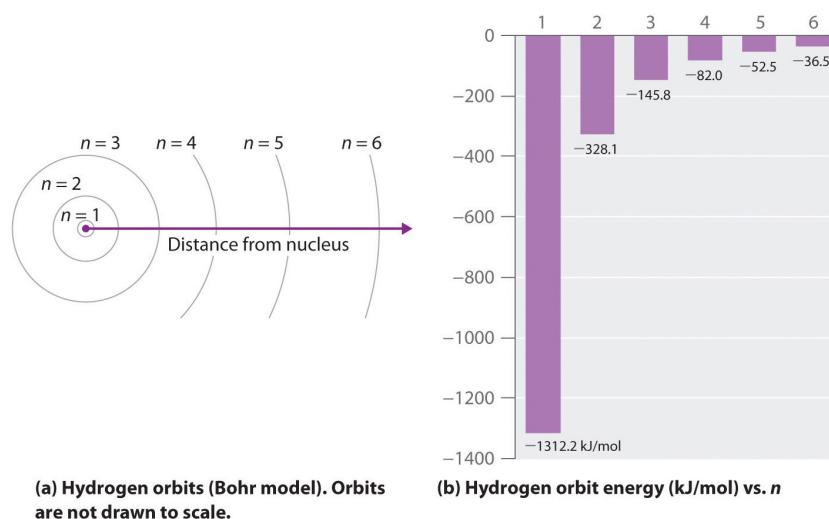
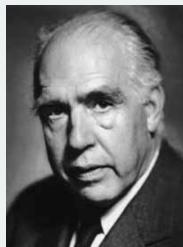


Figure 7.2.2: The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing n . (b) The energy of the orbit becomes increasingly less negative with increasing n .

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 7.2.3 indicates that the electron-nucleus pair is more tightly bound (i.e. at a lower potential energy) 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) 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 7.2.2a). A hydrogen atom with an electron in an orbit with $n > 1$ is therefore in an **excited state**, defined as any arrangement of electrons that is higher in energy than 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 7.2.1).

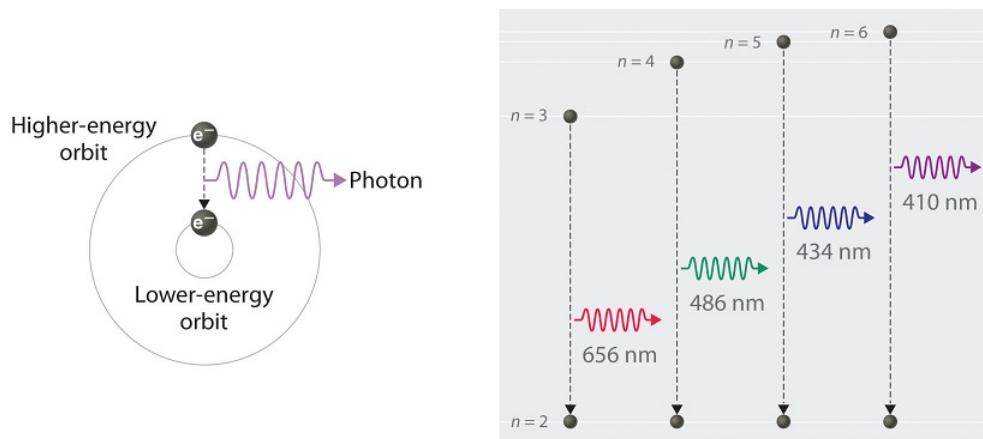


Figure 7.2.3: The Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with $n \geq 3$ 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 (ΔE) 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 7.2.3) for each energy value gives

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= -\frac{\mathfrak{R}hc}{n_2^2} - \left(-\frac{\mathfrak{R}hc}{n_1^2} \right) \\ &= -\mathfrak{R}hc \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)\end{aligned}$$

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 7.2.3. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\mathfrak{R}hc \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad (7.2.4)$$

Canceling hc on both sides gives

$$\frac{1}{\lambda} = -\mathfrak{R} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad (7.2.5)$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equations 7.2.4 and 7.2.5 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 \mathfrak{R} from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of $1.0974 \times 10^7 \text{ m}^{-1}$, 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 (7.2.3b); 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 (Figure 7.2.3a). 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 $n \geq 4$ levels. Consequently, the $n = 3$ to $n = 2$ transition is the most intense line, producing the characteristic

red color of a hydrogen discharge (Figure 7.2.1a). Other families of lines are produced by transitions from excited states with $n > 1$ to the orbit with $n = 1$ or to orbits with $n \geq 3$. These transitions are shown schematically in Figure 7.2.4.



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

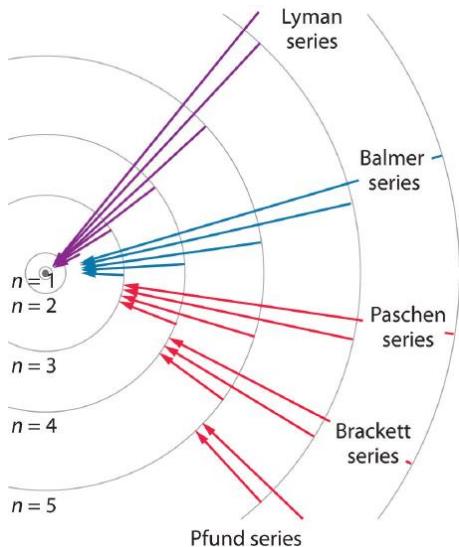


Figure 7.2.4: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit ($n = 1$); these transitions release a great deal of energy, corresponding 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.)

Using Atoms to Time

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 7.2.1: 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:

- Substitute the appropriate values into Equation 7.2.2 (the Rydberg equation) and solve for λ .
- Use Figure 2.2.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

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

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.

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

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} .

$$\tilde{u} = \frac{1}{\lambda} = 8.228 \times 10^6 \text{ } m^{-1} \left(\frac{\nu}{100 \text{ cm}} \right) = 82,280 \text{ } \text{cm}^{-1}$$

and

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

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 7.2.1: 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:

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 7.2.5). In fact, Bohr's model worked only for species that contained just one electron: H, He⁺, Li²⁺, 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.

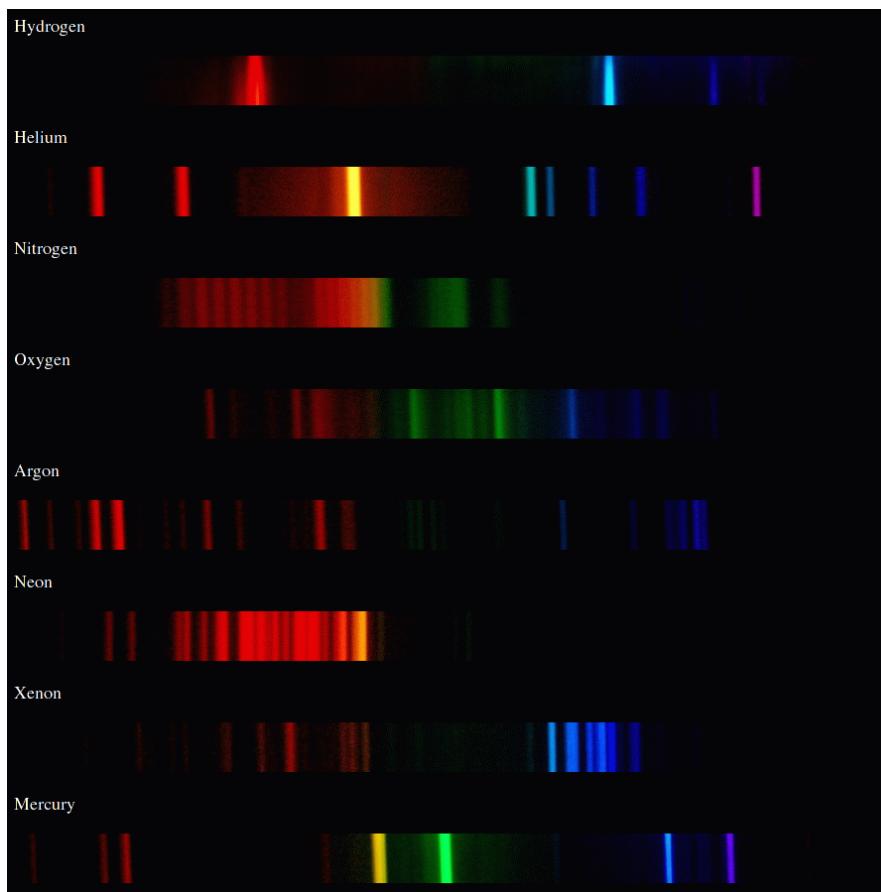


Figure 7.2.5: The atomic emission spectra for various elements. Each thin band in each spectrum corresponds to a single, unique transition between energy levels in an atom. [Astronomical spectra image](#)(opens in new window) from the Rochester Institute of Technology, CC BY-NC-SA 2.0(open in new window).

The Energy States of the Hydrogen Atom

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).

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.

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.

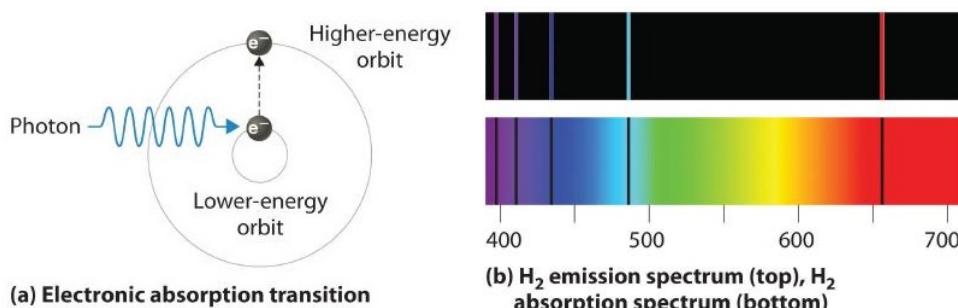


Figure 7.2.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n . (b) Images of the emission and absorption spectra of hydrogen are shown here. (CC BY-NC-SA 3.0; anonymous)

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 7.2.7. 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.

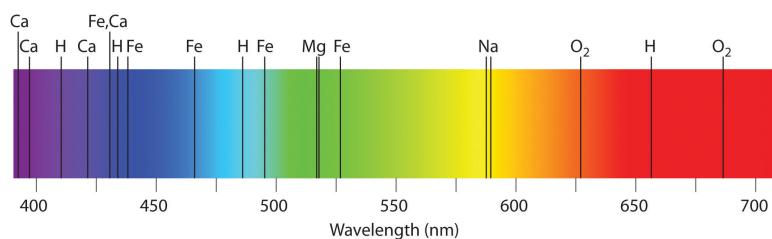


Figure 7.2.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere. (CC BY-NC-SA 3.0; anonymous)

The familiar red color of neon signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 7.2.5. 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 7.2.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.



Hg vapor spectrum (350-700 nm)

Low-pressure Na spectrum
(350-700 nm)High-pressure Na spectrum
(350-700 nm)

Figure 7.2.8: 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 caused by absorption of light in the cooler outer part of the lamp.

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. 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. Bohr's model revolutionized the understanding of the atom but could not explain the spectra of atoms heavier than hydrogen.

Key Concepts

- 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.

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7.3: The Wave-Particle Duality of Matter and Energy

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 famous equation:

$$E = hu = h \frac{c}{\lambda} = mc^2 \quad (7.3.1)$$

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

$$m = \frac{E}{c^2} = \frac{hu}{c^2} = \frac{h}{\lambda c} \quad (7.3.2)$$

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

$$\lambda = \frac{h}{mv} \quad (7.3.3)$$

where

- h 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 7.3.1, 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.



The de Broglie Equation: The de Broglie Equation, YouTube([opens in new window](#)) [youtu.be]

✓ Example 7.3.1: Wavelength of a Baseball in Motion

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:

- Convert the speed of the baseball to the appropriate SI units: meters per second.
- Substitute values into Equation 7.3.3 and solve for the wavelength.

Solution:

The wavelength of a particle is given by $\lambda = h/mv$. We know that $m = 0.149 \text{ kg}$, so all we need to find is the speed of the baseball:

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

B Recall that the joule is a derived unit, whose units are $(\text{kg} \cdot \text{m}^2)/\text{s}^2$. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{(0.149 \text{ kg})(44.69 \text{ m} \cdot \text{s})} = \frac{6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{s}}{(0.149 \text{ kg})(44.69 \text{ m} \cdot \text{s}^{-1})} = 9.95 \times 10^{-35} \text{ m}$$

(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 7.3.1: Wavelength of a Neutron in Motion

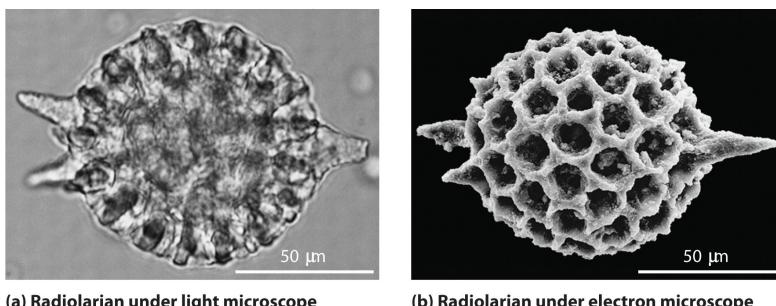
Calculate the wavelength of a neutron that is moving at $3.00 \times 10^3 \text{ m/s}$.

Answer

1.32 Å, or 132 pm

As you calculated in Example 7.3.1, 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, however, 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 7.3.1).



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

Figure 7.3.1: 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 And Interference

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 7.3.2A shows an arbitrary phase difference between two waves and Figure 7.3.2B shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 7.3.2C shows what happens when the two waves are in phase, exactly superimposed on each other. Again, the green line is the sum of the intensities. A pattern of constructive and destructive interference is obtained when two (or more) diffracting waves interact with each other. This principle of diffraction and interference was used to prove the wave properties of electrons and is the basis for how electron microscopes work.

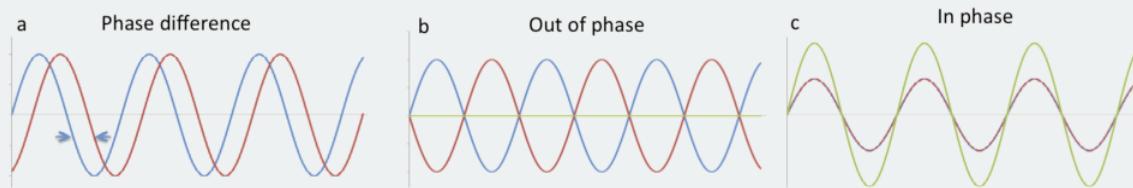
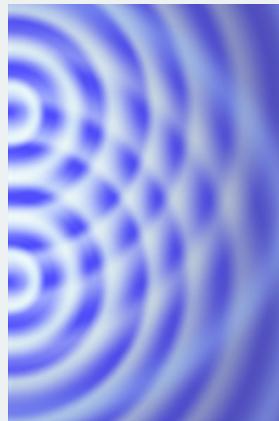


Figure 7.3.2: Phase. Two waves traveling together are displaced by a phase difference. If the phase difference is 0° then they lay on top of each other and reinforce. If the phase difference is 180° they completely cancel each other out.

