CHEM 210: GENERAL CHEMISTRY I, AN "ATOMS UP" APPROACH

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Camille Kaslan

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CHAPTER OVERVIEW

1: Chemistry is the Science of Everything

Chemistry: The Central Science

Chemistry is sometimes referred to as “the central science” due to its interconnectedness with a vast array of other STEM disciplines (STEM stands for areas of study in the science, technology, engineering, and math fields). Chemistry and the language of chemists play vital roles in biology, medicine, materials science, forensics, environmental science, and many other fields. The basic principles of physics are essential for understanding many aspects of chemistry, and there is extensive overlap between many sub-disciplines within the two fields, such as chemical physics and nuclear chemistry. Mathematics, computer science, and information theory provide important tools that help us calculate, interpret, describe, and generally make sense of the chemical world. Biology and chemistry converge in biochemistry, which is crucial to understanding the many complex factors and processes that keep living organisms (such as us) alive. Chemical engineering, materials science, and nanotechnology combine chemical principles and empirical findings to produce useful substances, ranging from gasoline to fabrics to electronics. Agriculture, food science, veterinary science, and brewing and wine making help provide sustenance in the form of food and drink to the world’s population. Medicine, pharmacology, biotechnology, and botany identify and produce substances that help keep us healthy. Environmental science, geology, oceanography, and atmospheric science incorporate many chemical ideas to help us better understand and protect our physical world. Chemical ideas are used to help understand the universe in astronomy and cosmology.

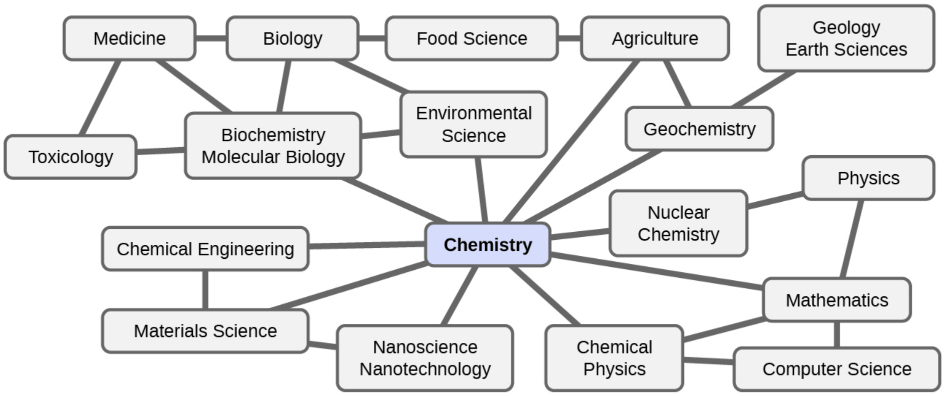

Figure 1: Knowledge of chemistry is central to understanding a wide range of scientific disciplines. This diagram shows just some of the interrelationships between chemistry and other fields.

Chapter Sections

Contributors and Attributions

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1.1: Thinking Scientifically - The Scientific Method

Learning Objectives

- To identify the components of the scientific method

Scientists search for answers to questions and solutions to problems by using a procedure called the **scientific method**. This procedure consists of making observations, formulating hypotheses, and designing experiments, which in turn lead to additional observations, hypotheses, and experiments in repeated cycles (Figure 1.1.1).

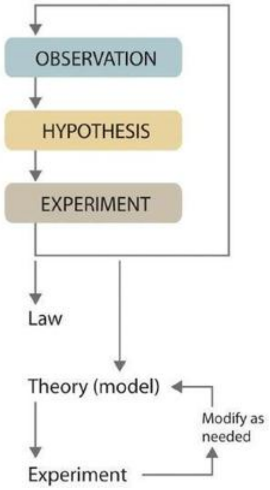

Figure 1.1.1: The Scientific Method. As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

Observations can be qualitative or quantitative. Qualitative observations describe properties or occurrences in ways that do not rely on numbers. Examples of qualitative observations include the following: the outside air temperature is cooler during the winter season, table salt is a crystalline solid, sulfur crystals are yellow, and dissolving a penny in dilute nitric acid forms a blue solution and a brown gas. Quantitative observations are measurements, which by definition consist of both a number and a unit. Examples of quantitative observations include the following: the melting point of crystalline sulfur is 115.21 °C, and 35.9 grams of table salt—whose chemical name is sodium chloride—dissolve in 100 grams of water at 20 °C. An example of a quantitative observation was the initial observation leading to the modern theory of the dinosaurs' extinction: iridium concentrations in sediments dating to 66 million years ago were found to be 20–160 times higher than normal. The development of this theory is a good exemplar of the scientific method in action (see Figure 1.1.2 below).

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

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

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

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

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

Whereas a law states only what happens, a **theory** attempts to explain why nature behaves as it does. Laws are unlikely to change greatly over time unless a major experimental error is discovered. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered. The theory developed to explain the extinction of the dinosaurs, for example, is that Earth occasionally encounters small- to medium-sized asteroids, and these encounters may have unfortunate implications for the continued existence of most species. This theory is by no means proven, but it is consistent with the bulk of evidence amassed to date. Figure 1.1.2 summarizes the application of the scientific method in this case.

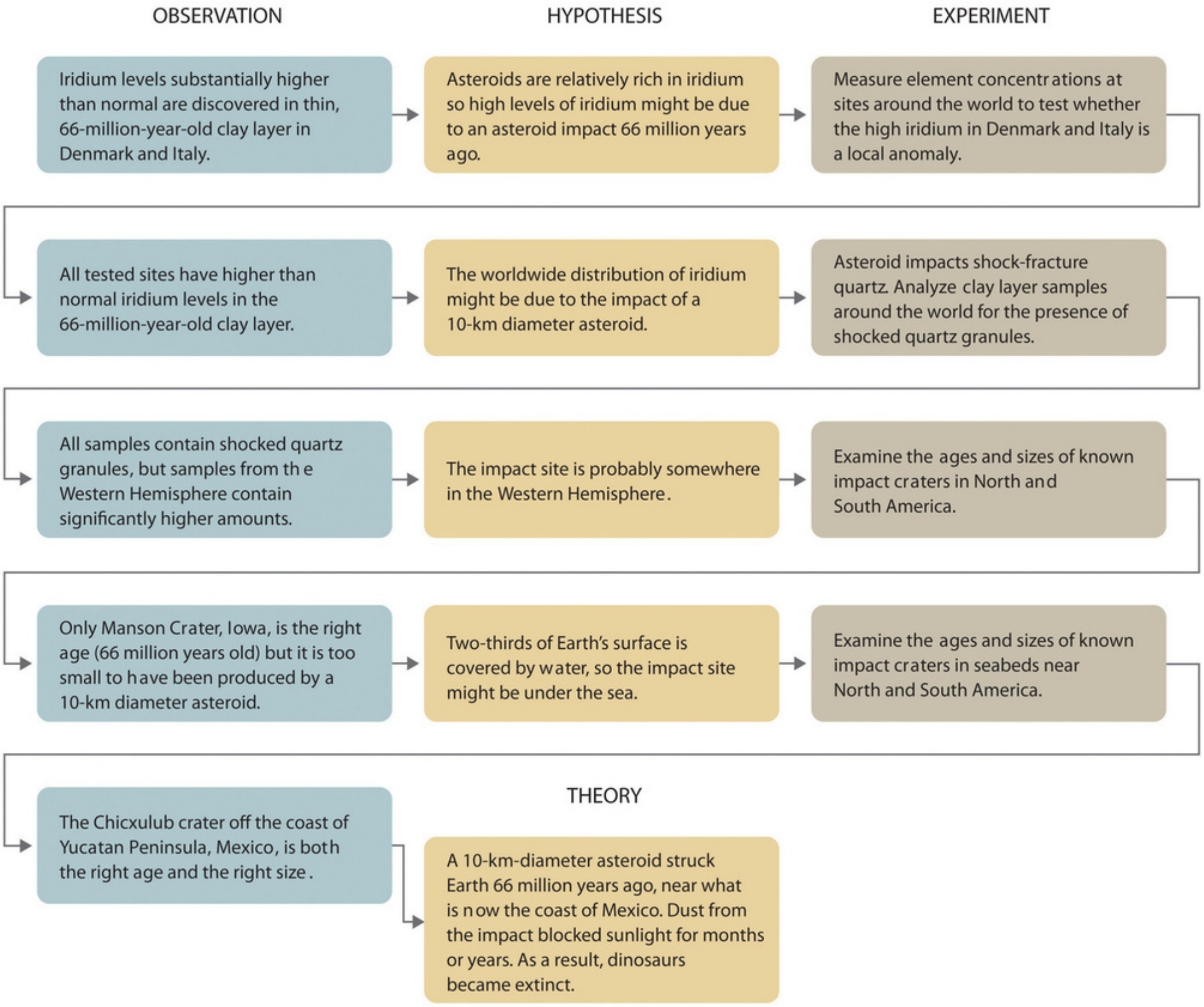

Figure 1.1.2: A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth

✓ Example 1.1.1

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

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

Given: components of the scientific method

Asked for: statement classification

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

Solution

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

? Exercise 1.1.1

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

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

Answer a

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

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

Summary

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

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

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1.2: Designing Experiments - What's Being Tested?

An **experiment** is a controlled method of testing a hypothesis. Experiments are designed to provide an opportunity to make observation that will help test a hypothesis. Experiments are best understood in term of three types of variables: independent variables, dependent variables, and controlled variables. A **variable** is some kind of parameter that is either directly recorded, set as constant, or something that affects a change in another parameter.

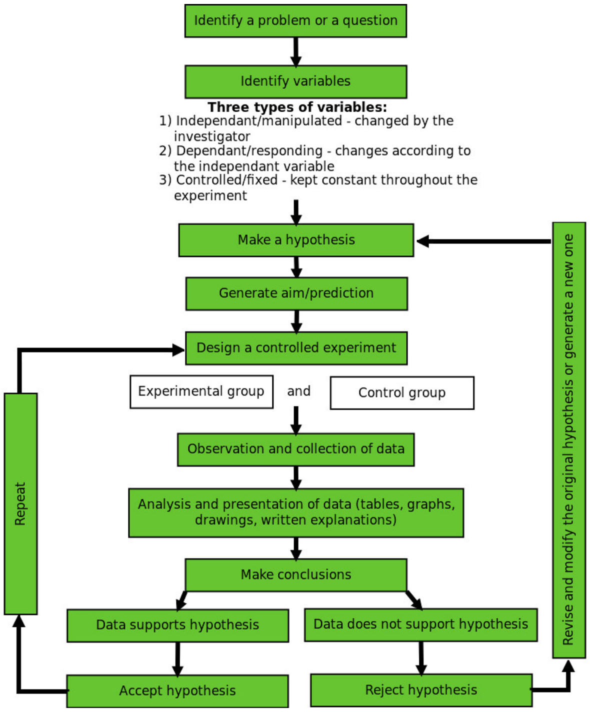


Figure 1.2.1: A recap of The Scientific Method that shows how a hypothesis is tested through experiments that have clearly defined experimental variables (measurements).

Experimental Variables

Most experiments are repeated multiple times with slight variations. These repetitions are often called trials. A variable that is purposely altered between trials is called an **independent variable**. Usually, it is a best practice to have a single independent variable in an experiment. It may be helpful to think of the independent variable as the "input" of the experiment.

If the independent variable is the "input" of an experiment, than the **dependent variable** is the "output." Dependent variables change in response to the independent variable (their name comes from the fact that they depend on the independent variable).

Finally, some variables, called **controlled variables**, are kept constant through all of the trials. Controlled variables are kept constant so that their fluctuations do not alter the dependent variable and cloud its relationship with the independent variable.

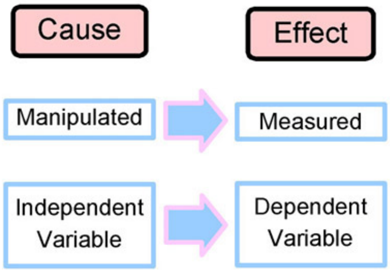
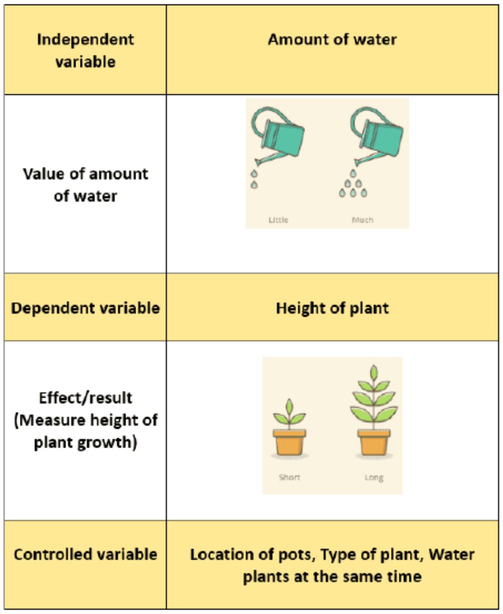


Figure 1.2.2: Experiments are designed such that the directly measured result (or something that can be used to calculate a desired result) is the dependent variable. Since hypotheses are inductive statements, i.e. statements that aim to predict or explain, the

dependent variable must be treated as an affected outcome that results from changes in specific causes of that outcome.

Example Experiment

Below is an example of an experiment that involves measuring plant growth by determining the height of the plant. In this experiment, the objective is to test a hypothesis that relates the amount of water (independent variable) to the height of the plant (dependent variable), specifically, "If little water is given to a plant, then the plant height will be lesser." If only those two variables are to be related, then all other factors that affect plant height must remain unchanged throughout the experiment. Can you design an experiment that will test this hypothesis?



Independent variable	Amount of water
Value of amount of water	Little Much
Dependent variable	Height of plant
Effect/result (Measure height of plant growth)	Short Long
Controlled variable	Location of pots, Type of plant, Water plants at the same time

Figure 1.2.3: Experimental variables involved in a plant growth experiment.

Image Attributions

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CHAPTER OVERVIEW

2: Matter - An Introduction

We are all familiar with "stuff" - what we call *matter*. The definition of **Matter** is anything that has mass and volume (takes up space). For most common objects that we deal with every day, it is fairly simple to demonstrate that they have mass and take up space. You might be able to imagine, however, the difficulty for people several hundred years ago to demonstrate that air has mass and volume. Air (and all other gases) are invisible to the eye, have very small masses compared to equal amounts of solids and liquids, and are quite easy to compress (change volume). Without sensitive equipment, it would have been difficult to convince people that gases are matter. Today, we can measure the mass of a small balloon when it is deflated and then blow it up, tie it off, and measure its mass again to detect the additional mass due to the air inside. The mass of air, under room conditions, that occupies a one quart jar is approximately 0.0002 pounds. This small amount of mass would have been difficult to measure in times before balances were designed to accurately measure very small masses. Later, scientists were able to compress gases into such a small volume that the gases turned into liquids, which made it clear that gases are matter.

Figure 2.2: Everything from an ant, to a truck, to the earth and even the entire galaxy is composed of matter. Images used with permission from Wikipedia (CC_SA-BY-3.0; credit High Contrast)

Even though the universe consists of "things" as wildly different as ants and galaxies, the matter that makes up all of these "things" is composed of a very limited number of building blocks. Like thousands of words comprise the English language, if those words are broken down to their "building blocks", we would have only 26 letters. In thie chapter, we will delve into the different types of matter according to their composition, properties, and behavior.

Chapter Sections

Contributors and Attributions

- Wikipedia
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- Henry Agnew (UC Davis)

2.1: Classifications of Matter

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.

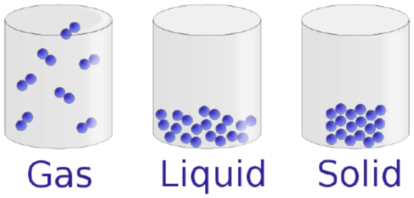

Figure 2.1.1: The Three States of Matter. Solids have a defined shape and volume. Liquids have a fixed volume but flow to assume the shape of their containers. Gases completely fill their containers, regardless of volume. Figure used with permission from Wikipedia

Three cylindrical containers containing spherical particles. From left to right. Particles are spread far apart, particles moderately closer to represent, particles that are tightly packed. Labeled gas, liquid, solid.

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 2.1.2: 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.

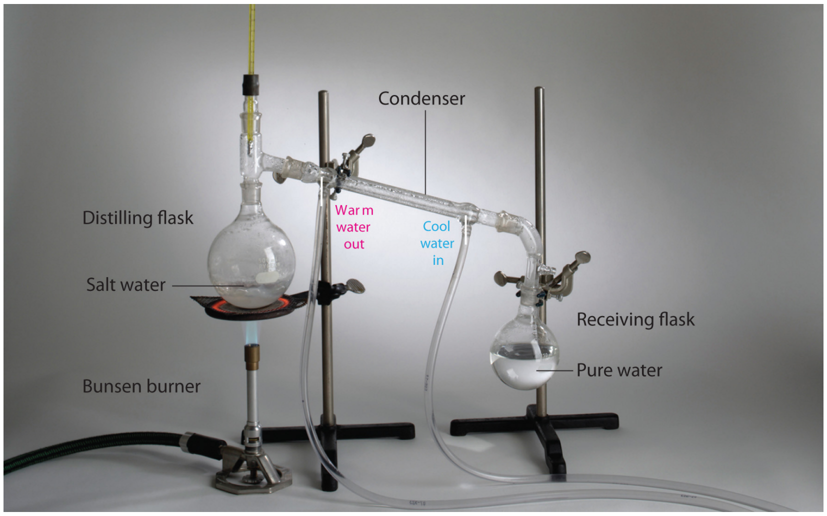

Figure 2.1.3: The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.