A shows two waves with a phase difference where the peaks are slightly misaligned. B shows two waves out of phase, the two waves are opposite of each other. C shows two waves in phase, the two waves peak at the same time.



The waves are the white circles that start from the left side. The waves intersect at multiple points.

Photograph of an interference pattern produced by circular water waves in a ripple tank.

For a mathematical analysis of phase aspects in sinusoids, check the math Libretexts library.

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 7.3.3). If the length of the string is L , then the lowest-energy vibration (the fundamental) has wavelength

$$\frac{\lambda}{2} = L \quad (7.3.4)$$

$$\lambda = 2L$$

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

$$\lambda = \frac{2L}{n} \quad (7.3.5)$$

where n has any integral value. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. Thus, we can think of the resonant frequencies of the string as being quantized. Notice in Figure 7.3.3 that all overtones have one or more nodes, points where the string does not move. The amplitude of the wave at a node is zero.

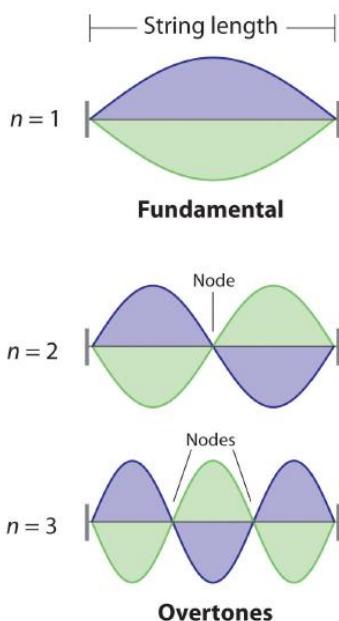
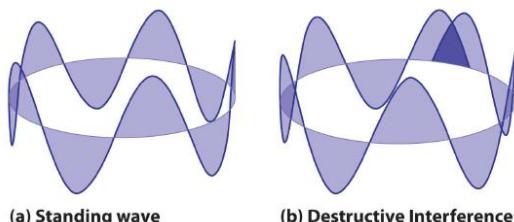


Figure 7.3.3: Standing Waves on a Vibrating String. The vibration with $\langle n = 1 \rangle$ is the fundamental and contains no nodes. Vibrations with higher values of n are called overtones; they contain $\langle n - 1 \rangle$ nodes.

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

$$2\pi r = n\lambda \quad (7.3.6)$$

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 7.3.4). 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 nonresonant 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 7.3.6, one complete wavelength would close the circle. Higher energy levels would have successively higher values of n with a corresponding number of nodes.



(a) Standing wave (b) Destructive Interference

Figure 7.3.4: Standing Circular Wave and Destructive Interference. (a) In a standing circular wave with $\lambda(n = 5)$, 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.

Like 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. 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 now 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.

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 it can be bent or spread out by passing through a narrow slit. 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. An "uncertainty principle" for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. De Broglie's idea of wave-particle duality means that particles such as electrons which exhibit wavelike characteristics will also undergo diffraction from slits whose size is on the order of the electron wavelength.

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** states that the uncertainty in the position of a particle (Δx) multiplied by the uncertainty in its momentum [$\Delta(mv)$] is greater than or equal to Planck's constant divided by 4π :

$$(\Delta x)(\Delta [mv]) \geq \frac{h}{4\pi} \quad (7.3.7)$$

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 ($\Delta x = 0$), then the uncertainty in its momentum must be infinite:

$$(\Delta [mv]) = \frac{h}{4\pi (\Delta x)} = \frac{h}{4\pi (0)} = \infty \quad (7.3.8)$$

Because the mass of the electron at rest (m) is both constant and accurately known, the uncertainty in $\Delta(mv)$ must be due to the Δv term, which would have to be infinitely large for $\Delta(mv)$ to equal infinity. That is, according to Equation 7.3.8, the more accurately we know the exact position of the electron (as $\Delta x \rightarrow 0$), the less accurately we know the speed and the kinetic energy of the electron ($1/2 mv^2$) because $\Delta(mv) \rightarrow \infty$. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as $\Delta(mv) \rightarrow 0$], then $\Delta x \rightarrow \infty$ 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 7.3.1: Quantum Nature of Baseballs

Calculate the minimum uncertainty in the position of the pitched baseball from Example 7.3.1 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:

- Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 7.3.7) to solve for the minimum uncertainty in the position of an object (Δx).
- Find Δv by converting the velocity of the baseball to the appropriate SI units: meters per second.
- Substitute the appropriate values into the expression for the inequality and solve for Δx .

Solution:

A The Heisenberg uncertainty principle (Equation 7.3.7) tells us that

$$(\Delta x)(\Delta(mv)) = h/4\pi$$

. Rearranging the inequality gives

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

B We know that $h = 6.626 \times 10^{-34}$ J·s and $m = 0.149$ kg. Because there is no uncertainty in the mass of the baseball, $\Delta(mv) = m\Delta v$ and $\Delta v = \pm 1$ mi/h. We have

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

C Therefore,

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

Inserting the definition of a joule ($1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$) gives

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

$$\Delta x \geq 7.92 \pm 10^{-34} \text{ m}$$

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 7.3.2

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 $\pm 0.1\%$. Assume its mass to be equal to its mass at rest.

Answer

$6 \times 10^{-10} \text{ m}$, 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.

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

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.

$$(\Delta x)(\Delta [mv]) \geq \frac{h}{4\pi}$$

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7.4: The Quantum-Mechanical Model of the Atom

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.

Erwin 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 *wavefunctions* that are the solutions of Schrödinger's equations.

Wavefunctions

A wavefunction (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 wavefunction is associated with a particular energy E . The properties of wavefunctions derived from quantum mechanics are summarized here:

- **A wavefunction 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 were the captain of a ship trying 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 7.4.1). 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.

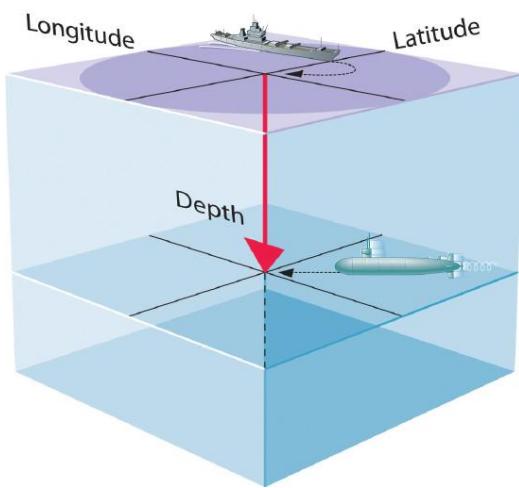


Figure 7.4.1: The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object

- **The magnitude of the wavefunction at a particular point in space is proportional to the amplitude of the wave at that point.** Many wavefunctions 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 wavefunction (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 wavefunction should *not* be confused with a positive or negative electrical charge.

- **The square of the wavefunction 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 wavefunction (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] and is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wavefunction 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 7.4.2.
- **Describing the electron distribution as a standing wave leads to sets of quantum numbers that are characteristic of each wavefunction.** From the patterns of one- and two-dimensional standing waves shown previously, 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 wavefunctions. 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 (wavefunctions), each of which is specified by a set of numbers called quantum numbers.
- **Each wavefunction 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.

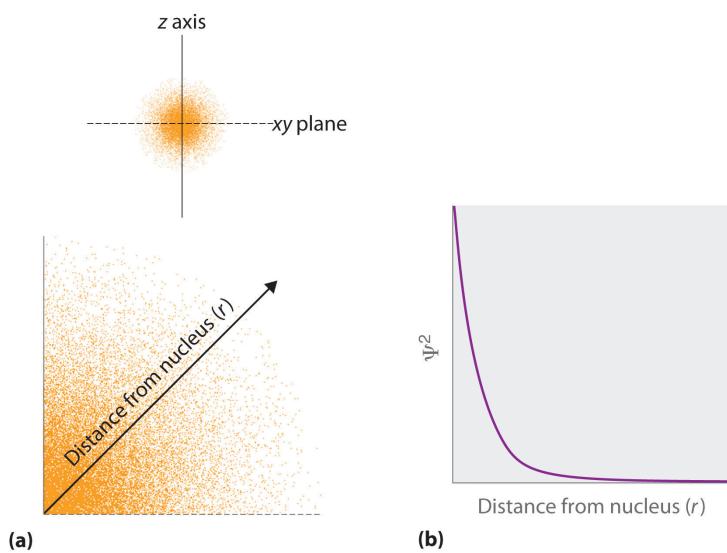


Figure 7.4.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at $r = 0$ (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.

Quantum Numbers

Schrödinger's approach uses three quantum numbers (n , l , and m_l) to specify any wavefunction. 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 .

The Principal Quantum Number

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

$$n = 1, 2, 3, 4, \dots \quad (7.4.1)$$

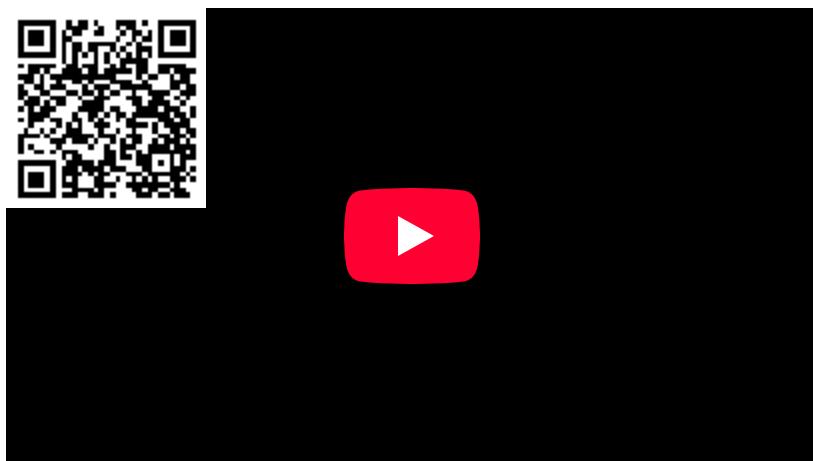
As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wavefunctions 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 $n - 1$:

$$l = 0, 1, 2, \dots, n - 1 \quad (7.4.2)$$

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 wavefunctions 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.



Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell:

[Principal quantum number \(\$n\$ \) & Orbital angular momentum \(\$l\$ \): The Orbital Subshell, YouTube](#)(opens in new window) [youtu.be]

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:

$$m_l = -l, -l + 1, \dots, 0, \dots, l - 1, l \quad (7.4.3)$$

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 wavefunction 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 7.4.1: $n=4$ 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 $n^2 = 16$

Exercise 7.4.1: $n=3$ 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:

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 historical terms for corresponding spectroscopic characteristics: sharp, principle, diffuse, and fundamental.) A 1s orbital has $n = 1$ and $l = 0$; a 2p subshell has $n = 2$ and $l = 1$ (and has three 2p orbitals, corresponding to $m_l = -1, 0$, and $+1$); a 3d subshell has $n = 3$ and $l = 2$ (and has five 3d 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 6.5.1):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible (1s); for $n = 2$, there are two subshells (2s and 2p); for $n = 3$, there are three subshells (3s, 3p, and 3d); 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 2d subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2d 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.

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

Table 7.4.1: Values of n , l , and m_l 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

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



Magnetic Quantum Number (m_l) & Spin Quantum Number (m_s): [Magnetic Quantum Number \(\$m_l\$ \) & Spin Quantum Number \(\$m_s\$ \) YouTube](#) (opens in new window) [youtu.be] (opens in new window)

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 **wavefunctions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wavefunctions have five important properties:

1. the wavefunction uses three variables (Cartesian axes x , y , and z) to describe the position of an electron;
2. the magnitude of the wavefunction 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 wavefunction 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 wavefunction; and
5. each spatial distribution of the electron described by a wavefunction 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 wavefunctions 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. Wavefunctions 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 wavefunction 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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7.E: Quantum Theory and Atomic Structure (Exercises)

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CHAPTER OVERVIEW

8: Electron Configuration and Chemical Periodicity

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII
XVIII XIX XX XXI XXII XXIII XXIV

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Topic hierarchy

- 8.1: Characteristics of Many-Electron Atoms
- 8.2: The Quantum-Mechanical Model and the Periodic Table
- 8.3: Trends in Three Atomic Properties
- 8.4: Atomic Properties and Chemical Reactivity
- 8.E: Electron Configuration and Chemical Periodicity (Exercises)

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8.1: Characteristics of Many-Electron Atoms

Learning Objectives

- To write the electron configuration of any element and relate its electron configuration to its position in the periodic table.

The quantum mechanical model allowed us to determine the energies of the hydrogen atomic orbitals; now we would like to extend this to describe the electronic structure of every element in the Periodic Table. 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; however, interactions between electrons make this process a bit more complicated than it sounds. 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 and the Pauli principle.

Orbitals and their Energies

Unlike in hydrogen-like atoms with only one electron, in multielectron atoms the values of quantum numbers n and l determine the energies of an orbital. The energies of the different orbitals for a typical multielectron atom are shown in Figure 8.1.1. Within a given principal shell of a multielectron atom, the orbital energies increase with increasing l . An ns orbital always lies below the corresponding np orbital, which in turn lies below the nd orbital.

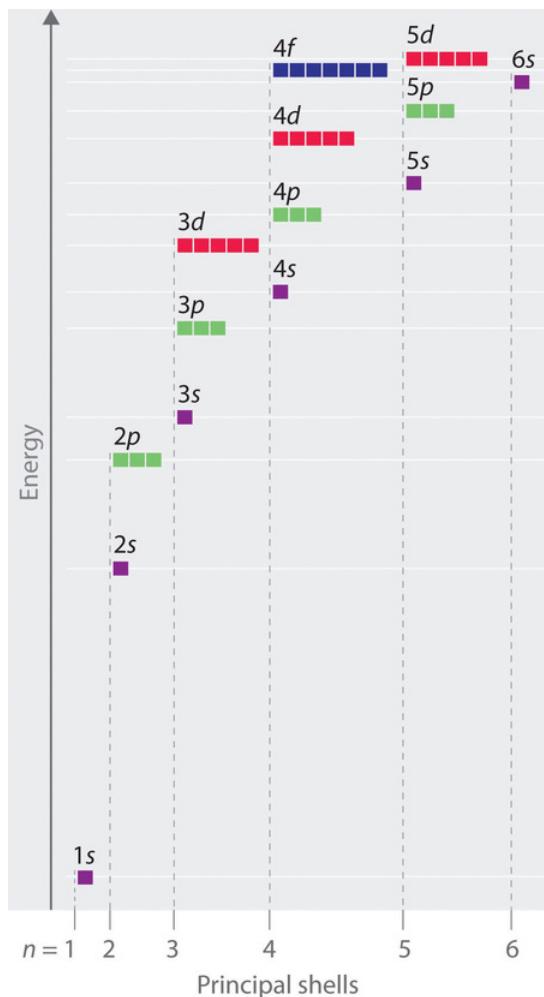


Figure 8.1.1: Orbital Energy Level Diagram for a Typical Multielectron Atom

These energy differences are caused by the effects of *shielding* and *penetration*, the extent to which a given orbital lies inside other filled orbitals. For example, an electron in the 2s orbital penetrates inside a filled 1s orbital more than an electron in a 2p orbital

does. Since electrons, all being negatively charged, repel each other, an electron closer to the nucleus partially *shields* an electron farther from the nucleus from the attractive effect of the positively charged nucleus. Hence in an atom with a filled 1s orbital, the **effective nuclear charge** (Z_{eff}) experienced by a 2s electron is greater than the Z_{eff} experienced by a 2p electron. Consequently, the 2s electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 8.1.1.