Distillation setup with distilling flask on the left being heated with a bunsen burner. A condenser connects the neck of the distilling flask to the flask containing pure water. The two flasks are being held up by clamps.

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 2.1.4: 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.

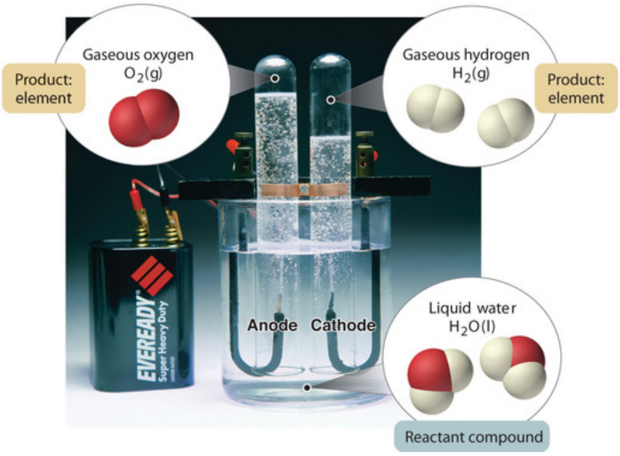

Figure 2.1.5: The Decomposition of Water to Hydrogen and Oxygen by Electrolysis. Water is a chemical compound; hydrogen and oxygen are elements.

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: YouTube, Different Definitions of Matter(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 2.1.5). 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 2.1.6.

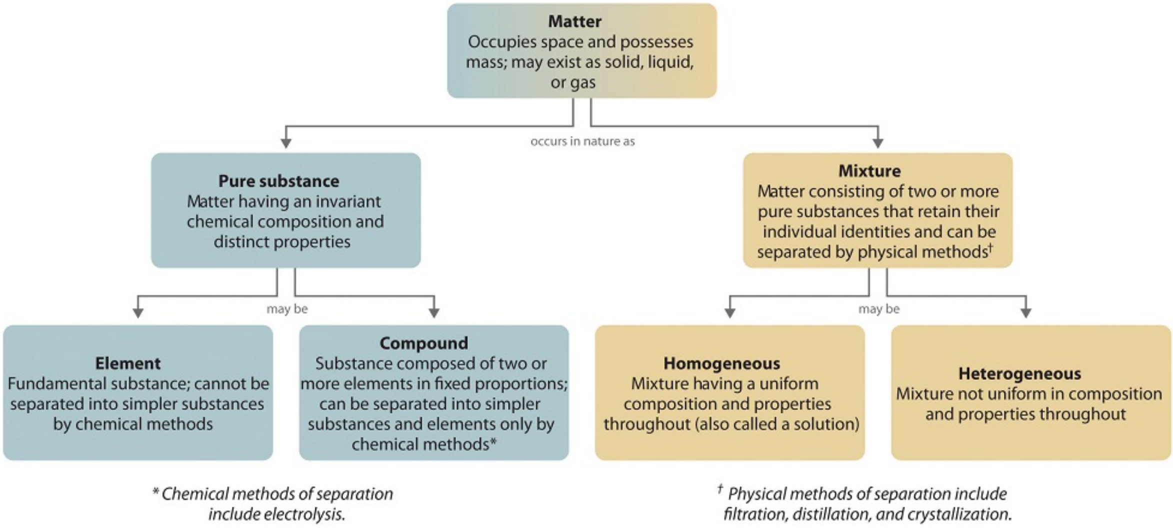

Figure 2.1.6: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

Example 2.1.1

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 2.1.1

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

2.2: Properties of Matter

Learning Objectives

- Describe the difference between physical and chemical properties or changed.
- Identify a property or transformation as either physical or chemical using symbolic, particulate, or macroscopic representations.
- Identify the properties of matter as extensive or intensive.
- Recognize and describe the parts of the NFPA hazard diamond.

The characteristics that enable us to distinguish one substance from another are called properties. A physical property is a characteristic of matter that is not associated with a change in its chemical composition. Familiar examples of physical properties include density, color, hardness, melting and boiling points, and electrical conductivity. We can observe some physical properties, such as density and color, without changing the physical state of the matter observed. Other physical properties, such as the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change. A physical change is a change in the state or properties of matter without any accompanying change in its chemical composition (the identities of the substances contained in the matter). We observe a physical change when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water (Figure $2.2.1$). Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding solids into powders (which can sometimes yield noticeable changes in color). In each of these examples, there is a change in the physical state, form, or properties of the substance, but no change in its chemical composition.

Figure $2.2.1$: (a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapor is changed into liquid water. (credit a: modification of work by "95jb14"/Wikimedia Commons; credit b: modification of work by "mjneuby"/Flickr).

The change of one type of matter into another type (or the inability to change) is a chemical property. Examples of chemical properties include flammability, toxicity, acidity, reactivity (many types), and heat of combustion. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize (Figure $2.2.2$). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.

Figure $2.2.2$: (a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by "Atoma"/Wikimedia Commons)

Comparison of two metal equipments. The first image shows a rusted brown appearance and the following image shows a shiny metallic appearance.

To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting (Figure 2.2.3).

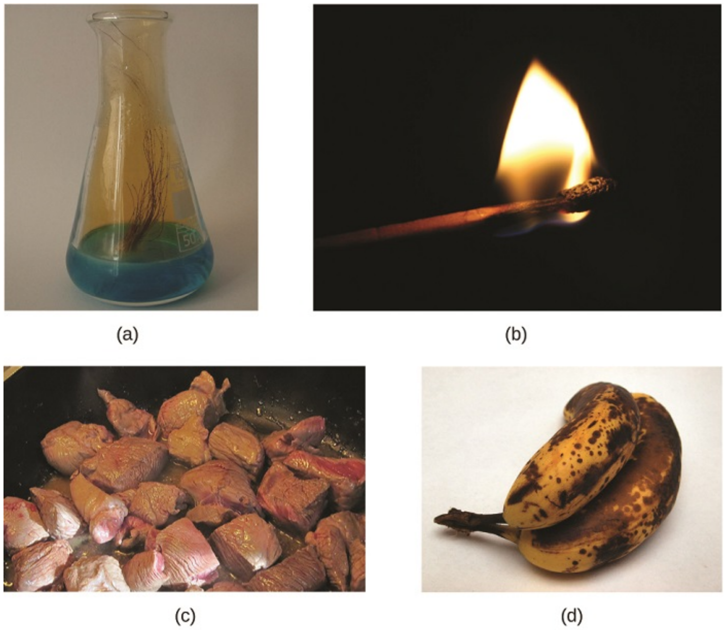

Figure 2.2.3: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo)

Four pictures. A. a flask with copper wires placed in a blue solution and also the presence of a gas. B. A lighted match. C. meat cubes being cooked on a pan. D. Bananas forming black spots on its peel.

Properties of matter fall into one of two categories. If the property depends on the amount of matter present, it is an extensive property. The mass and volume of a substance are examples of extensive properties; for instance, a gallon of milk has a larger mass and volume than a cup of milk. The value of an extensive property is directly proportional to the amount of matter in question. If the property of a sample of matter does not depend on the amount of matter present, it is an intensive property. Temperature is an example of an intensive property. If the gallon and cup of milk are each at 20 °C (room temperature), when they are combined, the temperature remains at 20 °C. As another example, consider the distinct but related properties of heat and temperature. A drop of hot cooking oil spattered on your arm causes brief, minor discomfort, whereas a pot of hot oil yields severe burns. Both the drop and the pot of oil are at the same temperature (an intensive property), but the pot clearly contains much more heat (extensive property).

Hazard Diamond

You may have seen the symbol shown in Figure 2.2.4 on containers of chemicals in a laboratory or workplace. Sometimes called a “fire diamond” or “hazard diamond,” this chemical hazard diamond provides valuable information that briefly summarizes the various dangers of which to be aware when working with a particular substance.

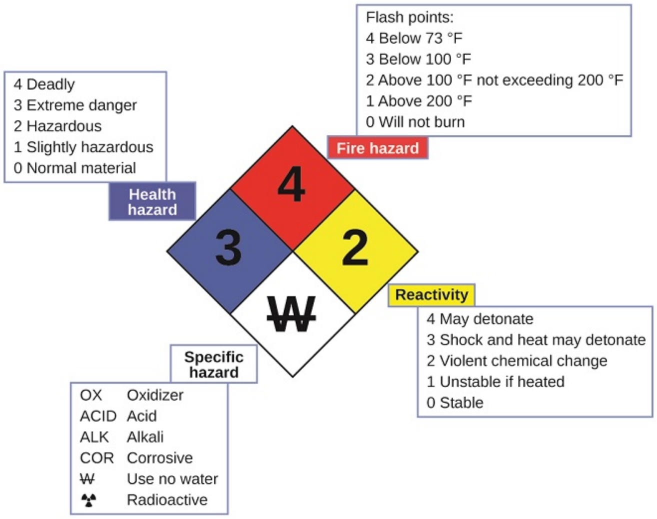

Figure 2.2.4: The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

The National Fire Protection Agency (NFPA) 704 Hazard Identification System was developed by NFPA to provide safety information about certain substances. The system details flammability, reactivity, health, and other hazards. Within the overall diamond symbol, the top (red) diamond specifies the level of fire hazard (temperature range for flash point). The blue (left) diamond indicates the level of health hazard. The yellow (right) diamond describes reactivity hazards, such as how readily the substance will undergo detonation or a violent chemical change. The white (bottom) diamond points out special hazards, such as if it is an oxidizer (which allows the substance to burn in the absence of air/oxygen), undergoes an unusual or dangerous reaction with water, is corrosive, acidic, alkaline, a biological hazard, radioactive, and so on. Each hazard is rated on a scale from 0 to 4, with 0 being no hazard and 4 being extremely hazardous.

While many elements differ dramatically in their chemical and physical properties, some elements have similar properties. We can identify sets of elements that exhibit common behaviors. For example, many elements conduct heat and electricity well, whereas others are poor conductors. These properties can be used to sort the elements into three classes: metals (elements that conduct well), nonmetals (elements that conduct poorly), and metalloids (elements that have properties of both metals and nonmetals).

The periodic table is a table of elements that places elements with similar properties close together (Figure 2.2.5). You will learn more about the periodic table as you continue your study of chemistry.

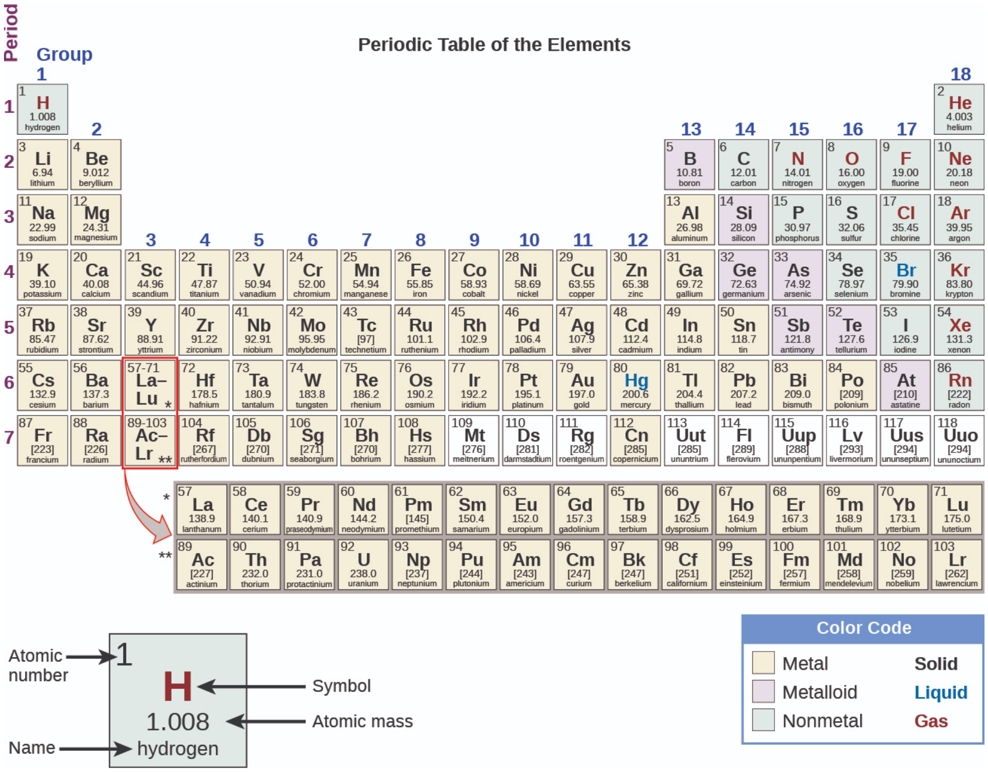

Figure 2.2.5: The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

Summary

All substances have distinct physical and chemical properties, and may undergo physical or chemical changes. Physical properties, such as hardness and boiling point, and physical changes, such as melting or freezing, do not involve a change in the composition of matter. Chemical properties, such flammability and acidity, and chemical changes, such as rusting, involve production of matter that differs from that present beforehand.

Measurable properties fall into one of two categories. Extensive properties depend on the amount of matter present, for example, the mass of gold. Intensive properties do not depend on the amount of matter present, for example, the density of gold. Heat is an example of an extensive property, and temperature is an example of an intensive property.

Glossary

chemical change

change producing a different kind of matter from the original kind of matter

chemical property

behavior that is related to the change of one kind of matter into another kind of matter

extensive property

property of a substance that depends on the amount of the substance

intensive property

property of a substance that is independent of the amount of the substance

physical change

change in the state or properties of matter that does not involve a change in its chemical composition

physical property

characteristic of matter that is not associated with any change in its chemical composition

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2.3: Intensive vs. Extensive Properties

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 2.3.1). 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.

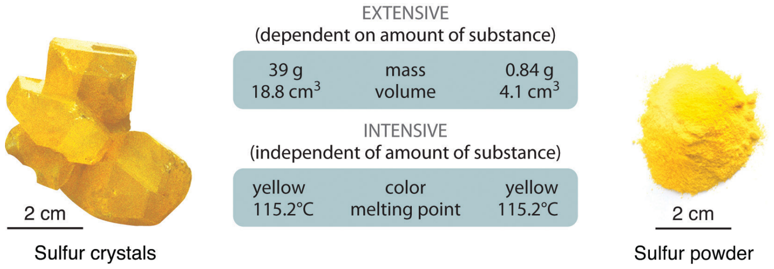

Figure 2.3.2.1.1: The Difference between Extensive and Intensive Properties of Matter. Because they differ in size, the two samples of sulfur have different extensive properties, such as mass and volume. In contrast, their intensive properties, including color, melting point, and electrical conductivity, 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/cm^3). 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:

$$density = \frac{mass}{volume} \rightarrow \rho = \frac{m}{v} \tag{2.3.1}$$

Pure water, for example, has a density of 0.998 g/cm^3 at 25°C. The average densities of some common substances are in Table 2.3.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table 2.3.1: Densities of Common Substances

Substance	Density at 25°C (g/cm3)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

References

1. Petrucci, Bissonnette, Herring, Madura. General Chemistry: Principles and Modern Applications. Tenth ed. Upper Saddle River, NJ 07458: Pearson Education Inc., 2011.
2. Cracolice, Peters. Basics of introductory Chemistry An active Learning Approach. Second ed. Belmont, CA 94001:Brooks/Cole, 2007.

Contributors and Attributions

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2.4: Changes in Matter

Learning Objectives

- Label a change as chemical or physical.
- List evidence that can indicate a chemical change occurred.

Change is happening all around us all of the time. Just as chemists have classified elements and compounds, they have also classified types of changes. Changes are classified as either physical or chemical changes. Chemists learn a lot about the nature of matter by studying the changes that matter can undergo. Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.

Physical Change

Physical changes are changes in which no 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. A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not. When liquid water is heated, it changes to water vapor. However, even though the physical properties have changed, the molecules are exactly the same as before. We still have each water molecule containing two hydrogen atoms and one oxygen atom covalently bonded. When you have a jar containing a mixture of pennies and nickels and you sort the mixture so that you have one pile of pennies and another pile of nickels, you have not altered the identity of the pennies or the nickels—you've merely separated them into two groups. This would be an example of a physical change. Similarly, if you have a piece of paper, you don't change it into something other than a piece of paper by ripping it up. What was paper before you started tearing is still paper when you are done. Again, this is an example of a physical change.

Figure 2.4.1: Ice melting is a physical change. When liquid water (H_2O) freezes into a solid state (ice), it appears changed; however, this change is only physical, as the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (Public Domain; Moussa).

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.

Chemical 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 a candle. The act of burning paper actually results in the formation of new chemicals (carbon dioxide and water) from the burning of the wax. Another example of a chemical change is what occurs when natural gas is burned in your furnace. This time, on the left there is a molecule of methane, $\mathrm{CH_4}$, and two molecules of oxygen, $\mathrm{O_2}$; on the right are two molecules of water, $\mathrm{H_2O}$, and one molecule of carbon dioxide, $\mathrm{CO_2}$. 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.

Figure $2.4.2$: Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

We can't actually see molecules breaking and forming bonds, although that's what defines chemical changes. We have to make other observations to indicate that a chemical change has happened. Some of the evidence for chemical change will involve the energy changes that occur in chemical changes, but some evidence involves the fact that new substances with different properties are formed in a chemical change.

Observations that help to indicate chemical change include:

- Temperature changes (either the temperature increases or decreases).
- Light given off.
- Unexpected color changes (a substance with a different color is made, rather than just mixing the original colors together).
- Bubbles are formed (but the substance is not boiling—you made a substance that is a gas at the temperature of the beginning materials, instead of a liquid).
- Different smell or taste (do not taste your chemistry experiments, though!).
- A solid forms if two clear liquids are mixed (look for *floaties*—technically called a precipitate).