Due to electron shielding, Z_{eff} increases more rapidly going across a row of the periodic table than going down a column.

Notice in Figure 8.1.1 that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3d orbitals in most atoms is actually *between* the energies of the 4s and the 4p orbitals.

Electron Spin: The Fourth Quantum Number

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**.

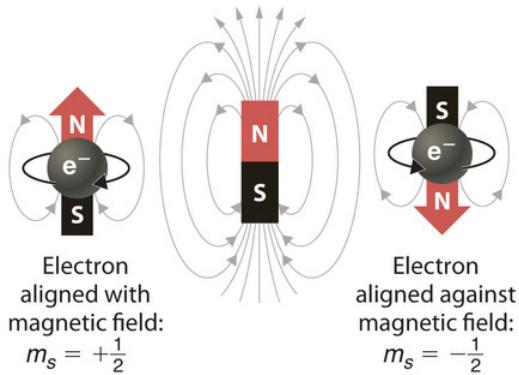


Figure 8.1.2: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure 8.1.2). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated $+1/2$ (up) and $-1/2$ (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 Pauli Exclusion Principle

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 ($+1/2$ or $-1/2$), 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 8.1.1

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

Given: orbital

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

Strategy:

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

Solution:

A For a $2p$ orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l, (-l + 1), \dots, (l - 1), l$. 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 $+\frac{1}{2}$ and $-\frac{1}{2}$, there are six possible combinations of (n , l , m_l , m_s): $(2, 1, 1, +\frac{1}{2})$, $(2, 1, 1, -\frac{1}{2})$, $(2, 1, 0, +\frac{1}{2})$, $(2, 1, 0, -\frac{1}{2})$, $(2, 1, -1, +\frac{1}{2})$, and $(2, 1, -1, -\frac{1}{2})$.

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

? Exercise 8.1.1

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

$(6, 0, 0, +\frac{1}{2}), (6, 0, 0, -\frac{1}{2})$; two electrons



Magnetic Quantum Number (m_l) & Spin Quantum Number (m_s): [Magnetic Quantum Number \(\$m_l\$ \) & Spin Quantum Number \(\$m_s\$ \)](#),
[YouTube](#)(opens in new window) [youtu.be] (opens in new window)

Summary

The arrangement of atoms in the periodic table arises from the lowest energy arrangement of electrons in the valence shell. 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 $+\frac{1}{2}$ or $-\frac{1}{2}$ 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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8.2: The Quantum-Mechanical Model and the Periodic Table

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 8.2.1, recognizing that each orbital can hold two electrons, one with spin up \uparrow , corresponding to $m_s = +\frac{1}{2}$, which is arbitrarily written first, and one with spin down \downarrow , corresponding to $m_s = -\frac{1}{2}$. A filled orbital is indicated by $\uparrow\downarrow$, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

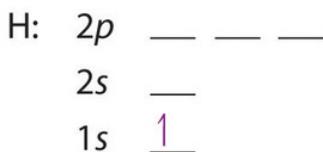
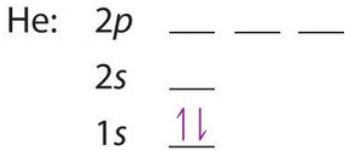


Figure 8.2.1: One electron in.

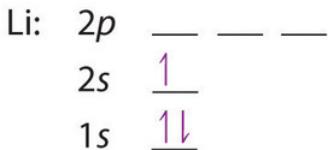
From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number n and their value of l (s , p , d , or f), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1s orbital, which is the orbital lowest in energy (Figure 8.2.1), 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



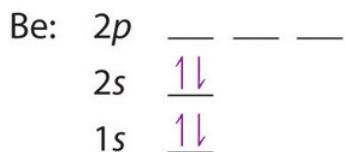
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

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; the third electron must enter a higher energy orbital. Figure 6.29 tells us that the next lowest energy orbital is 2s, so the orbital diagram for lithium is

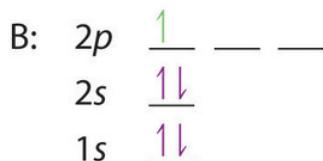


This electron configuration is written as $1s^22s^1$.

The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1s and 2s orbitals to achieve a $1s^22s^2$ electron configuration:

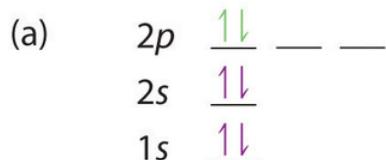


When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the $2p$ orbitals. Because all three $2p$ orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^22s^22p^1$:

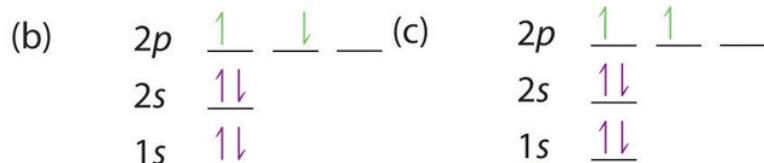


Boron has one electron pair in the $1s$ orbital, one electron pair in the $2s$ orbital, and one electron in the $2p$ orbital.

At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same $2p$ orbital that already has an electron, or should it go in one of the empty $2p$ orbitals? If it goes in an empty $2p$ 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 $2p$ orbitals are degenerate?



Three diagrams on where the sixth electron should go, a) paired with the lone electron in the $2p$ orbital, b) unpaired with the lone electron and pointing downward, and c) unpaired with the lone electron



Because of electron-electron interactions, 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 $1s^22s^22p^2$, 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

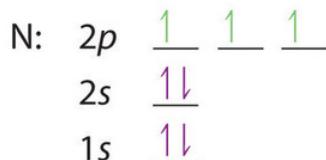
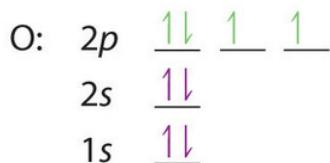


Figure 8.2.1: Copy and Paste Caption here. (Copyright; author via source)

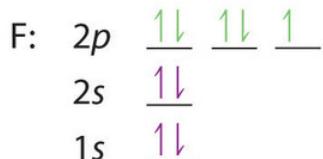
with three unpaired electrons. The electron configuration of nitrogen is thus $1s^22s^22p^3$.

At oxygen, with $Z = 8$ and eight electrons, we have no choice. One electron must be paired with another in one of the $2p$ orbitals, which gives us two unpaired electrons and a $1s^22s^22p^4$ electron configuration. Because all the $2p$ orbitals are degenerate, it doesn't matter which one has the pair of electrons.



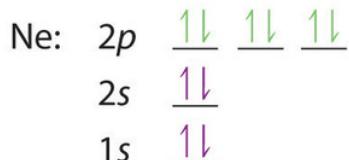
Oxygen has one electron pair in the 1 s orbital, one electron pair in the 2 s pair, and one electron pair, and 2 unpaired electrons in the 2 p orbitals.

Similarly, fluorine has the electron configuration $1s^22s^22p^5$:



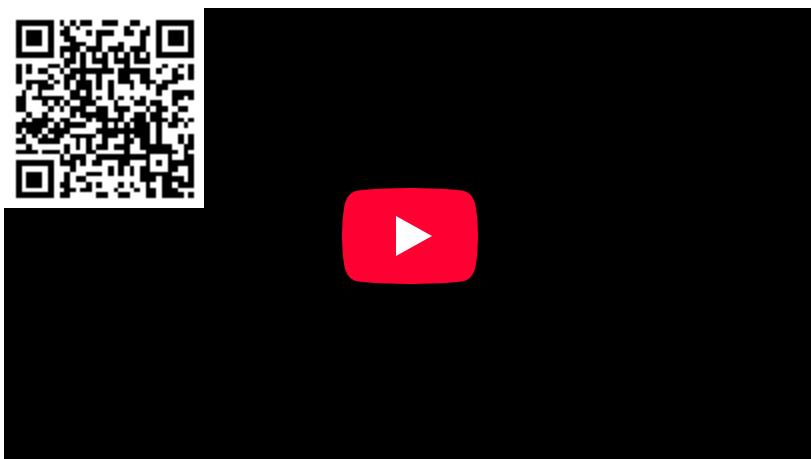
Fluorine has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and 2 electrons pairs with one unpaired electron in the 2 p orbital.

When we reach neon, with $Z = 10$, we have filled the $2p$ subshell, giving a $1s^22s^22p^6$ electron configuration:



Neon has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and 3 electron pairs in the 2 p orbital.

Notice that for neon, as for helium, all the orbitals through the $2p$ 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.



Electron Configuration of Atoms: [Electron Configuration of Atoms, YouTube](#)(opens in new window) [youtu.be]

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 $1s^22s^22p^6$ electron configuration of neon ($Z = 10$), so the electron configuration of sodium, with $Z = 11$, which is $1s^22s^22p^63s^1$, is written as $[Ne]3s^1$:

Electron Configuration of Neon and Sodium

Neon	$Z = 10$	$1s^22s^22p^6$
------	----------	----------------

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

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:

Electron Configuration of Sodium and Lithium

Sodium	$1s^2 2s^2 2p^6 3s^1 = [\text{Ne}]3s^1$
Lithium	$1s^2 2s^1 = [\text{He}]2s^1$

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 3s and 3p orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration $[\text{Ne}]3s^2 3p^6$, corresponding to a filled valence shell.

✓ Example 8.2.1: Electronic Configuration of Phosphorus

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

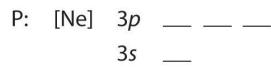
Strategy:

- 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.
- Referring to Figure 8.2.1, 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.
- Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

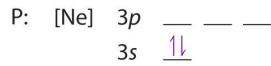
Solution:

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.

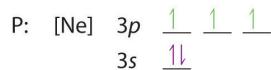
B The additional five electrons are placed in the next available orbitals, which Figure 8.2.1 tells us are the 3s and 3p orbitals:



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



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



The electron configuration is $[\text{Ne}]3s^2 3p^3$.

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 $3s^23p^3$.

? Exercise 8.2.1

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

Answer

[Ne] $3s^23p^5$; $3s^23p^5$



Definition of Valence Electrons: [Definition of Valence Electrons, YouTube](#)(opens in new window) [youtu.be]

The general order in which orbitals are filled is depicted in Figure 8.2.2. 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 $3d$ 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 $3d$ orbitals are filled by the next 10 elements, the transition metals, followed by three $4p$ orbitals. Notice that the last member of this row is the noble gas krypton ($Z = 36$), $[Ar]4s^23d^{10}4p^6 = [Kr]$, which has filled $4s$, $3d$, and $4p$ orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the $5s$, $4d$, and $5p$ orbitals are filled sequentially.

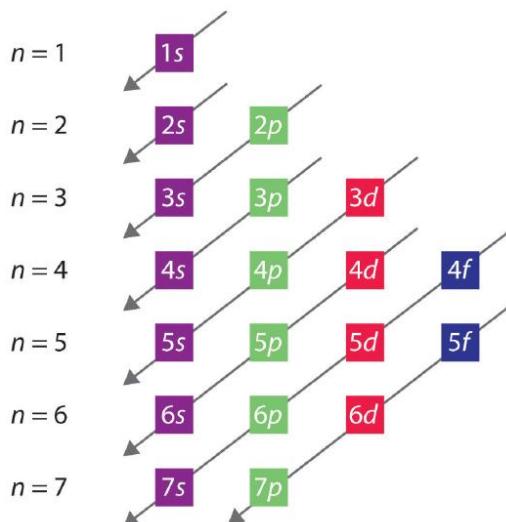


Figure 8.2.2: Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.

The sixth row of the periodic table will be different from the preceding two because the $4f$ orbitals, which can hold 14 electrons, are filled between the $6s$ and the $5d$ orbitals. The elements that contain $4f$ orbitals in their valence shell are the lanthanides. When the $6p$ orbitals are finally filled, we have reached the next noble gas, radon ($Z = 86$), $[Xe]6s^24f^{14}5d^{10}6p^6 = [Rn]$. In the last row, the $5f$ orbitals are filled between the $7s$ and the $6d$ orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

✓ Example 8.2.2: Electron Configuration of Mercury

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 8.2.1 and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

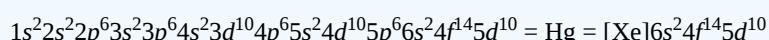
Solution:

By placing the electrons in orbitals following the order shown in Figure 8.2.2 and using the periodic table as a guide, we obtain

Solution to Example 6.8.2

$1s^2$	row 1	2 electrons
$2s^22p^6$	row 2	8 electrons
$3s^23p^6$	row 3	8 electrons
$4s^23d^{10}4p^6$	row 4	18 electrons
$5s^24d^{10}5p^6$	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 8.2.2, we need to fill the $6s$ (2 electrons), $4f$ (14 electrons), and $5d$ (10 electrons) orbitals. The result is mercury's electron configuration:



with a filled $5d$ subshell, a $6s^24f^{14}5d^{10}$ 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 8.2.2: Electron Configuration of Flerovium

Although element 114 is not stable enough to occur in nature, atoms of element 114 were created for the first time in a nuclear reactor in 1998 by a team of Russian and American scientists. The element is named after the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research in Dubna, Russia, where the element was discovered. The name of the laboratory, in turn, honors the Russian physicist Georgy Flyorov. Write the complete electron configuration for element 114.

Answer

$$s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^67s^25f^{14}6d^{10}7p^2$$

The electron configurations of the elements are presented in Figure 8.2.2, 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 8.2.1. Some of these anomalies occur as the $3d$ orbitals are filled. For example, the observed ground state electron configuration of chromium is $[Ar]4s^13d^5$ rather than the predicted $[Ar]4s^23d^4$. Similarly, the observed electron configuration of copper is $[Ar]4s^13d^{10}$ instead of $[Ar]s^23d^9$. 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. (In fact, this "special stability" is really another consequence of the *instability* caused by pairing an electron with another in the same orbital, as illustrated by Hund's rule.) 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 many additional anomalies. For example, cerium has an electron configuration of $[Xe]6s^24f^15d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

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



Electron Configuration of Transition Metals: [Electron Configuration of Transition Metals, YouTube](#)(opens in new window)
[youtu.be]

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**.

Learning Objectives

- To correlate the arrangement of atoms in the periodic table results in blocks corresponding to filling of the ns , np , nd , and nf orbitals

As you have learned, the electron configurations of the elements explain the otherwise peculiar shape of the periodic table. Although the table was originally organized on the basis of physical and chemical similarities between the elements within groups, these similarities are ultimately attributable to orbital energy levels and the Pauli principle, which cause the individual subshells to be filled in a particular order. As a result, the periodic table can be divided into “blocks” corresponding to the type of subshell that is being filled, as illustrated in Figure 8.2.1. For example, the two columns on the left, known as the *s* block, consist of elements in which the ns orbitals are being filled. The six columns on the right, elements in which the np orbitals are being filled, constitute the *p* block. In between are the 10 columns of the *d* block, elements in which the $(n - 1)d$ orbitals are filled. At the bottom lie the 14 columns of the *f* block, elements in which the $(n - 2)f$ orbitals are filled. Because two electrons can be accommodated per orbital, the number of columns in each block is the same as the maximum electron capacity of the subshell: 2 for ns , 6 for np , 10 for $(n - 1)d$, and 14 for $(n - 2)f$. Within each column, each element has the same valence electron configuration—for example, ns^1 (group 1) or ns^2np^1 (group 13). As you will see, this is reflected in important similarities in the chemical reactivity and the bonding for the elements in each column.