✓ Example $2.4.1$

Label each of the following changes as a physical or chemical change. Give evidence to support your answer.

a. Boiling water.
b. A nail rusting.
c. A green solution and colorless solution are mixed. The resulting mixture is a solution with a pale green color.
d. Two colorless solutions are mixed. The resulting mixture has a yellow precipitate.

Solution

a. Physical: boiling and melting are physical changes. When water boils, no bonds are broken or formed. The change could be written: $\mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2O}\,(g)$
b. Chemical: The dark grey nail changes color to form an orange flaky substance (the rust); this must be a chemical change. Color changes indicate chemical change. The following reaction occurs: $\mathrm{Fe} + \mathrm{O_2} \rightarrow \mathrm{Fe_2O_3}$

c. Physical: because none of the properties changed, this is a physical change. The green mixture is still green and the colorless solution is still colorless. They have just been spread together. No color *change* occurred or other evidence of chemical change.
d. Chemical: the formation of a precipitate and the color change from colorless to yellow indicate a chemical change.

? Exercise 2.4.1

Label each of the following changes as a physical or chemical change.

a. A mirror is broken.
b. An iron nail corroded in moist air
c. Copper metal is melted.
d. A catalytic converter changes nitrogen dioxide to nitrogen gas and oxygen gas.

Answer a:

physical change

Answer b:

chemical change

Answer c:

physical change

Answer d:

chemical change

Separating Mixtures Through Physical Changes

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.

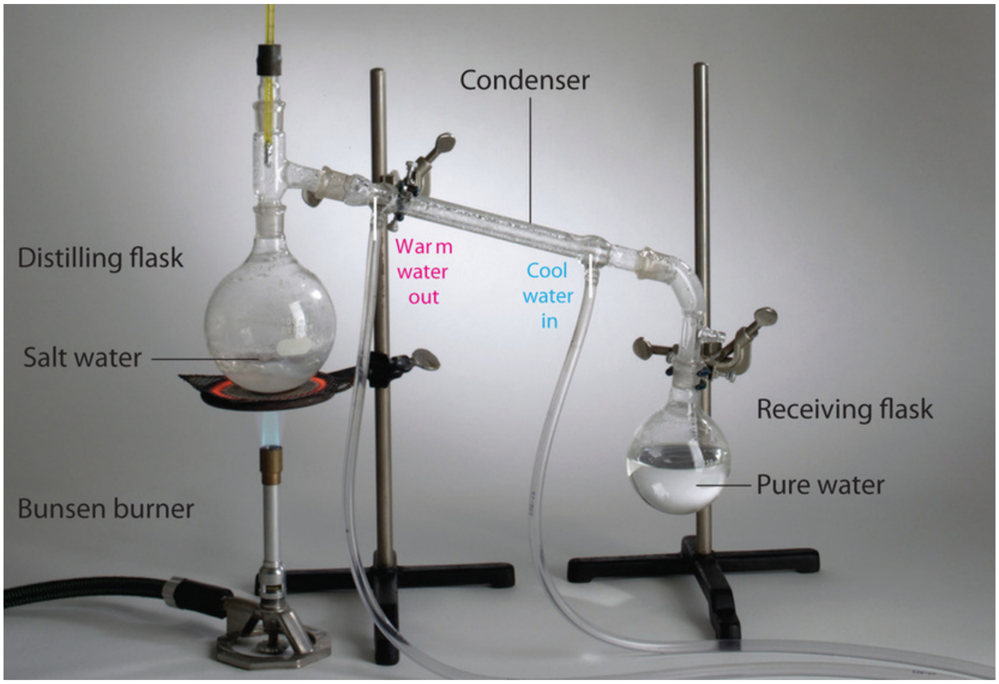

Figure 2.4.3: *The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.*

Parts of a distillation setup: Bunsen burner, salt water in distilling flask, condenser with cool water in and warm water out, pure water in 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.

Another example for using physical properties to separate mixtures is filtration (Figure 2.4.4). Filtration is any mechanical, physical or biological operation that separates solids from fluids (liquids or gases) by adding a medium through which only the fluid can pass. The fluid that passes through is called the filtrate. There are many different methods of filtration; all aim to attain the separation of substances. Separation is achieved by some form of interaction between the substance or objects to be removed and the filter. The substance that is to pass through the filter must be a fluid, i.e. a liquid or gas. Methods of filtration vary depending on the location of the targeted material, i.e. whether it is dissolved in the fluid phase or suspended as a solid.

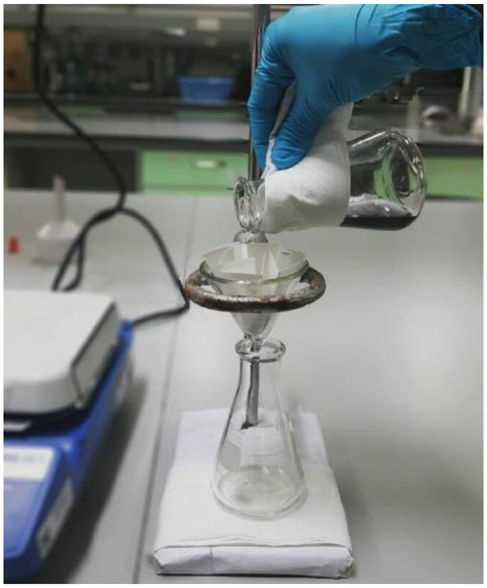

Figure 2.4.4**:** *Filtration for the separation of solids from a hot solution. (CC BY-SA 4.0; Suman6395).*

Summary

- Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.
- Physical changes are changes that do not alter the identity of a substance.
- Chemical changes are changes that occur when one substance is turned into another substance.
- Chemical changes are frequently harder to reverse than physical changes. Observations that indicate a chemical change has occurred include color change, temperature change, light given off, formation of bubbles, formation of a precipitate, etc.

Contributions & Attributions

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- Boundless (www.boundless.com)

2.5: Energy - What Drives Changes in Matter

Learning Objectives

- To understand the concept of energy and its various forms.
- To know the relationship between energy, work, and heat.

Because energy takes many forms, only some of which can be seen or felt, it is defined by its effect on matter. For example, microwave ovens produce energy to cook food, but we cannot see that energy. In contrast, we can see the energy produced by a light bulb when we switch on a lamp. In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 2.5.1). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperature of an object is a measure of its thermal energy content. Radiant energy is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energy results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energy is stored in the nucleus of an atom, and chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

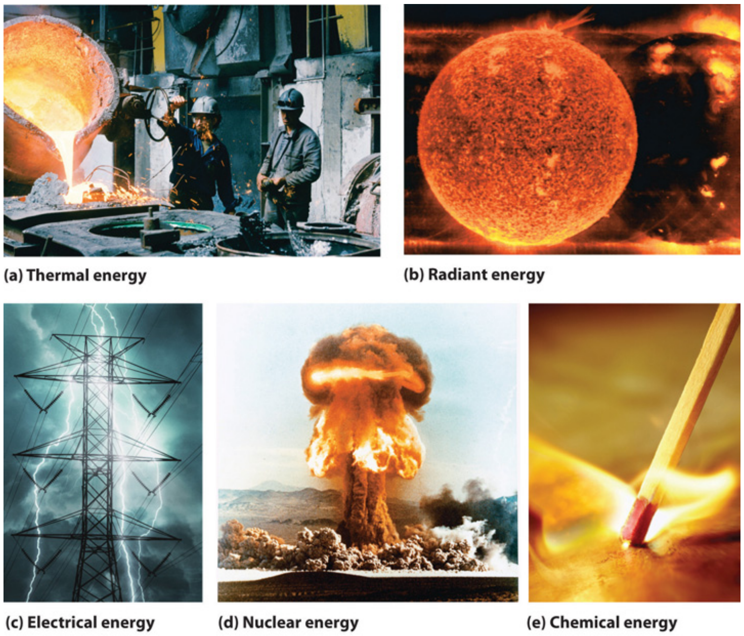


Figure 2.5.1: Forms of Energy. (a) *Thermal energy* results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, which is due to the flow of electrically charged particles. (d) *Nuclear energy* is released when particles in the nucleus of the atom are rearranged. (e) *Chemical energy* results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds.

Electrical energy, nuclear energy, and chemical energy are different forms of potential energy (PE), which is energy stored in an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, kinetic energy (KE) is energy due to the motion of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is then transferred to the object on the ground that it strikes. The electrostatic attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure 2.5.2) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

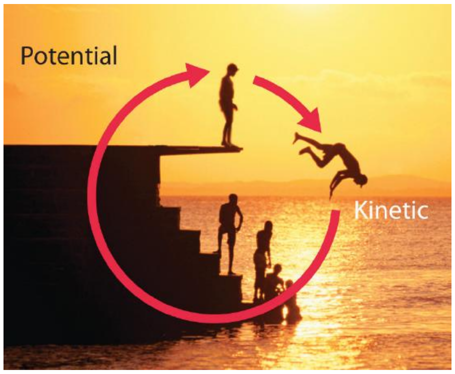


Figure 2.5.2: Interconversion of Forms of Energy. When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the **law of conservation of energy**: *Energy cannot be created or destroyed.*

Energy, Heat, and Work

One definition of energy is the capacity to do work. The easiest form of work to visualize is mechanical work (Figure 2.5.3), which is the energy required to move an object a distance d when opposed by a force F, such as gravity:

work = force x distance

$$w = F\,d \tag{2.5.1}$$

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), we can also write Equation 2.5.1 as follows:

work= mass x acceleration x distance

$$w = m\,a\,d \tag{2.5.2}$$

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth.

Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the force of gravity. The amount of work done (*w*) and thus the energy required depends on three things:

1. the height of the second floor (the distance *d*);
2. your mass, which must be raised that distance against the downward acceleration due to gravity; and
3. your path.

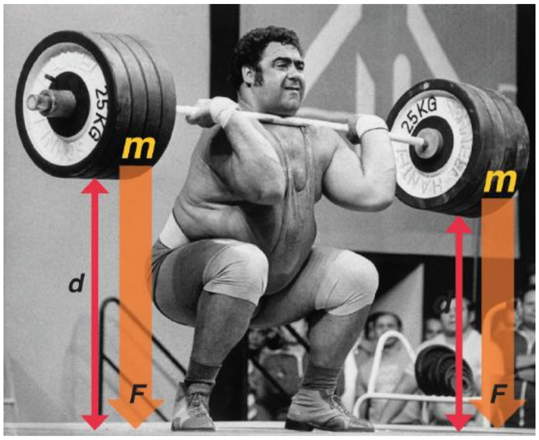


Figure 2.5.2: An Example of Mechanical Work. One form of energy is mechanical work, the energy required to move an object of mass *m* a distance *d* when opposed by a force *F*, such as gravity.

In contrast, heat (q) is thermal energy that can be transferred from an object at one temperature to an object at another temperature. The net transfer of thermal energy stops when the two objects reach the same temperature.

Energy is an *extensive* property of matter—for example, the amount of **thermal energy** in an object is proportional to both its mass and its temperature. A water heater that holds 150 L of water at 50°C contains much more thermal energy than does a 1 L pan of water at 50°C. Similarly, a bomb contains much more chemical energy than does a firecracker. We now present a more detailed description of kinetic and potential energy.

Kinetic and Potential Energy

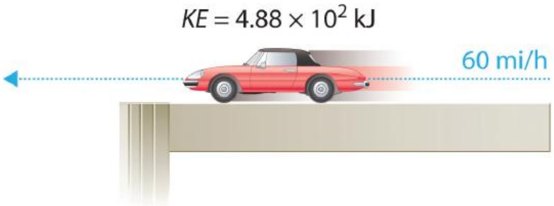
The kinetic energy of an object is related to its mass m and velocity v:

$$KE = \frac{1}{2}mv^2 \tag{2.5.3}$$

For example, the kinetic energy of a 1360 kg (approximately 3000 lb) automobile traveling at a velocity of 26.8 m/s (approximately 60 mi/h) is

$$KE = \frac{1}{2}(1360 kg)(26.8 ms)^2 = 4.88 \times 10^5 g \cdot m^2 \tag{2.5.4}$$

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J), is named after the British physicist James Joule (1818–1889), an early worker in the field of energy. is defined as 1 kilogram·meter^2/second^2 (kg·m^2/s^2). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10^3 J). For example, the kinetic energy of the 1360 kg car traveling at 26.8 m/s is 4.88×10^5 J or 4.88×10^2 kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.



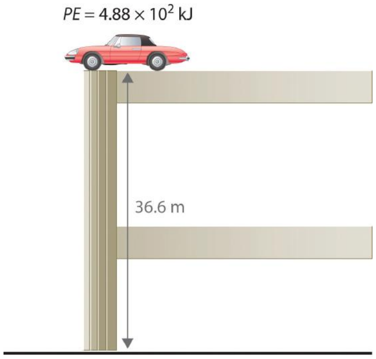
To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is $w = Fd$. According to Equation 2.5.2, the force (F) exerted by gravity on any object is equal to its mass (m, in this case, 1360 kg) times the acceleration (a) due to gravity (g, 9.81 m/s^2 at Earth's surface). The distance (d) is the height (h) above street level (in this case, 36.6 m). Thus the potential energy of the car is as follows:

$$PE = F\ d = m\ a\ d = m\ g\ h \tag{2.5.5}$$

$$PE = (1360, Kg)\left(\frac{9.81\, m}{s^2}\right)(36.6\ m) = 4.88 \times 10^5\ \frac{Kg \cdot m}{s^2} \tag{2.5.6}$$

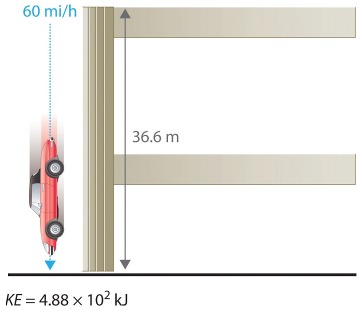
$$= 4.88 \times 10^5 J = 488\ kJ \tag{2.5.7}$$

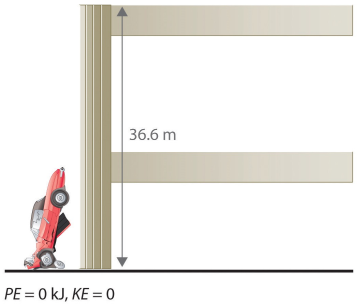
The units of potential energy are the same as the units of kinetic energy. Notice that in this case the potential energy of the stationary automobile at the top of a 36.6 m high parking garage is the same as its kinetic energy at 60 mi/h.



If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic energy would both be zero.

Potential energy is usually defined relative to an arbitrary standard position (in this case, the street was assigned an elevation of zero). As a result, we usually calculate only differences in potential energy: in this case, the difference between the potential energy of the car on the top level of the parking garage and the potential energy of the same car on the street at the base of the garage.





Units of Energy

The units of energy are the same for all forms of energy. Energy can also be expressed in the non-SI units of calories (cal), where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5°C to 15.5°C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1°C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0°C–100°C. The name is derived from the Latin *calor*, meaning "heat." Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$$1\ cal = 4.184\ J \text{ exactly} \tag{2.5.8}$$

$$1\ J = 0.2390\ cal \tag{2.5.9}$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information.

✓ Example 2.5.1

a. If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?
b. A batter hits a pop fly, and the baseball (with a mass of 149 g) reaches an altitude of 250 ft. If we assume that the ball was 3 ft above home plate when hit by the batter, what is the increase in its potential energy?

Given: mass and velocity or height

Asked for: kinetic and potential energy

Strategy:

Use Equation 5.1.4 to calculate the kinetic energy and Equation 5.1.6 to calculate the potential energy, as appropriate.

Solution:

a. The kinetic energy of an object is given by $\frac{1}{2}mv^2$ In this case, we know both the mass and the velocity, but we must convert the velocity to SI units:

$$v = \left(\frac{100\ \cancel{mi}}{1\ \cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.61\ \cancel{km}}{1\ \cancel{mi}}\right)\left(\frac{1000\ m}{1\ \cancel{km}}\right) = 44.7\ m/s$$

The kinetic energy of the baseball is therefore

$$KE = 1492\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{44.7\ m}{s}\right)^2 = 1.49\times 10^2\ \frac{kg\cdot m^2}{s^2} = 1.49\times 10^2\ J$$

b. The increase in potential energy is the same as the amount of work required to raise the ball to its new altitude, which is (250 − 3) = 247 feet above its initial position. Thus

$$PE = 149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{9.81\ m}{s^2}\right)\left(247\ \cancel{ft}\right)\left(\frac{0.3048\ m}{1\ \cancel{ft}}\right) = 1.10\times 10^2\ \frac{kg\cdot m^2}{s^2} = 1.10\times 10^2\ J$$

? Exercise 2.5.1

a. In a bowling alley, the distance from the foul line to the head pin is 59 ft, 10 13/16 in. (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)
b. What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

Answer a

3.10×10^2 J

Answer b

65 J

Summary

All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work. *Thermochemistry* is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. **Energy** is the capacity to do work. **Mechanical work** is the amount of energy required to move an object a given distance when opposed by a force. **Thermal energy** is due to the random motions of atoms, molecules, or ions in a substance. The **temperature** of an object is a measure of the amount of thermal energy it contains. **Heat (*q*)** is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of **potential energy (*PE*)**, energy caused by the relative position or orientation of an object. **Kinetic energy (*KE*)** is the energy an object possesses due to its motion. The most common units of energy are the **joule (J)**, defined as 1 (kg·m^2)/s^2, and the **calorie**, defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C (1 cal = 4.184 J).