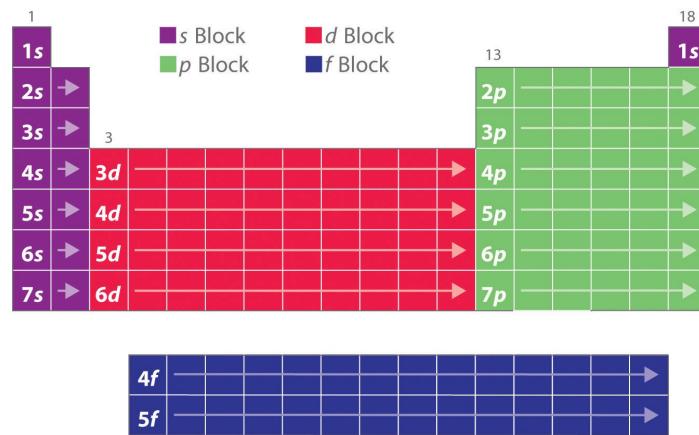


Figure 8.2.1: The Periodic Table, Showing How the Elements Are Grouped According to the Kind of Subshell (*s*, *p*, *d*, *f*) Being Filled with Electrons in the Valence Shell of Each Element. The electron configurations of the elements are in Figure 6.9.2.

Because each orbital can have a maximum of 2 electrons, there are 2 columns in the *s* block, 6 columns in the *p* block, 10 columns in the *d* block, and 14 columns in the *f* block.

Hydrogen and helium are placed somewhat arbitrarily. Although hydrogen is not an alkali metal, its $1s^1$ electron configuration suggests a similarity to lithium ($[He]2s^1$) and the other elements in the first column. Although helium, with a filled ns subshell, should be similar chemically to other elements with an ns^2 electron configuration, the closed principal shell dominates its chemistry, justifying its placement above neon on the right.

Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	$1s^1$	37	Rb	$[Kr]5s^1$	73	Ta	$[Xe]6s^24f^45d^3$
2	He	$1s^2$	38	Sr	$[Kr]5s^2$	74	W	$[Xe]6s^24f^45d^4$
3	Li	$[He]2s^1$	39	Y	$[Kr]5s^24d^1$	75	Re	$[Xe]6s^24f^45d^5$
4	Be	$[He]2s^2$	40	Zr	$[Kr]5s^24d^2$	76	Os	$[Xe]6s^24f^45d^6$
5	B	$[He]2s^22p^1$	41	Nb	$[Kr]5s^14d^4$	77	Ir	$[Xe]6s^24f^45d^7$
6	C	$[He]2s^22p^2$	42	Mo	$[Kr]5s^14d^5$	78	Pt	$[Xe]6s^14f^45d^9$
7	N	$[He]2s^22p^3$	43	Tc	$[Kr]5s^24d^5$	79	Au	$[Xe]6s^14f^45d^{10}$
8	O	$[He]2s^22p^4$	44	Ru	$[Kr]5s^14d^7$	80	Hg	$[Xe]6s^24f^45d^{10}$
9	F	$[He]2s^22p^5$	45	Rh	$[Kr]5s^14d^8$	81	Tl	$[Xe]6s^24f^45d^{10}6p^1$
10	Ne	$[He]2s^22p^6$	46	Pd	$[Kr]4d^{10}$	82	Pb	$[Xe]6s^24f^45d^{10}6p^2$
11	Na	$[Ne]3s^1$	47	Ag	$[Kr]5s^14d^{10}$	83	Bi	$[Xe]6s^24f^45d^{10}6p^3$
12	Mg	$[Ne]3s^2$	48	Cd	$[Kr]5s^24d^{10}$	84	Po	$[Xe]6s^24f^45d^{10}6p^4$
13	Al	$[Ne]3s^23p^1$	49	In	$[Kr]5s^24d^{10}5p^1$	85	At	$[Xe]6s^24f^45d^{10}6p^5$
14	Si	$[Ne]3s^23p^2$	50	Sn	$[Kr]5s^24d^{10}5p^2$	86	Rn	$[Xe]6s^24f^45d^{10}6p^6$
15	P	$[Ne]3s^23p^3$	51	Sb	$[Kr]5s^24d^{10}5p^3$	87	Fr	$[Rn]7s^1$
16	S	$[Ne]3s^23p^4$	52	Te	$[Kr]5s^24d^{10}5p^4$	88	Ra	$[Rn]7s^2$
17	Cl	$[Ne]3s^23p^5$	53	I	$[Kr]5s^24d^{10}5p^5$	89	Ac	$[Rn]7s^26d^1$
18	Ar	$[Ne]3s^23p^6$	54	Xe	$[Kr]5s^24d^{10}5p^6$	90	Th	$[Rn]7s^26d^2$
19	K	$[Ar]4s^1$	55	Cs	$[Xe]6s^1$	91	Pa	$[Rn]7s^35f^6d^1$
20	Ca	$[Ar]4s^2$	56	Ba	$[Xe]6s^2$	92	U	$[Rn]7s^35f^6d^1$
21	Sc	$[Ar]4s^23d^1$	57	La	$[Xe]6s^25d^1$	93	Np	$[Rn]7s^35f^6d^1$
22	Ti	$[Ar]4s^23d^2$	58	Ce	$[Xe]6s^24f^5d^1$	94	Pu	$[Rn]7s^25f^6$
23	V	$[Ar]4s^23d^3$	59	Pr	$[Xe]6s^24f^8$	95	Am	$[Rn]7s^25f^6$
24	Cr	$[Ar]4s^23d^5$	60	Nd	$[Xe]6s^24f^4$	96	Cm	$[Rn]7s^25f^6d^1$
25	Mn	$[Ar]4s^23d^5$	61	Pm	$[Xe]6s^24f^6$	97	Bk	$[Rn]7s^25f^6$
26	Fe	$[Ar]4s^23d^6$	62	Sm	$[Xe]6s^24f^6$	98	Cf	$[Rn]7s^25f^{10}$
27	Co	$[Ar]4s^23d^7$	63	Eu	$[Xe]6s^24f^7$	99	Es	$[Rn]7s^25f^{11}$
28	Ni	$[Ar]4s^23d^8$	64	Gd	$[Xe]6s^24f^5d^1$	100	Fm	$[Rn]7s^25f^{12}$
29	Cu	$[Ar]4s^23d^{10}$	65	Tb	$[Xe]6s^24f^9$	101	Md	$[Rn]7s^25f^{13}$
30	Zn	$[Ar]4s^23d^{10}$	66	Dy	$[Xe]6s^24f^{10}$	102	No	$[Rn]7s^25f^{14}$
31	Ga	$[Ar]4s^23d^{10}4p^1$	67	Ho	$[Xe]6s^24f^{11}$	103	Lr	$[Rn]7s^25f^46d^1$
32	Ge	$[Ar]4s^23d^{10}4p^2$	68	Er	$[Xe]6s^24f^{12}$	104	Rf	$[Rn]7s^25f^46d^2$
33	As	$[Ar]4s^23d^{10}4p^3$	69	Tm	$[Xe]6s^24f^{13}$	105	Db	$[Rn]7s^25f^46d^3$
34	Se	$[Ar]4s^23d^{10}4p^4$	70	Yb	$[Xe]6s^24f^{14}$	106	Sg	$[Rn]7s^25f^46d^4$
35	Br	$[Ar]4s^23d^{10}4p^5$	71	Lu	$[Xe]6s^24f^{14}5d^1$	107	Bh	$[Rn]7s^25f^46d^5$
36	Kr	$[Ar]4s^23d^{10}4p^6$	72	Hf	$[Xe]6s^24f^{14}5d^2$	108	Hs	$[Rn]7s^25f^46d^6$
						109	Mt	$[Rn]7s^25f^46d^7$
						110	Ds	$[Rn]7s^25f^46d^9$
						111	Rg	$[Rn]7s^25f^46d^{10}$

Figure 8.2.2: Electron Configurations of the Elements. The electron configurations of elements indicated in red are exceptions due to the added stability associated with half-filled and filled subshells. The electron configurations of the elements indicated in blue are also anomalous, but the reasons for the observed configurations are more complex. For elements after No, the electron configurations are tentative.

Example 8.2.1

Use the periodic table to predict the valence electron configuration of all the elements of group 2 (beryllium, magnesium, calcium, strontium, barium, and radium).

Given: series of elements

Asked for: valence electron configurations

Strategy:

- Identify the block in the periodic table to which the group 2 elements belong. Locate the nearest noble gas preceding each element and identify the principal quantum number of the valence shell of each element.
- Write the valence electron configuration of each element by first indicating the filled inner shells using the symbol for the nearest preceding noble gas and then listing the principal quantum number of its valence shell, its valence orbitals, and the number of valence electrons in each orbital as superscripts.

Solution:

A The group 2 elements are in the s block of the periodic table, and as group 2 elements, they all have two valence electrons. Beginning with beryllium, we see that its nearest preceding noble gas is helium and that the principal quantum number of its

valence shell is $n = 2$.

B Thus beryllium has an $[\text{He}]s^2$ electron configuration. The next element down, magnesium, is expected to have exactly the same arrangement of electrons in the $n = 3$ principal shell: $[\text{Ne}]s^2$. By extrapolation, we expect all the group 2 elements to have an ns^2 electron configuration.

?

Exercise 8.2.1

Use the periodic table to predict the characteristic valence electron configuration of the halogens in group 17.

Answer

All have an ns^2np^5 electron configuration, one electron short of a noble gas electron configuration. (Note that the heavier halogens also have filled $(n - 1)d^{10}$ subshells, as well as an $(n - 2)f^{14}$ subshell for Rn; these do not, however, affect their chemistry in any significant way.)

Summary

The arrangement of atoms in the periodic table results in blocks corresponding to filling of the ns , np , nd , and nf orbitals to produce the distinctive chemical properties of the elements in the **s block**, **p block**, **d block**, and **f block**, respectively.

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8.3: Trends in Three Atomic Properties

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; however, some atoms are larger or smaller than others, and this influences their chemistry. 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 8.3.1 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.

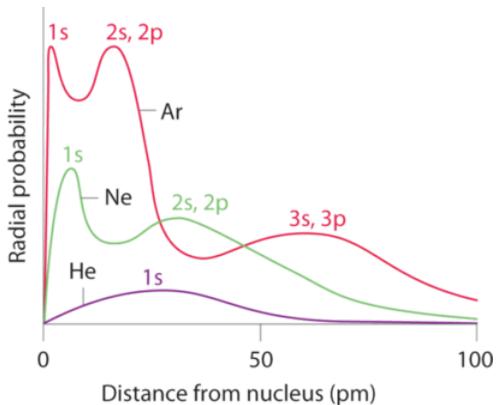


Figure 8.3.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1s electrons have a maximum radial probability at ≈ 30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈ 8 pm, and the 2s and 2p electrons combine to form another maximum 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 8.3.1 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 8.3.1 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 (Figure 8.3.2a). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1 \text{ \AA} = 1 \times 10^{-10} \text{ m} = 100 \text{ pm}$.

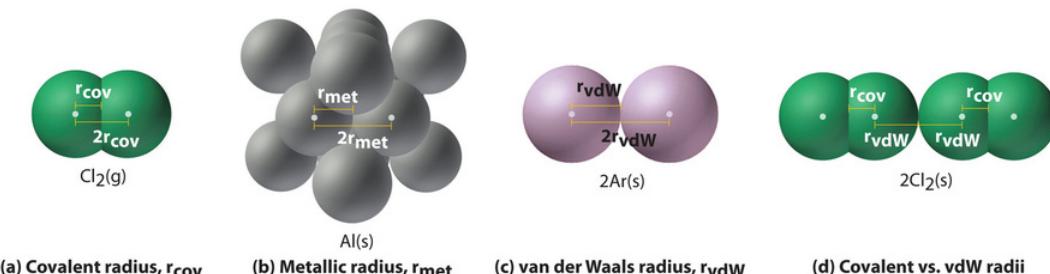


Figure 8.3.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov} , is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2 . (b) The metallic atomic radius, r_{met} , is half the distance between the nuclei of two adjacent 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 half the distance between the two chlorine atoms in a single molecule of Cl_2 . The van der Waals radius is half 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 $77 \text{ pm} + 99 \text{ pm} = 176 \text{ pm}$ 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 in the solid (Figure 8.3.2b). 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 (Figure 8.3.2c). 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, $\text{Cl}_2(\text{s})$ at low temperatures). These radii are generally not the same (Figure 8.3.2d).

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 8.3.3).

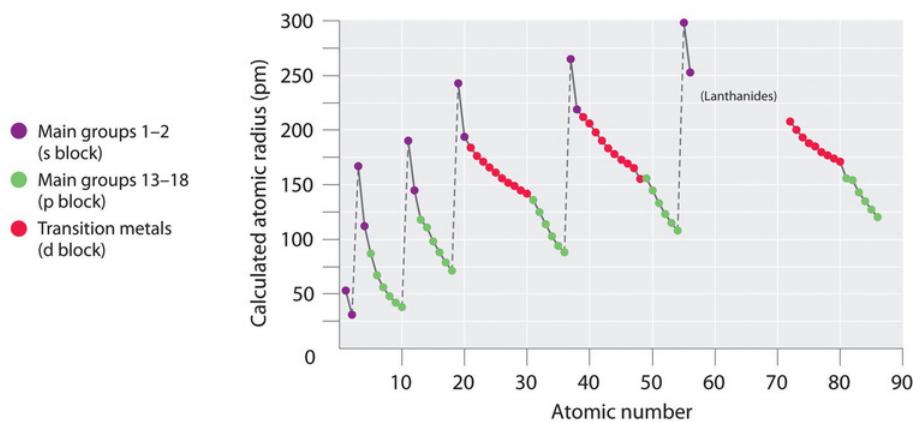


Figure 8.3.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table

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 8.3.4).