CHAPTER OVERVIEW

3: Units, Measurements, and Conversions

A coffee maker’s instructions tell you to fill the coffeepot with 4 cups of water and use 3 scoops of coffee. When you follow these instructions, you are *measuring*. When you visit a doctor’s office, a nurse checks your temperature, height, weight, and perhaps blood pressure (Figure 3.1); the nurse is also measuring. Chemists measure the properties of matter using a variety of devices or measuring tools, many of which are similar to those used in everyday life. Rulers are used to measure length, balances (scales) are used to measure mass (weight), and graduated cylinders or pipettes are used to measure volume. Measurements made using these devices are expressed as quantities. A **quantity** is an amount of something and consists of a **number** and a **unit**. To understand chemistry, we need a clear understanding of the units chemists work with and the rules they follow for expressing numbers.

Figure 3.1: Measuring Blood Pressure. A nurse or a doctor measuring a patient’s blood pressure is taking a measurement. (GNU Free Documentation License; Pia von Lützau via Wikipedia).

Chapter Sections

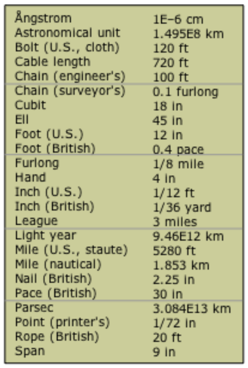
Contributors and Attributions

3.1: Base Units and Derived Units

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).



Ångstrom	1E–6 cm
Astronomical unit	1.495E8 km
Bolt (U.S., cloth)	120 ft
Cable length	720 ft
Chain (engineer's)	100 ft
Chain (surveyor's)	0.1 furlong
Cubit	18 in
Ell	45 in
Foot (U.S.)	12 in
Foot (British)	0.4 pace
Furlong	1/8 mile
Hand	4 in
Inch (U.S.)	1/12 ft
Inch (British)	1/36 yard
League	3 miles
Light year	9.46E12 km
Mile (U.S., staute)	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 3.1.1: Current and past units of distance

Table showing various forms of units for measuring distanced 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 the 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 *Systeme Internationale* (*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 3.1.1), with each base unit defined by a standard described in the NIST Web site.

Table 3.1.1: 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 3.1.2) 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 6.02x10^{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 3.1.2).

Table 3.1.2: Prefixes used to scale up or down base units

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 L = 1 dm^3 = 10^{-3} m^3
metric ton	t	1 t = 10^3 kg
united atomic mass unit (amu)	u	1 u = 1.66054×10^{-27} 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 Q 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 3.1.1

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 3.1.1.

Table 3.1.3: 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
-	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

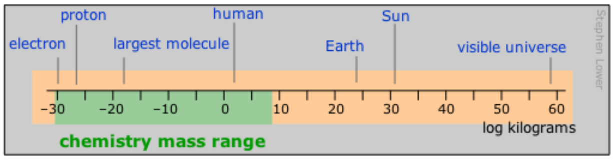
Dimensional analysis is widely employed when it is necessary to convert one kind of unit into another, and chemistry students often use it in "chemical arithmetic" calculations, in which context it is also known as the "Factor-Label" method. In this section, we will look at some of the quantities that 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 gravational field:

$$f = ma = mg \tag{3.1.1}$$

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.



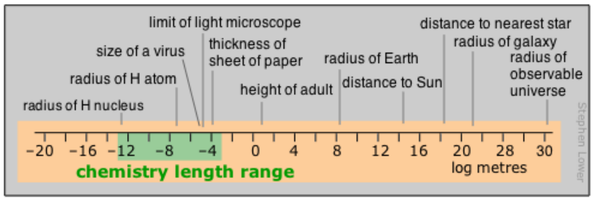
Numeric scale in terms of log kilogram. Range is negative 30 to 60 with intervals of 10. The range from negative 30 to 8 is highlighted in green to show chemistry mass range.

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 enivonmental 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

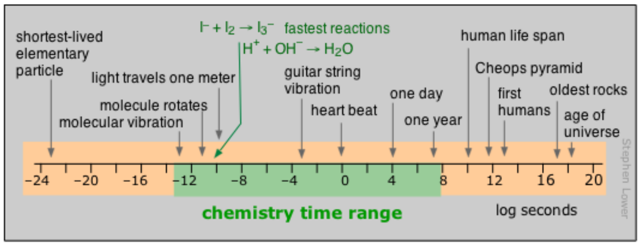
Chemists tend to work mostly in the moderately-small part of the distance range. Those who live in the lilliputian world of crystal- and molecular structures and atomic radii find the *picometer* a convenient currency, but one still sees the older non-SI unit called the *Ångstrom* used in this context; 1Å = 10^{-10} m = 100pm. 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.

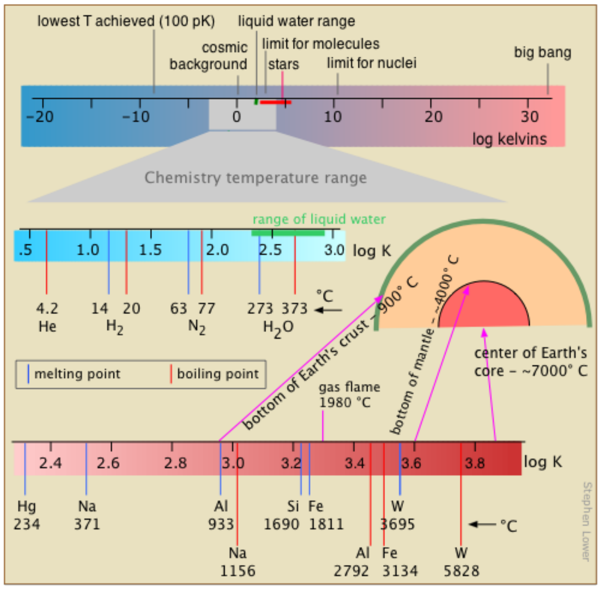


Numeric scale in terms of log seconds. Range is negative 24 to 20 with intervals of 4. The range from negative 12 to 8 is highlighted in green to show chemistry time range.

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 in 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° 100/180 = 5/9 the magnitude of the C°. Note the distinction between "°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 °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:

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

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

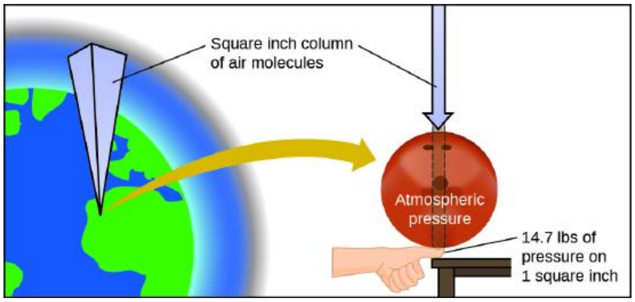


Figure 3.1.1: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

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.

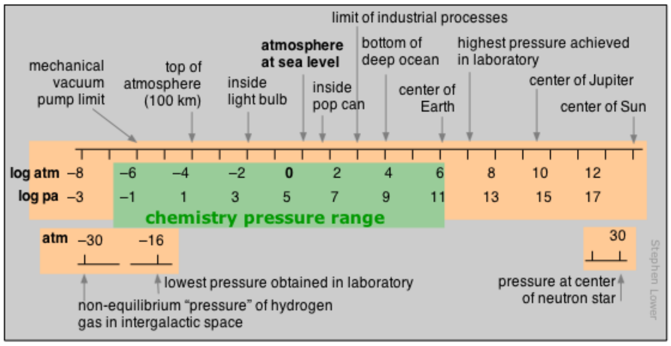
Video 3.1.1: A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased. A smaller scale demonstration of this phenomenon is briefly explained.

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 gravitional acceleration g exerts on this mass is

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

resulting in a pressure of 1.013 × 10^5 n m^{-2} = 1.013 × 10^5 Pa. The actual pressure at sea level varies with atmospheric conditions, so it is customary to define standard atmospheric pressure as 1 atm = 1.01325 x 10^5 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 × 10^5 = 0.967 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 Evangalisto 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 under its own weight until the downward force 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.

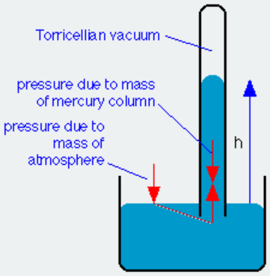


Diagram showing a barometer setup with arrows pointing on the surface of the liquid to indicate pressure due to atmosphere as well as arrow pointing up in the vertical tube to show height of liquid in the tube.

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

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- 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).

3.2: Scientific Notation - Writing Large and Small Numbers

Learning Objectives

- Express a large number or a small number in scientific notation.
- Convert a number in scientific notation to standard conventional form.