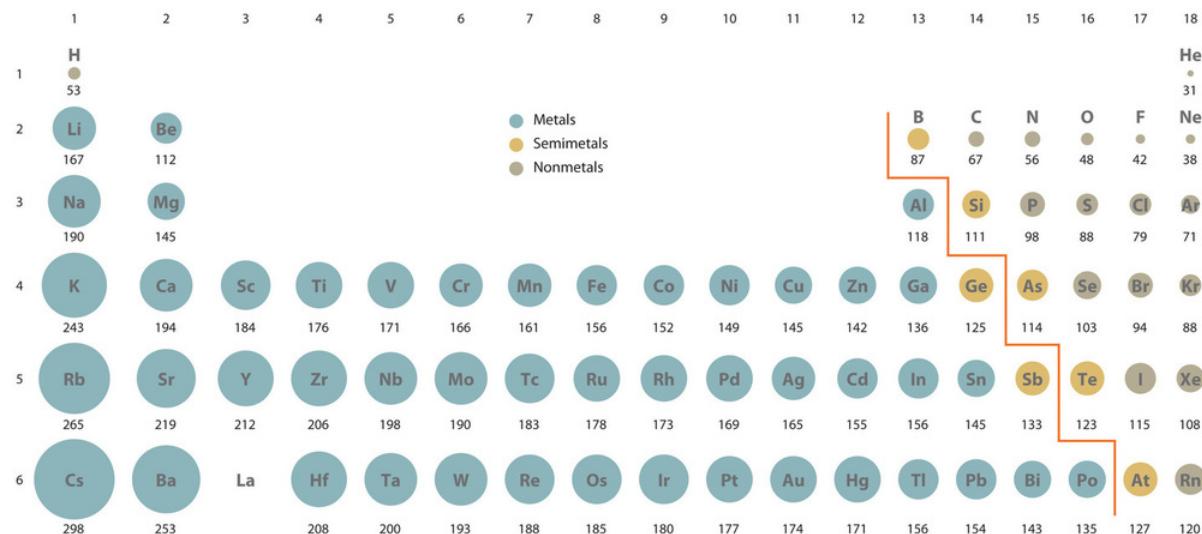


Figure 8.3.4 Calculated Atomic Radii (in Picometers) of the *s*-, *p*-, and *d*-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: [Web elements](http://www.webelements.com) [www.webelements.com]. Web Elements is an excellent online source for looking up atomic properties.

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.

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

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 2s and 2p orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2s 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 2s 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 2s 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 2s and 2p orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size (Figure 8.3.5).

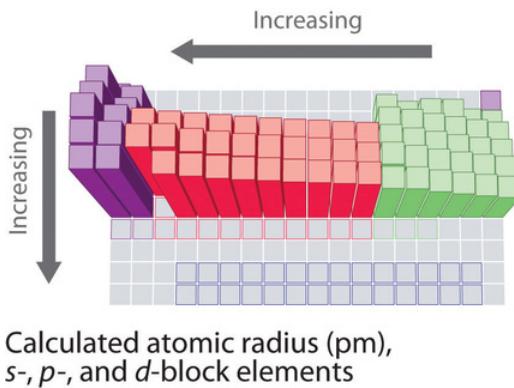


Figure 8.3.5: The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.

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 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.

💡 Not all Electrons shield equally

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 8.3.1

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:

- 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.
- 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.

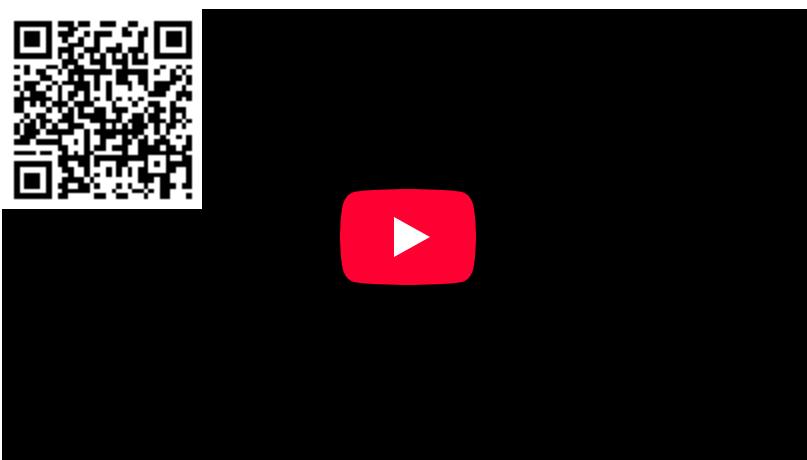
B Combining the two inequalities gives the overall order: $C < Si < Al$.

❓ Exercise 8.3.1

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

Answer

$O < S < P < K$



Atomic Radius: [Atomic Radius, YouTube](#)(opens in new window) [youtu.be]

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom to form a positive ion (cation) or when additional electrons attach themselves to neutral atoms to form a negative one (anion). 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.

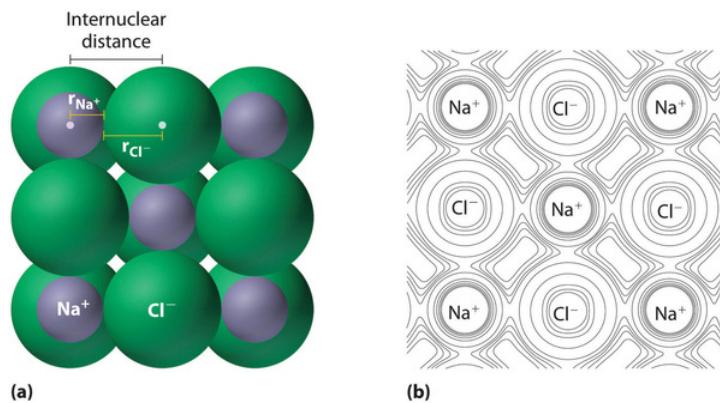


Figure 8.3.6: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for 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^+ .

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charged 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 8.3.6, 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.

A comparison of ionic radii with atomic radii (Figure 8.3.7) shows that *a 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 are 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 and the ion shrinks (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 and the ion expands (compare F at 42 pm with F^- at 133 pm).

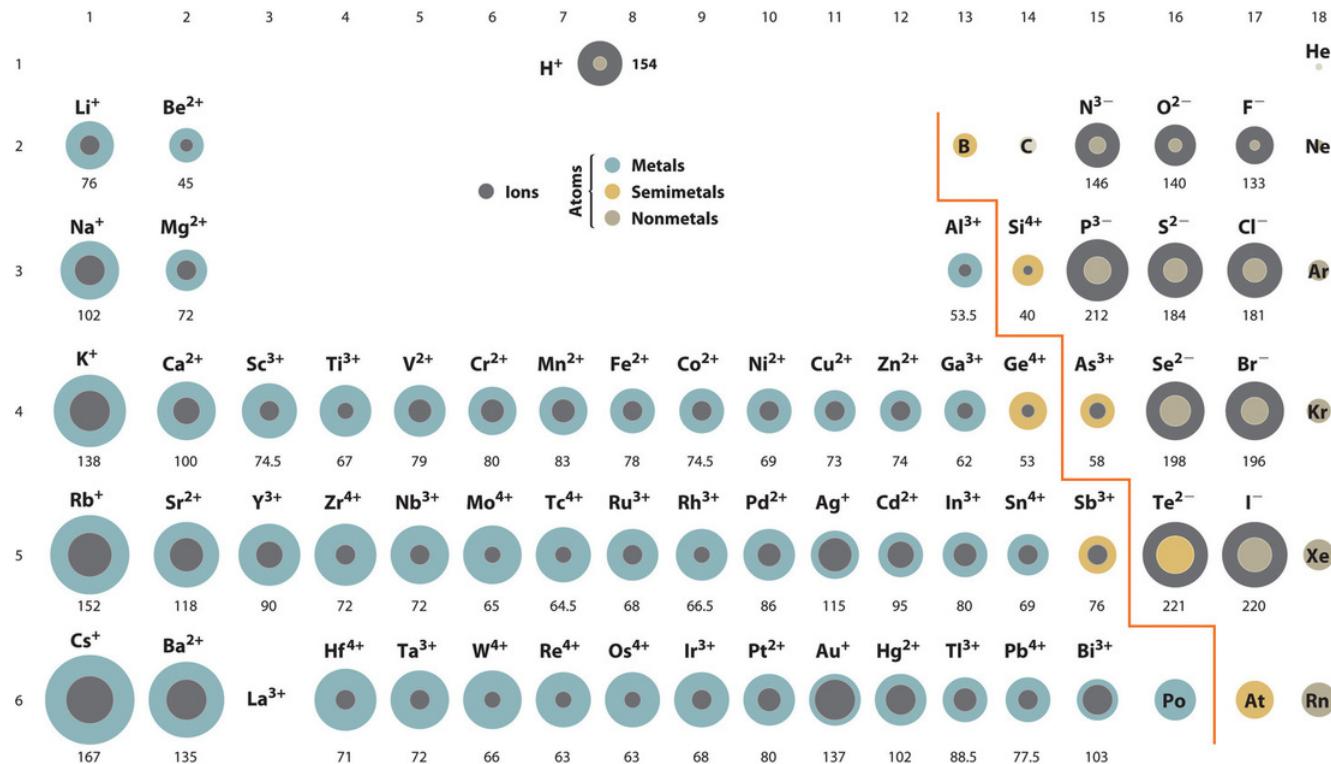


Figure 8.3.7: Ionic Radii (in Picometers) of the Most Common Ionic States of the s-, p-, and d-Block Elements. Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms. Source: Ionic radius data from R. D. Shannon, “Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides,” *Acta Crystallographica* 32, no. 5 (1976): 751–767.

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 8.3.1. 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.

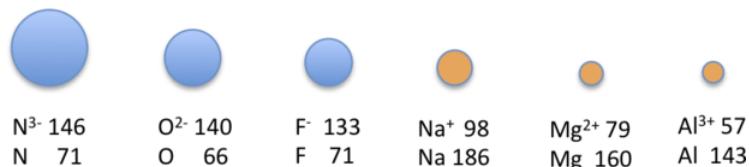
Table 8.3.1: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	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 ($1s^22s^22p^6$) is shown in Table 8.3.3.



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 8.3.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table 8.3.3: 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 8.3.2

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:

- 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.
- 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 8.3.2

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br⁻, Ca²⁺, Rb⁺, and Sr²⁺.

Answer



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)

Learning Objectives

- To master the concept of electron affinity as a measure of the energy required to add 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 or ion:



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 (Figure 8.3.1).

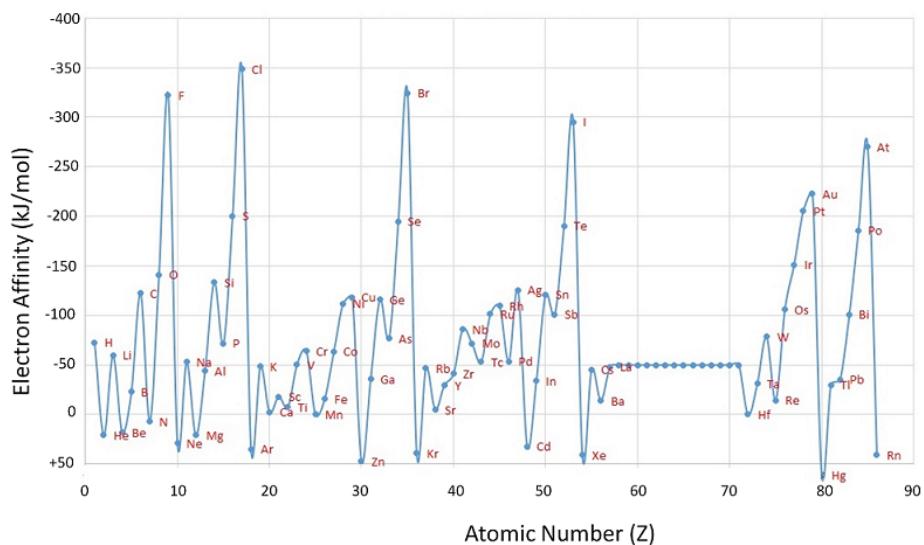
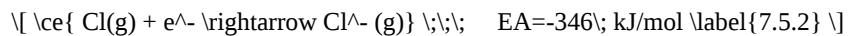


Figure 8.3.1: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies).

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:



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



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:



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

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.

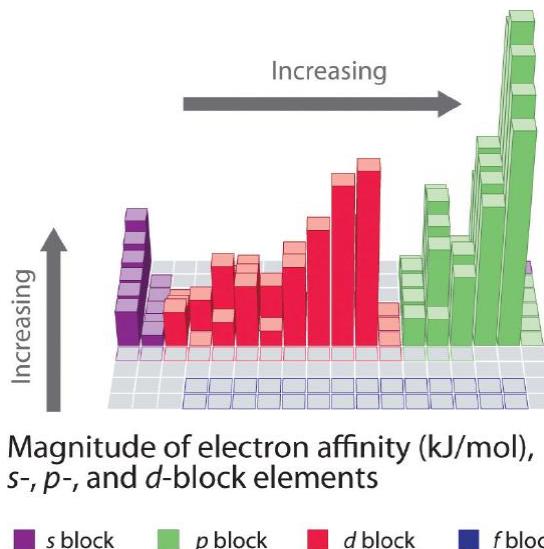


Figure 8.3.2: Electron Affinities (in kJ/mol) of the s-, p-, and d-Block Elements.

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electron affinity increases from left to right and bottom to top.

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 $2p$ 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.

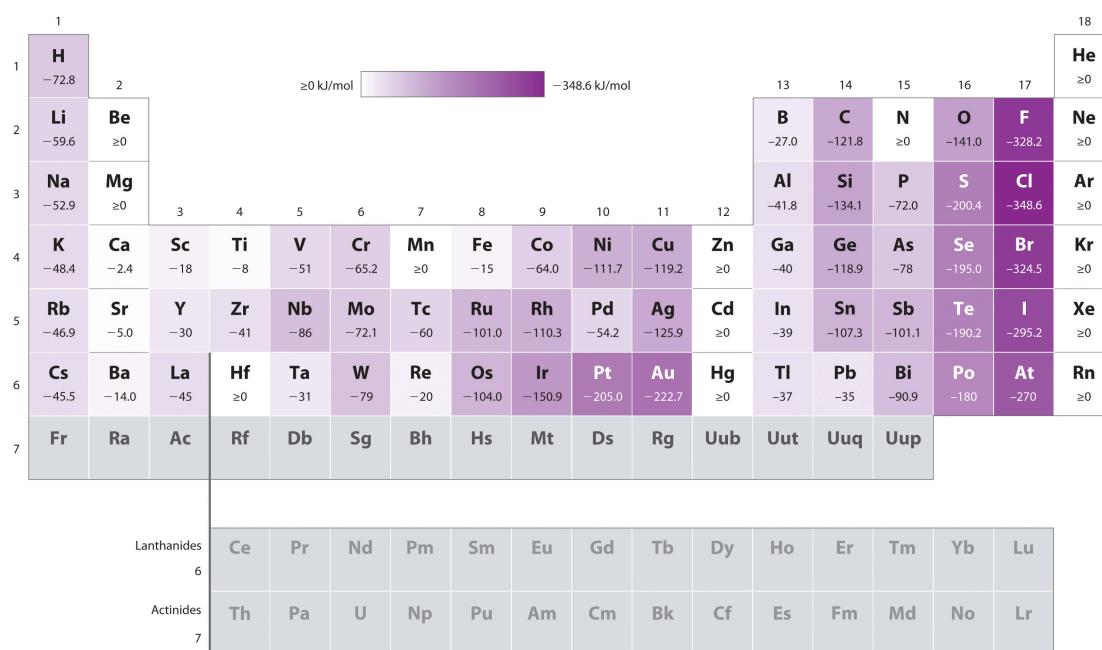
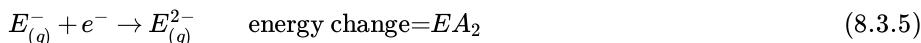
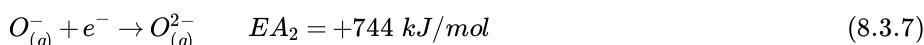
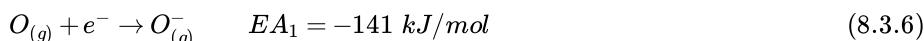


Figure 8.3.3: There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from *Journal of Physical and Chemical Reference Data* 28, no. 6 (1999).

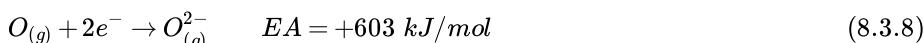
The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:



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 $+744 \text{ kJ/mol}$:



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



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

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



Electron Affinity: [Electron Affinity, YouTube](#)(opens in new window) [youtu.be] (opens in new window)

If energy is required to form both positively charged cations 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 8.3.1: 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:

- 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.
- 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 8.3.1: 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

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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8.4: Atomic Properties and Chemical Reactivity

Learning Objectives

- To understand the basic properties separating Metals from Nonmetals and Metalloids

An element is the simplest form of matter that cannot be split into simpler substances or built from simpler substances by any ordinary chemical or physical method. There are 118 elements known to us, out of which 92 are naturally occurring, while the rest have been prepared artificially. Elements are further classified into metals, non-metals, and metalloids based on their properties, which are correlated with their placement in the periodic table.

Table 8.4.1: Characteristic properties of metallic and non-metallic elements:

Metallic Elements	Nonmetallic elements
Distinguishing luster (shine)	Non-lustrous, various colors
Malleable and ductile (flexible) as solids	Brittle, hard or soft
Conduct heat and electricity	Poor conductors
Metallic oxides are basic, ionic	Nonmetallic oxides are acidic, covalent
Form cations in aqueous solution	Form anions, oxyanions in aqueous solution

Metals

With the exception of hydrogen, all elements that form positive ions by losing electrons during chemical reactions are called metals. Thus metals are electropositive elements with relatively low ionization energies. They are characterized by bright luster, hardness, ability to resonate sound and are excellent conductors of heat and electricity. Metals are solids under normal conditions except for Mercury.

Physical Properties of Metals

Metals are lustrous, malleable, ductile, good conductors of heat and electricity. Other properties include:

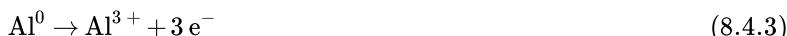
- State:** Metals are solids at room temperature with the exception of mercury, which is liquid at room temperature (Gallium is liquid on hot days).
- Luster:** Metals have the quality of reflecting light from their surface and can be polished e.g., gold, silver and copper.
- Malleability:** Metals have the ability to withstand hammering and can be made into thin sheets known as foils. For example, a sugar cube sized chunk of gold can be pounded into a thin sheet that will cover a football field.
- Ductility:** Metals can be drawn into wires. For example, 100 g of silver can be drawn into a thin wire about 200 meters long.
- Hardness:** All metals are hard except sodium and potassium, which are soft and can be cut with a knife.
- Valency:** Metals typically have 1 to 3 electrons in the outermost shell of their atoms.
- Conduction:** Metals are good conductors because they have free electrons. Silver and copper are the two best conductors of heat and electricity. Lead is the poorest conductor of heat. Bismuth, mercury and iron are also poor conductors
- Density:** Metals have high density and are very heavy. Iridium and osmium have the highest densities whereas lithium has the lowest density.
- Melting and Boiling Points:** Metals have high melting and boiling points. Tungsten has the highest melting and boiling points whereas mercury has the lowest. Sodium and potassium also have low melting points.

Chemical Properties of Metals

Metals are electropositive elements that generally form *basic* or *amphoteric* oxides with oxygen. Other chemical properties include:

- Electropositive Character:** Metals tend to have low ionization energies, and *typically lose electrons (i.e. are oxidized) when they undergo chemical reactions*. They normally do not accept electrons. For example:
 - Alkali metals are always 1^+ (lose the electron in s subshell)
 - Alkaline earth metals are always 2^+ (lose both electrons in s subshell)

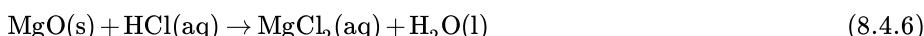
- Transition metal ions do not follow an obvious pattern, 2^+ is common (lose both electrons in s subshell), and 1^+ and 3^+ are also observed



Compounds of metals with non-metals tend to be **ionic** in nature. Most metal oxides are basic oxides and dissolve in water to form **metal hydroxides**:



Metal oxides exhibit their **basic** chemical nature by reacting with **acids** to form metal **salts** and water:



✓ Example 8.4.1

What is the chemical formula for aluminum oxide?

Solution

Al has a 3+ charge, the oxide ion is O^{2-} , thus Al_2O_3 .

✓ Example 8.4.2

Would you expect it to be solid, liquid or gas at room temperature?

Solutions

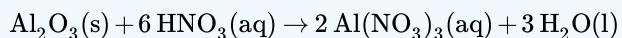
Oxides of metals are characteristically solid at room temperature

✓ Example 8.4.3

Write the balanced chemical equation for the reaction of aluminum oxide with nitric acid:

Solution

Metal oxide + acid → salt + water



Nonmetals

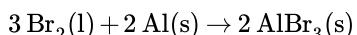
Elements that tend to gain electrons to form anions during chemical reactions are called non-metals. These are electronegative elements with high ionization energies. They are non-lustrous, brittle and poor conductors of heat and electricity (except graphite). Non-metals can be gases, liquids or solids.

Physical Properties of Nonmetals

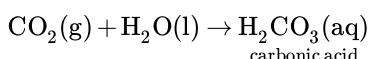
- Physical State:** Most of the non-metals exist in two of the three states of matter at room temperature: gases (oxygen) and solids (carbon). Only bromine exists as a liquid at room temperature.
- Non-Malleable and Ductile:** Non-metals are very brittle, and cannot be rolled into wires or pounded into sheets.
- Conduction:** They are poor conductors of heat and electricity.
- Luster:** These have no metallic luster and do not reflect light.
- Melting and Boiling Points:** The melting points of non-metals are *generally* lower than metals, but are highly variable.
- Seven non-metals exist under standard conditions as *diatomic molecules*: $\text{H}_2(g)$, $\text{N}_2(g)$, $\text{O}_2(g)$, $\text{F}_2(g)$, $\text{Cl}_2(g)$, $\text{Br}_2(l)$, $\text{I}_2(s)$.

Chemical Properties of Nonmetals

Non-metals have a tendency to gain or share electrons with other atoms. They are electronegative in character. Nonmetals, when reacting with metals, tend to gain electrons (typically *attaining noble gas electron configuration*) and become **anions**:

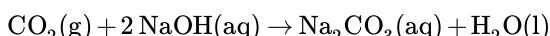


Compounds composed entirely of nonmetals are covalent substances. They generally form acidic or neutral oxides with oxygen that dissolve in water to form acids:



As you may know, carbonated water is slightly acidic (carbonic acid).

Nonmetal oxides can combine with bases to form salts.



Metalloids

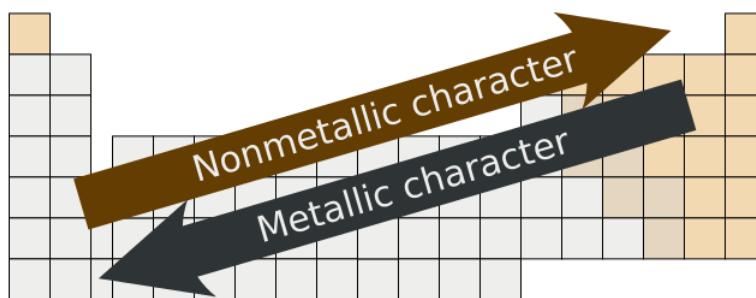
Metalloids have properties intermediate between the metals and nonmetals. Metalloids are useful in the semiconductor industry. Metalloids are all solid at room temperature. They can form alloys with other metals. Some metalloids, such as silicon and germanium, can act as electrical conductors under the right conditions, thus they are called semiconductors. Silicon for example appears lustrous, but is *not* malleable nor ductile (it is *brittle* - a characteristic of some nonmetals). It is a much poorer conductor of heat and electricity than the metals. The physical properties of metalloids tend to be metallic, but their chemical properties tend to be non-metallic. The oxidation number of an element in this group can range from +5 to -2, depending on the group in which it is located.

Table 8.4.2: Elements categorized into metals, non-metals and metalloids.

Metals	Non-metals	Metalloids
Gold	Oxygen	Silicon
Silver	Carbon	Boron
Copper	Hydrogen	Arsenic
Iron	Nitrogen	Antimony
Mercury	Sulfur	Germanium
Zinc	Phosphorus	

Trends in Metallic and Nonmetallic Character

Metallic character is strongest for the elements in the leftmost part of the periodic table, and tends to decrease as we move to the right in any period (nonmetallic character increases with increasing electronegativity and ionization energy values). Within any group of elements (columns), the metallic character increases from top to bottom (the electronegativity and ionization energy values generally decrease as we move down a group). This general trend is not necessarily observed with the transition metals.



Non metallic character increases bottom to top and left to right with the most nonmetal element in the top right corner. metallic character shows the opposite trend with the most metallic element being in the bottom left.

Contributors and Attributions

- Mike Blaber (Florida State University)
- Binod Shrestha (University of Lorraine)

The elements within the same group of the periodic table tend to exhibit similar physical and chemical properties. Four major factors affect reactivity of metals: nuclear charge, atomic radius, shielding effect and sublevel arrangement (of electrons). Metal reactivity relates to ability to lose electrons (oxidize), form basic hydroxides, form ionic compounds with non-metals. In general, the bigger the atom, the greater the ability to lose electrons. The greater the shielding, the greater the ability to lose electrons. Therefore, metallic character increases going down the table, and decreases going across -- so the most active metal is towards the left and down.

Group 1: The Alkali Metals

The word "alkali" is derived from an Arabic word meaning "ashes". Many sodium and potassium compounds were isolated from wood ashes (Na_2CO_3 and K_2CO_3 are still occasionally referred to as "soda ash" and "potash"). In the alkali group, as we go down the group we have elements Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs) and Francium (Fr). Several physical properties of these elements are compared in Table 8.4.1. These elements have all only one electron in their outermost shells. All the elements show metallic properties and have valence +1, hence they give up electron easily.

Table 8.4.1: General Properties of Group I Metals

Element	Electronic Configuration	Melting Point (°C)	Density (g/cm³)	Atomic Radius	Ionization Energy (kJ/mol)
Lithium	[He]2s ¹	181	0.53	1.52	520
Sodium	[Ne]3s ¹	98	0.97	1.86	496
Potassium	[Ar]4s ¹	63	0.86	2.27	419
Rubidium	[Kr]5s ¹	39	1.53	2.47	403
Cesium	[Xe]6s ¹	28	1.88	2.65	376

As we move down the group (from Li to Fr), the following trends are observed (Table 8.4.1):

- All have a single electron in an 's' valence orbital
- The melting point decreases
- The density increases
- The atomic radius increases
- The ionization energy decreases (first ionization energy)

The alkali metals have the lowest I_1 values of the elements

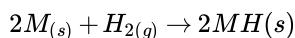
This represents the relative ease with which the lone electron in the outer 's' orbital can be removed.

The alkali metals are very reactive, readily losing 1 electron to form an ion with a 1+ charge:



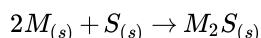
Due to this reactivity, the alkali metals are found in nature only as compounds. The alkali metals combine directly with most nonmetals:

- React with hydrogen to form solid *hydrides*

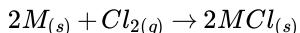


(Note: hydrogen is present in the metal hydride as the **hydride** H^- ion)

- React with sulfur to form solid *sulfides*



React with chlorine to form solid *chlorides*



Alkali metals react with water to produce hydrogen gas and alkali metal hydroxides; this is a very exothermic reaction (Figure 8.4.1).

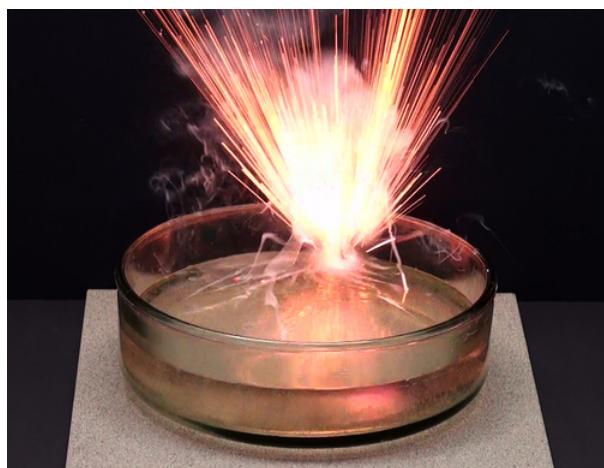
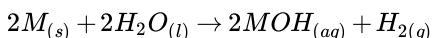
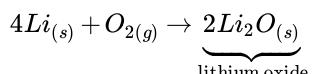


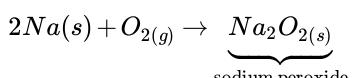
Figure 8.4.1: A small piece of potassium metal explodes as it reacts with water. (CC SA-BY 3.0; Tavoromann)

The reaction between alkali metals and oxygen is more complex:

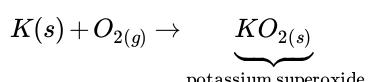
- A common reaction is to form metal oxides which contain the O^{2-} ion



Other alkali metals **can** form metal peroxides (contains O_2^{2-} ion)



K, Rb and Cs **can** also form superoxides (O_2^- ion)



💡 Colors via Absorption

The color of a chemical is produced when a valence electron in an atom is excited from one energy level to another by visible radiation. In this case, the particular frequency of light that excites the electron is **absorbed**. Thus, the remaining light that you see is white light devoid of one or more wavelengths (thus appearing colored). Alkali metals, having lost their outermost electrons, have no electrons that can be excited by visible radiation. Alkali metal salts and their aqueous solution are colorless unless they contain a colored anion.

💡 Colors via Emission

When alkali metals are placed in a flame the ions are reduced (gain an electron) in the lower part of the flame. The electron is excited (jumps to a higher orbital) by the high temperature of the flame. When the excited electron falls back down to a lower orbital a photon is released. The transition of the valence electron of sodium from the 3p down to the 3s subshell results in release of a photon with a wavelength of 589 nm (yellow)

Flame colors:

- Lithium: crimson red
- Sodium: yellow
- Potassium: lilac

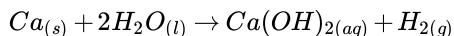
Group 2: The Alkaline Earth Metals

Compared with the alkali metals, the alkaline earth metals are typically harder, more dense, melt at a higher temperature. The first ionization energies (I_1) of the alkaline earth metals are not as low as the alkali metals. The alkaline earth metals are therefore less reactive than the alkali metals (Be and Mg are the least reactive of the alkaline earth metals). Several physical properties of these elements are compared in Table 8.4.2.

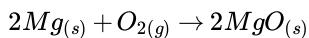
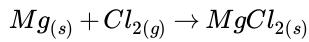
Table 8.4.2: General Properties of Group 2 Metals

Element	Electronic Configuration	Melting Point (°C)	Density (g/cm³)	Atomic Radius	Ionization Energy (kJ/mol)
Beryllium	[He]2s ²	1278	1.85	1.52	899
Magnesium	[Ne]3s ²	649	1.74	1.60	738
Calcium	[Ar]4s ²	839	1.54	1.97	590
Strontium	[Kr]5s ²	769	2.54	2.15	549
Barium	[Xe]6s ²	725	3.51	2.17	503

Calcium, and elements below it, react readily with water at room temperature:



The tendency of the alkaline earths to lose their two valence electrons is demonstrated in the reactivity of Mg towards chlorine gas and oxygen:



The 2+ ions of the alkaline earth metals have a noble gas like electron configuration and are thus form colorless or white compounds (unless the anion is itself colored). Flame colors:

- Calcium: brick red
- Strontium: crimson red
- Barium: green

Contributors and Attributions

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Learning Objectives

- To gain a descriptive understanding of the chemical properties of Hydrogen, the group 16, 17 and 18 elements.

Non-metallic character is the ability to be reduced (be an oxidizing agent), form acidic hydroxides, form covalent compounds with non-metals. These characteristics increase with a larger nuclear charge and smaller radius, with no increase in shielding. The most active non-metal would be the one farthest up and to the right -- not including the noble gases (non-reactive.)

Hydrogen

Hydrogen has a 1s¹ electron configuration and is placed above the alkali metal group. Hydrogen is a **non-metal**, which occurs as a **gas** (H₂) under normal conditions.

- Its ionization energy is considerably higher (due to lack of shielding, and thus higher Z_{eff}) than the rest of the Group 1 metals and is more like the **nonmetals**

- Hydrogen generally reacts with other nonmetals to form molecular compounds (typically highly exothermic)
- Hydrogen reacts with active metals to form metal hydrides which contain the **H^- hydride ion**:



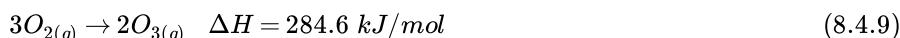
- Hydrogen can also lose an electron to yield the aqueous $H_{(aq)}^+$ hydronium ion.

Group 16: The Oxygen Family

As we proceed down group 16 the elements become more metallic in nature:

- Oxygen is a gas, the rest are solids
- Oxygen, sulfur and selenium are nonmetals
- Tellurium is a metalloid with some metal properties
- Polonium is a metal

Oxygen can be found in two molecular forms, O_2 and O_3 (ozone). These two forms of oxygen are called **allotropes** (*different forms of the same element in the same state*)



the reaction is endothermic, thus ozone is less stable than O_2

Oxygen has a great tendency to attract electrons from other elements (i.e. to "oxidize" them)

- Oxygen in combination with metals is almost always present as the O^{2-} ion (which has noble gas electronic configuration and is particularly stable)
- Two other oxygen anions are observed: **peroxide (O_2^{2-}) and superoxide (O_2^-)**

Sulfur

Sulfur also exists in several allotropic forms, the most common stable allotrope is the yellow solid S_8 (an 8 member ring of sulfur atoms). Like oxygen, **sulfur has a tendency to gain electrons** from other elements, and to form **sulfides** (which contain the S^{2-} ion). This is particular true for the active metals:



Note: most sulfur in nature is present as a metal-sulfur compound. Sulfur chemistry is more complex than that of oxygen.

Group 17: The Halogens

"Halogens" is derived from the Greek meaning "salt formers"

- Astatine is radioactive and rare, and some of its properties are unknown
- All the halogens are **nonmetals**
- Each element consists of diatomic molecules under standard conditions

Colors of diatomic halogens: (not flame colors)

- Fluorine: pale yellow
- Chlorine: yellow green
- Bromine: reddish brown
- Iodine: violet vapor

The halogens have some of the most negative electron affinities (i.e. large exothermic process in gaining an electron from another element)



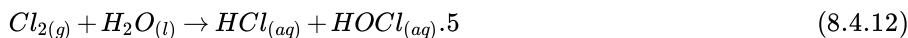
- Fluorine and chlorine are the most reactive halogens (highest electron affinities). Fluorine will remove electrons from almost any substance (including several of the noble gases from Group 18).

Note

The chemistry of the halogens is dominated by their tendency to gain electrons from other elements (forming a halide ion)

In 1992, **22.3 billion pounds** of chlorine was produced. Both chlorine and sodium can be produced by electrolysis of molten sodium chloride (table salt). The electricity is used to strip electrons from chloride ions and transfer them to sodium ions to produce chlorine gas and solid sodium metal

Chlorine reacts slowly with water to produce hydrochloric acid and hypochlorous acid:



Hypochlorous acid is a disinfectant, thus chlorine is a useful addition to swimming pool water

The halogens react with most metals to form ionic halides:



Group 18: The Noble Gases

- Nonmetals
- Gases at room temperature
- monoatomic
- completely filled 's' and 'p' subshells
- large first ionization energy, **but this decreases somewhat as we move down the group**

Rn is highly radioactive and some of its properties are unknown

They are exceptionally unreactive. It was reasoned that if any of these were reactive, they would most likely be Rn, Xe or Kr where the first ionization energies were lower.

Note

In order to react, they would have to be combined with an element which had a high tendency to remove electrons from other atoms. Such as fluorine.

Compounds of noble gases to date:



only one compound with Kr has been made



No compounds observed with He, Ne, or Ar; they are truly inert gases.

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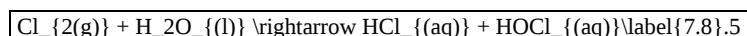
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- Mike Blaber (Florida State University)

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8.E: Electron Configuration and Chemical Periodicity (Exercises)

7.1: Development of the Periodic Table

Conceptual Problems

- Johannes Dobereiner is credited with developing the concept of chemical triads. Which of the group 15 elements would you expect to compose a triad? Would you expect B, Al, and Ga to act as a triad? Justify your answers.
- Despite the fact that Dobereiner, Newlands, Meyer, and Mendeleev all contributed to the development of the modern periodic table, Mendeleev is credited with its origin. Why was Mendeleev's periodic table accepted so rapidly?
- How did Moseley's contribution to the development of the periodic table explain the location of the noble gases?
- The *eka-* naming scheme devised by Mendeleev was used to describe undiscovered elements.
 - Use this naming method to predict the atomic number of *eka*-mercury, *eka*-astatine, *eka*-thallium, and *eka*-hafnium.
 - Using the *eka*-prefix, identify the elements with these atomic numbers: 79, 40, 51, 117, and 121.

Numerical Problem

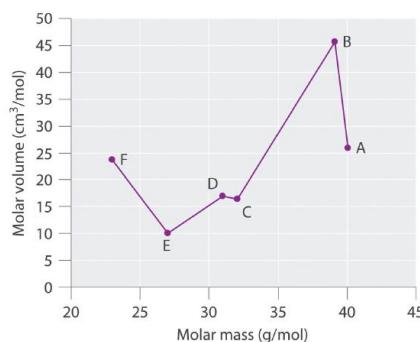
- Based on the data given, complete the table.

Species	Molar Mass (g/mol)	Density (g/cm ³)	Molar Volume (cm ³ /mol)
A	40.078		25.85
B	39.09	0.856	
C	32.065		16.35
D		1.823	16.98
E	26.98		9.992
F	22.98	0.968	

Plot molar volume versus molar mass for these substances. According to Meyer, which would be considered metals and which would be considered nonmetals?

Numerical Answer

Species	Molar Mass (g/mol)	Density (g/cm ³)	Molar Volume (cm ³ /mol)
A	40.078	1.550	25.85
B	39.09	0.856	45.67
C	32.065	1.961	16.35
D	30.95	1.823	16.98
E	26.98	2.700	9.992
F	22.98	0.968	23.7



2. Meyer found that the alkali metals had the highest molar volumes, and that molar volumes decreased steadily with increasing atomic mass, then leveled off, and finally rose again. The elements located on the rising portion of a plot of molar volume versus molar mass were typically nonmetals. If we look at the plot of the data in the table, we can immediately identify those elements with the largest molar volumes (A, B, F) as metals located on the left side of the periodic table. The element with the smallest molar volume (E) is aluminum. The plot shows that the subsequent elements (C, D) have molar volumes that are larger than that of E, but smaller than those of A and B. Thus, C and D are most likely to be nonmetals (which is the case: C = sulfur, D = phosphorus).

7.2: Effective Nuclear Charge

Conceptual Problems

1. What happens to the energy of a given orbital as the nuclear charge Z of a species increases? In a multielectron atom and for a given nuclear charge, the Z_{eff} experienced by an electron depends on its value of l . Why?
2. The electron density of a particular atom is divided into two general regions. Name these two regions and describe what each represents.
3. As the principal quantum number increases, the energy difference between successive energy levels decreases. Why? What would happen to the electron configurations of the transition metals if this decrease did not occur?
4. Describe the relationship between electron shielding and Z_{eff} on the outermost electrons of an atom. Predict how chemical reactivity is affected by a decreased effective nuclear charge.
5. If a given atom or ion has a single electron in each of the following subshells, which electron is easier to remove?
 - 2s, 3s
 - 3p, 4d
 - 2p, 1s
 - 3d, 4s

7.3: Sizes of Atoms and Ions

Conceptual Problems

1. The electrons of the 1s shell have a stronger electrostatic attraction to the nucleus than electrons in the 2s shell. Give two reasons for this.
2. Predict whether Na or Cl has the more stable $1s^2$ shell and explain your rationale.
3. Arrange K, F, Ba, Pb, B, and I in order of decreasing atomic radius.
4. Arrange Ag, Pt, Mg, C, Cu, and Si in order of increasing atomic radius.
5. Using the periodic table, arrange Li, Ga, Ba, Cl, and Ni in order of increasing atomic radius.
6. Element M is a metal that forms compounds of the type MX_2 , MX_3 , and MX_4 , where X is a halogen. What is the expected trend in the ionic radius of M in these compounds? Arrange these compounds in order of decreasing ionic radius of M.
7. The atomic radii of Na and Cl are 190 and 79 pm, respectively, but the distance between sodium and chlorine in NaCl is 282 pm. Explain this discrepancy.
8. Are shielding effects on the atomic radius more pronounced across a row or down a group? Why?
9. What two factors influence the size of an ion relative to the size of its parent atom? Would you expect the ionic radius of S^{2-} to be the same in both MgS and Na_2S ? Why or why not?
10. Arrange Br^- , Al^{3+} , Sr^{2+} , F^- , O^{2-} , and I^- in order of increasing ionic radius.
11. Arrange P^{3-} , N^{3-} , Cl^- , In^{3+} , and S^{2-} in order of decreasing ionic radius.
12. How is an isoelectronic series different from a series of ions with the same charge? Do the cations in magnesium, strontium, and potassium sulfate form an isoelectronic series? Why or why not?
13. What isoelectronic series arises from fluorine, nitrogen, magnesium, and carbon? Arrange the ions in this series by

1. increasing nuclear charge.
 2. increasing size.
14. What would be the charge and electron configuration of an ion formed from calcium that is isoelectronic with
1. a chloride ion?
 2. Ar^+ ?

Conceptual Answers

1. The 1s shell is closer to the nucleus and therefore experiences a greater electrostatic attraction. In addition, the electrons in the 2s subshell are shielded by the filled 1s² shell, which further decreases the electrostatic attraction to the nucleus.
- 2.
3. $\text{Ba} > \text{K} > \text{Pb} > \text{I} > \text{B} > \text{F}$
- 4.
- 5.
- 6.
7. The sum of the calculated atomic radii of sodium and chlorine *atoms* is 253 pm. The sodium cation is significantly smaller than a neutral sodium atom (102 versus 154 pm), due to the loss of the single electron in the 3s orbital. Conversely, the chloride ion is much larger than a neutral chlorine atom (181 versus 99 pm), because the added electron results in greatly increased electron-electron repulsions within the filled $n = 3$ principal shell. Thus, transferring an electron from sodium to chlorine decreases the radius of sodium by about 50%, but causes the radius of chlorine to almost double. The net effect is that the distance between a sodium ion and a chloride ion in NaCl is *greater* than the sum of the atomic radii of the neutral atoms.

Numerical Problems

1. Plot the ionic charge versus ionic radius using the following data for Mo: Mo³⁺, 69 pm; Mo⁴⁺, 65 pm; and Mo⁵⁺, 61 pm. Then use this plot to predict the ionic radius of Mo⁶⁺. Is the observed trend consistent with the general trends discussed in the chapter? Why or why not?
2. Internuclear distances for selected ionic compounds are given in the following table.

1. If the ionic radius of Li⁺ is 76 pm, what is the ionic radius of each of the anions?

	LiF	LiCl	LiBr	LiI
Distance (pm)	209	257	272	296

- What is the ionic radius of Na⁺?

	NaF	NaCl	NaBr	NaI
Distance (pm)	235	282	298	322

- Arrange the gaseous species Mg²⁺, P³⁻, Br⁻, S²⁻, F⁻, and N³⁻ in order of increasing radius and justify your decisions.

7.4: Ionization Energy

Conceptual Problems

1. Identify each statement as either true or false and explain your reasoning.
 - a. Ionization energies increase with atomic radius.
 - b. Ionization energies decrease down a group.
 - c. Ionization energies increase with an increase in the magnitude of the electron affinity.
 - d. Ionization energies decrease diagonally across the periodic table from He to Cs.
 - e. Ionization energies depend on electron configuration.
 - f. Ionization energies decrease across a row.

2. Based on electronic configurations, explain why the first ionization energies of the group 16 elements are lower than those of the group 15 elements, which is contrary to the general trend.
3. The first through third ionization energies do not vary greatly across the lanthanides. Why? How does the effective nuclear charge experienced by the ns electron change when going from left to right (with increasing atomic number) in this series?
4. Most of the first row transition metals can form at least two stable cations, for example iron(II) and iron(III). In contrast, scandium and zinc each form only a single cation, the Sc^{3+} and Zn^{2+} ions, respectively. Use the electron configuration of these elements to provide an explanation.
5. Of the elements Nd, Al, and Ar, which will readily form(s) +3 ions? Why?
6. Orbital energies can reverse when an element is ionized. Of the ions B^{3+} , Ga^{3+} , Pr^{3+} , Cr^{3+} , and As^{3+} , in which would you expect this reversal to occur? Explain your reasoning.
7. The periodic trends in electron affinities are not as regular as periodic trends in ionization energies, even though the processes are essentially the converse of one another. Why are there so many more exceptions to the trends in electron affinities compared to ionization energies?
8. Elements lying on a lower right to upper left diagonal line cannot be arranged in order of increasing electronegativity according to where they occur in the periodic table. Why?
9. Why do ionic compounds form, if energy is required to form gaseous cations?
10. Why is Pauling's definition of electronegativity considered to be somewhat limited?
11. Based on their positions in the periodic table, arrange Sb, O, P, Mo, K, and H in order of increasing electronegativity.
12. Based on their positions in the periodic table, arrange V, F, B, In, Na, and S in order of decreasing electronegativity.

Conceptual Answers

5. Both Al and Nd will form a cation with a +3 charge. Aluminum is in Group 13, and loss of all three valence electrons will produce the Al^{3+} ion with a noble gas configuration. Neodymium is a lanthanide, and all of the lanthanides tend to form +3 ions because the ionization potentials do not vary greatly across the row, and a +3 charge can be achieved with many oxidants.

11. $\text{K} < \text{Mo} \approx \text{Sb} < \text{P} \approx \text{H} < \text{O}$

Numerical Problems

1. The following table gives values of the first and third ionization energies for selected elements:

N	u	m	b	e	r	o	f	E	Element	$I_1 (\text{E} \rightarrow \text{E}^+ + \text{e}^- \text{, kJ/mol})$	Element	$I_3 (\text{E}^{2+} \rightarrow \text{E}^{3+} + \text{e}^- \text{, kJ/mol})$
l	e	c	t	r	o	n	s					
1		Na		495.9		Al						2744.8

1 2	Mg	737.8	Si	3231.6
1 3	Al	577.6	P	2914.1
1 4	Si	786.6	S	3357
1 5	P	1011.9	Cl	3822
1 6	S	999.6	Ar	3931
1 7	Cl	1251.2	K	4419.6
1 8	Ar	1520.6	Ca	4912.4

Plot the ionization energies versus the number of electrons. Explain why the slopes of the I_1 and I_3 plots are different, even though the species in each row of the table have the same electron configurations.

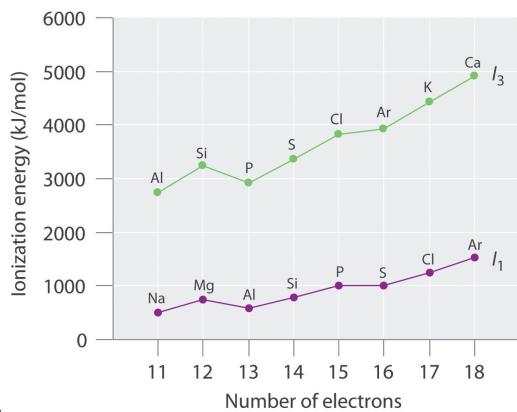
- Would you expect the third ionization energy of iron, corresponding to the removal of an electron from a gaseous Fe^{2+} ion, to be larger or smaller than the fourth ionization energy, corresponding to the removal of an electron from a gaseous Fe^{3+} ion? Why? How would these ionization energies compare to the first ionization energy of Ca?
- Which would you expect to have the highest first ionization energy: Mg, Al, or Si? Which would you expect to have the highest third ionization energy? Why?
- Use the values of the first ionization energies given in Figure 7.11 to construct plots of first ionization energy versus atomic number for (a) boron through oxygen in the second period; and (b) oxygen through tellurium in group 16. Which plot shows more variation? Explain the reason for the variation in first ionization energies for this group of elements.
- Arrange Ga, In, and Zn in order of increasing first ionization energies. Would the order be the same for second and third ionization energies? Explain your reasoning.
- Arrange each set of elements in order of increasing magnitude of electron affinity.
 - Pb, Bi, and Te
 - Na, K, and Rb
 - P, C, and Ge
- Arrange each set of elements in order of decreasing magnitude of electron affinity.
 - As, Bi, and N
 - O, F, and Ar
 - Cs, Ba, and Rb
- Of the species F^- , O^- , Al^{3+} , and Li^+ , which has the highest electron affinity? Explain your reasoning.
- Of the species O^- , N^{2-} , Hg^{2+} , and H^+ , which has the highest electron affinity? Which has the lowest electron affinity? Justify your answers.
- The Mulliken electronegativity of element A is 542 kJ/mol. If the electron affinity of A is -72 kJ/mol, what is the first ionization energy of element A? Use the data in the following table as a guideline to decide if A is a metal, a nonmetal, or a semimetal. If 1 g of A contains 4.85×10^{21} molecules, what is the identity of element A?

	Na	Al	Si	S	Cl
EA (kJ/mol)	-59.6	-41.8	-134.1	-200.4	-348.6

	Na	Al	Si	S	Cl
I (kJ/mol)	495.8	577.5	786.5	999.6	1251.2

11. Based on their valence electron configurations, classify the following elements as either electrical insulators, electrical conductors, or substances with intermediate conductivity: S, Ba, Fe, Al, Te, Be, O, C, P, Sc, W, Na, B, and Rb.
12. Using the data in Problem 10, what conclusions can you draw with regard to the relationship between electronegativity and electrical properties? Estimate the approximate electronegativity of a pure element that is very dense, lustrous, and malleable.
13. Of the elements Al, Mg, O₂, Ti, I₂, and H₂, which, if any, would you expect to be a good reductant? Explain your reasoning.
14. Of the elements Zn, B, Li, Se, Co, and Br₂, which if any, would you expect to be a good oxidant? Explain your reasoning.
15. Determine whether each species is a good oxidant, a good reductant, or neither.
1. Ba
 2. Mo
 3. Al
 4. Ni
 5. O₂
 6. Xe
16. Determine whether each species is a good oxidant, a good reductant, or neither.
1. Ir
 2. Cs
 3. Be
 4. B
 5. N
 6. Po
 7. Ne
17. Of the species I₂, O⁻, Zn, Sn²⁺, and K⁺, choose which you would expect to be a good oxidant. Then justify your answer.
18. Based on the valence electron configuration of the noble gases, would you expect them to have positive or negative electron affinities? What does this imply about their most likely oxidation states? their reactivity?

Numerical Answers



1.

The general features of both plots are roughly the same, with a small peak at 12 electrons and an essentially level region from 15–16 electrons. The slope of the I_3 plot is about twice as large as the slope of the I_1 plot, however, because the I_3 values correspond to removing an electron from an ion with a +2 charge rather than a neutral atom. The greater charge increases the effect of the steady rise in effective nuclear charge across the row.

2.

3. Electron configurations: Mg, $1s^2 2s^2 2p^6 3s^2$; Al, $1s^2 2s^2 2p^6 3s^2 3p^1$; Si, $1s^2 2s^2 2p^6 3s^2 3p^2$; First ionization energies increase across the row due to a steady increase in effective nuclear charge; thus, Si has the highest first ionization energy. The third ionization energy corresponds to removal of a 3s electron for Al and Si, but for Mg it involves removing a 2p electron from a filled inner shell; consequently, the third ionization energy of Mg is the highest.
- 4.
- 5.
- 6.
7. 1. Bi > As > N
2. F > O >> Ar
3. Rb > Cs > Ba
- 8.
9. $Hg^{2+} > H^+ > O^- > N^{2-}$; Hg^{2+} has the highest positive charge plus a relatively low energy vacant set of orbitals (the 6p subshell) to accommodate an added electron, giving it the greatest electron affinity; N^{2-} has a greater negative charge than O^- , so electron-electron repulsions will cause its electron affinity to be even lower (more negative) than that of O^- .
- 10.
11. insulators: S, O, C (diamond), P; conductors: Ba, Fe, Al, C (graphite), Be, Sc, W, Na, Rb; Te and B are semimetals and semiconductors.
- 12.
13. Mg, Al, Ti, and H₂
- 14.
15. 1. reductant
2. neither
3. reductant
4. reductant
5. oxidant
6. neither
- 16.
17. I₂ is the best oxidant, with a moderately strong tendency to accept an electron to form the I⁻ ion, with a closed shell electron configuration. O⁻ would probably also be an oxidant, with a tendency to add an electron to form salts containing the oxide ion, O²⁻. Zn and Sn²⁺ are all reductants, while K⁺ has no tendency to act as an oxidant or a reductant.

7.5: Electron Affinities

see above question to tease out

7.6: Metals, Nonmetals, and Metalloids

7.7: Group Trends fo the Active Metals

7.8: Group Trends for Selected Nonmetals

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CHAPTER OVERVIEW

9: Models of Chemical Bonding

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- 9.1: Atomic Properties and Chemical Bonds
- 9.2: The Ionic Bonding Model
- 9.3: The Covalent Bonding Model
- 9.4: Bond Energy and Chemical Change
- 9.5: Between the Extremes- Electronegativity and Bond Polarity
- 9.6: An Introduction to Metallic Bonding
- 9.E: Models of Chemical Bonding (Exercises)

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9.1: Atomic Properties and Chemical Bonds

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9.4: Bond Energy and Chemical Change

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CHAPTER OVERVIEW

10: The Shapes of Molecules

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- 10.1: Depicting Molecules and Ions with Lewis Structures
- 10.2: Valence-Shell Electron-Pair Repulsion (VSEPR) Theory
- 10.3: Molecular Shape and Molecular Polarity
- 10.E: The Shapes of Molecules (Exercises)

Thumbnail: Structural formula of sulfur tetrafluoride, showing dimensions. (Public Domain; Benjah-bmm27).

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10.1: Depicting Molecules and Ions with Lewis Structures

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10.3: Molecular Shape and Molecular Polarity

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10.E: The Shapes of Molecules (Exercises)

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11: Theories of Covalent Bonding

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- [11.1: Valence Bond \(VB\) Theory and Orbital Hybridization](#)
- [11.2: Modes of Orbital Overlap and the Types of Covalent Bonds](#)
- [11.3: Molecular Orbital \(MO\) Theory and Electron Delocalization](#)
- [11.E: Theories of Covalent Bonding \(Exercises\)](#)

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CHAPTER OVERVIEW

12: Intermolecular Forces- Liquids, Solids, and Phase Change

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- 12.1: An Overview of Physical States and Phase Changes
- 12.2: Quantitative Aspects of Phase Changes
- 12.3: Properties of the Liquid State
- 12.4: Types of Intermolecular Forces
- 12.5: The Uniqueness of Water
- 12.6: The Solid State- Structure, Properties, and Bonding
- 12.7: Advanced Materials
- 12.8: Advanced Materials
- 12.E: Intermolecular Forces - Liquids, Solids, and Phase Changes (Exercises)

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CHAPTER OVERVIEW

13: The Properties of Mixtures- Solutions and Colloids

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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- [13.2: Intermolecular Forces and Biological Macromolecules](#)
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14: Periodic Patterns in the Main-Group Elements

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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14.5: Group 13 - The Boron Family

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14.6: Group 14 - The Carbon Family

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14.7: Group 15 - The Nitrogen Family

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14.9: Group 17 - The Halogens

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CHAPTER OVERVIEW

15: Organic Compounds and the Atomic Properties of Carbon

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- 15.1: The Special Nature of Carbon and the Characteristics of Organic Molecules
- 15.2: The Structures and Classes of Hydrocarbons
- 15.3: Some Important Classes of Organic Reactions
- 15.4: Properties and Reactivities of Common Functional Groups
- 15.5: The Monomer-Polymer Theme I - Synthetic Macromolecules
- 15.6: The Monomer-Polymer Theme II - Biological Macromolecules
- 15.E: Organic Compounds and the Atomic Properties of Carbon (Exercises)

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CHAPTER OVERVIEW

16: Kinetics- Rates and Mechanisms of Chemical Reactions

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- 16.1: Focusing on Reaction Rate
- 16.2: Expressing the Reaction Rate
- 16.3: The Rate Law and Its Components
- 16.4: Integrated Rate Laws - Concentration Changes over Time
- 16.5: Theories of Chemical Kinetics
- 16.6: Reaction Mechanisms - The Steps from Reactant to Product
- 16.7: Catalysis - Speeding Up a Reaction
- 16.E: Kinetics- Rates and Mechanisms of Chemical Reactions (Exercises)

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CHAPTER OVERVIEW

17: Equilibrium - The Extent of Chemical Reactions

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- [17.1: The Equilibrium State and the Equilibrium Constant](#)
- [17.2: The Reaction Quotient and the Equilibrium Constant](#)
- [17.3: Expressing Equilibria with Pressure Terms - Relation Between Kc and Kp](#)
- [17.4: Comparing Q and K to Determine Reaction Direction](#)
- [17.5: How to Solve Equilibrium Problems](#)
- [17.6: Reaction Conditions and Equilibrium - Le Châtelier's Principle](#)
- [17.E: Equilibrium - The Extent of Chemical Reactions \(Exercises\)](#)

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17.3: Expressing Equilibria with Pressure Terms - Relation Between K_c and K_p

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CHAPTER OVERVIEW

18: Acid-Base Equilibria

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- 18.1: Acids and Bases in Water
- 18.2: Autoionization of Water and the pH Scale
- 18.3: Proton Transfer and the Brønsted-Lowry Acid-Base Definition
- 18.4: Solving Problems Involving Weak-Acid Equilibria
- 18.5: Molecular Properties and Acid Strength
- 18.6: Weak Bases and Their Relation to Weak Acids
- 18.7: Acid-Base Properties of Salt Solutions
- 18.8: Generalizing the Brønsted-Lowry Concept - The Leveling Effect
- 18.9: Electron-Pair Donation and the Lewis Acid-Base Definition
- 18.E: Acid-Base Equilibria (Exercises)

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18.2: Autoionization of Water and the pH Scale

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CHAPTER OVERVIEW

19: Ionic Equilibria in Aqueous Systems

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- 19.1: Equilibria of Acid-Base Buffers
- 19.2: Acid-Base Titration Curves
- 19.3: Equilibria of Slightly Soluble Ionic Compounds
- 19.4: Equilibria Involving Complex Ions
- 19.E: Ionic Equilibria in Aqueous Systems (Exercises)

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CHAPTER OVERVIEW

20: Thermodynamics- Entropy, Free Energy, and the Direction of Chemical Reactions

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- 20.1: The Second Law of Thermodynamics - Predicting Spontaneous Change
- 20.2: Calculating the Change in Entropy of a Reaction
- 20.3: Entropy, Gibbs Energy, and Work
- 20.4: Gibbs Energy, Equilibrium, and Reaction Direction
- 20.E: Thermodynamics (Exercises)

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CHAPTER OVERVIEW

21: Electrochemistry- Chemical Change and Electrical Work

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- 21.1: Redox Reactions and Electrochemical Cells
- 21.2: Voltaic Cells - Using Spontaneous Reactions to Generate Electrical Energy
- 21.3: Cell Potential - Output of a Voltaic Cell
- 21.4: Gibbs Energy and Electrical Work
- 21.5: Electrochemical Processes in Batteries
- 21.6: Corrosion - An Environmental Voltaic Cell
- 21.7: Electrolytic Cells- Using Electrical Energy to Drive Nonspontaneous Reactions
- 21.E: Electrochemistry - Chemical Change and Electrical Work (Exercises)

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21.1: Redox Reactions and Electrochemical Cells

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CHAPTER OVERVIEW

22: The Elements in Nature and Industry

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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Topic hierarchy

- [22.1: How the Elements Occur in Nature](#)
- [22.2: The Cycling of Elements Through the Environment](#)
- [22.3: Metallurgy - Extracting a Metal from Its Ore](#)
- [22.4: Tapping the Crust - Isolation and Uses of Selected Elements](#)
- [22.5: Chemical Manufacturing - Two Case Studies](#)
- [22.E: The Elements in Nature and Industry \(Exercises\)](#)

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22.1: How the Elements Occur in Nature

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22.5: Chemical Manufacturing - Two Case Studies

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CHAPTER OVERVIEW

23: Transition Elements and Their Coordination Compounds

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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[Template](#):[HideTOC](#)

Topic hierarchy

- [23.1: Properties of the Transition Elements](#)
- [23.2: The Inner Transition Elements](#)
- [23.3: Coordination Compounds](#)
- [23.4: Theoretical Basis for the Bonding and Properties of Complexes](#)
- [23.E: Transition Elements and Their Coordination Compounds \(Exercises\)](#)

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23.1: Properties of the Transition Elements

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23.2: The Inner Transition Elements

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CHAPTER OVERVIEW

24: Nuclear Reactions and Their Applications

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Molecular Nature of Matter and Change

by Martin Silberberg

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