The instructions for making a pot of coffee specified 3 scoops (rather than 12,000 grounds) because any measurement is expressed more efficiently with units that are appropriate in size. In science, however, we often must deal with quantities that are extremely small or incredibly large. For example, you may have 5,000,000,000,000 red blood cells in a liter of blood, and the diameter of an iron atom is 0.000000014 inches. Numbers with many zeros can be cumbersome to work with, so scientists use scientific notation.

Scientific notation is a system for expressing very large or very small numbers in a compact manner. It uses the idea that such numbers can be rewritten as a simple number multiplied by 10 raised to a certain exponent, or power.

Let us look first at very large numbers. Suppose a spacecraft is 1,500,000 miles from Mars. The number 1,500,000 can be thought of as follows:

$$1.5 \times \underbrace{\underbrace{1{,}000{,}000}_{10 \times 10 \times 10 \times 10 \times 10 \times 10}}_{10^6} = 1.5 \times 10^6$$

That is, 1,500,000 is the same as 1.5 times 1 million, and 1 million is 10 × 10 × 10 × 10 × 10 × 10, or 10^6 (which is read as “ten to the sixth power”). Therefore, 1,500,000 can be rewritten as 1.5 times 10^6, or 1.5×10^6. The distance of the spacecraft from Mars can therefore be expressed as 1.5×10^6 miles.

Recall that:

- $10^0 = 1$
- $10^1 = 10$
- $10^2 = 100$
- $10^3 = 1{,}000$
- $10^4 = 10{,}000$
- and so forth

The standard convention for expressing numbers in scientific notation is to write a single *nonzero* first digit, a decimal point, and the rest of the digits, excluding any trailing zeros (see rules for significant figures in the next section for more details on what to exclude). This number is followed by a multiplication sign and then by 10 raised to the power necessary to reproduce the original number. For example, although 1,500,000 can also be written as $15. \times 10^5$ (which would be $15. \times 100{,}000$), the convention is to have only one digit before the decimal point. How do we know to what power 10 is raised? The power is the number of places you have to move the decimal point to the *left* to place it after the <u>first digit</u>, so that the number being multiplied is *between 1 and 10*:

$$1{,}\underset{\curvearrowleft\curvearrowleft\curvearrowleft\,\curvearrowleft\curvearrowleft\curvearrowleft}{500{,}000} = 1.5 \times 10^{6}$$

✓ Example 3.2.1: Scientific Notation

Express each number in scientific notation.

a. 67,000,000,000
b. 1,689
c. 12.6

Answer a

Moving the decimal point 10 places to the left gives 6.7×10^{10}.

Answer b

The decimal point is assumed to be at the end of the number, so moving it three places to the left gives 1.689×10^3.

Answer c

In this case, we need to move the decimal point only one place to the left, which yields 1.26 × 10^1.

Exercise 3.2.1

Express each number in scientific notation.

a. 1,492
b. 102,000,000
c. 101,325

Answer a

Moving the decimal point 3 places to the left gives 1.492 × 10^3.

Answer b

The decimal point is assumed to be at the end of the number, so moving it 8 places to the left gives 1.02 × 10^8.

Answer c

Moving the decimal point 5 places to the left yields 1.01325 × 10^5.

To change a number in **scientific notation** to **standard form**, we reverse the process, moving the decimal point to the right. Add zeros to the end of the number being converted, if necessary, to produce a number of the proper magnitude. Lastly, we drop the number 10 and its power.

$$1.5 \times 10^{6} = 1.\underbrace{500000}. = 1{,}500{,}000$$

Example 3.2.2

Express each number in standard, or conventional notation.

a. 5.27 × 10^4
b. 1.0008 × 10^6

Answer a

Moving the decimal four places to the right and adding zeros give 52,700.

Answer b

Moving the decimal six places to the right and adding zeros give 1,000,800.

Exercise 3.2.2

Express each number in standard, or conventional notation.

a. 6.98×10^8
b. 1.005×10^2

Answer a

Moving the decimal point eight places to the right and adding zeros give 698,000,000.

Answer b

Moving the decimal point two places to the right gives 100.5

We can also use scientific notation to express numbers whose magnitudes are less than 1. For example, the quantity 0.006 centimeters can be expressed as follows:

$$6 \times \underbrace{\frac{1}{1,000}}_{\underbrace{\frac{1}{10} \times \frac{1}{10} \times \frac{1}{10}}_{10^{-3}}} = 6 \times 10^{-3}$$

That is, 0.006 centimeters is the same as 6 *divided by* one thousand, which is the same as 6 *divided* by 10 x 10 x 10 or 6 *times* 10^{-3} (which is read as "ten to the negative third power"). Therefore, 0.006 centimeters can be rewritten as 6 times 10^{-3}, or 6×10^{-3} centimeters.

Recall that:

- $10^{-1} = 1/10$
- $10^{-2} = 1/100$
- $10^{-3} = 1/1,000$
- $10^{-4} = 1/10,000$
- $10^{-5} = 1/100,000$
- and so forth

We use a negative number as the power to indicate the number of places we have to move the decimal point to the right to make it follow the first nonzero digit so that the number is between 1 and 10. This is illustrated as follows:

$$0.\underset{\smile}{0}\underset{\smile}{0}\underset{\smile}{6} = 6 \times 10^{-3}$$

Note:

In writing scientific notations, the convention is to have only one digit before the decimal point.

- Numbers that are greater than one have a positive power in scientific notation. If the decimal point is moved to the left n places, the power (n) of 10 is positive. $1,\underset{\smile}{5}\underset{\smile}{0}\underset{\smile}{0},\underset{\smile}{0}\underset{\smile}{0}\underset{\smile}{0} = 1.5 \times 10^{6}$
- Numbers that are less than one have a negative power in scientific notation. If the decimal point is moved to the right n places, the power (n) of 10 is negative. $0.\underset{\smile}{0}\underset{\smile}{0}\underset{\smile}{6} = 6 \times 10^{-3}$

Example 3.2.3

Express each number in scientific notation.

a. 0.000006567
b. −0.0004004
c. 0.000000000000123

Answer a

Move the decimal point six places to the right to get 6.567×10^{-6}.

Answer b

Move the decimal point four places to the right to get -4.004×10^{-4}. The negative sign on the number itself does not affect how we apply the rules of scientific notation.

Answer c

Move the decimal point 13 places to the right to get 1.23×10^{-13}.

Exercise 3.2.3

Express each number in scientific notation.

a. 0.000355
b. 0.314159

c. −0.051204

Answer a

Moving the decimal point four places to the right gives 3.55×10^{-4}.

Answer b

Moving the decimal point one place to the right gives 3.14159×10^{-1}.

Answer c

Moving the decimal point one place to the right gives -5.1204×10^{-2}.

As with numbers with positive powers of 10, when changing from **scientific** notation to **standard or conventional** format, we reverse the process.

$$6 \times 10^{-3} = \underset{\curvearrowleft\curvearrowleft\curvearrowleft}{.006.} = 0.006$$

Note

Changing a number in scientific notation to standard form:

- If the scientific notation has a positive power, the standard number is greater than one. Example: $8 \times 10^{4} = 80{,}000$
- If the scientific notation has a negative power, then the standard number is less than one. Example: $8 \times 10^{-2} = 0.08$

✓ Example 3.2.4

Change the number in scientific notation to standard form.

a. 6.22×10^{-2}
b. 9.9×10^{-9}

Answer a

0.0622

Answer b

0.0000000099

? Exercise 3.2.4

Change the number in scientific notation to standard form.

a. 9.98×10^{-5}
b. 5.109×10^{-8}

Answer a

0.0000998

Answer b

0.00000005109

Although calculators can show 8 to 10 digits in their display windows, that is not always enough when working with very large or very small numbers. For this reason, many calculators are designed to handle scientific notation. The method for entering scientific notation differs for each calculator model, so take the time to learn how to do it properly on your calculator, *asking your instructor for assistance if necessary*. If you do not learn to enter scientific notation into your calculator properly, you will not get the correct final answer when performing a calculation.

Concept Review Exercises

1. Why it is easier to use scientific notation to express very large or very small numbers?
2. What is the relationship between how many places a decimal point moves and the power of 10 used in changing a conventional number into scientific notation?

Answers

1. Scientific notation is more convenient than listing a large number of zeros.
2. The number of places the decimal point moves equals the power of 10. The power of 10 is positive if the decimal point moves to the left and negative if the decimal point moves to the right.

Key Takeaway

- Large or small numbers are expressed in scientific notation, which use powers of 10.

3.3: The Reliability of Measurement

Learning Objectives

- Compare and contrast exact and uncertain numbers.
- Correctly represent uncertainty in quantities using significant figures.
- Identify the number of significant figures in value.
- Solve problems that involve various calculations and report the results with the appropriate number of significant figures.
- Apply proper rounding rules to computed quantities
- Define accuracy and precision, and use accuracy and precision to describe data sets.

Counting is the only type of measurement that is free from uncertainty, provided the number of objects being counted does not change while the counting process is underway. The result of such a counting measurement is an example of an exact number. If we count eggs in a carton, we know *exactly* how many eggs the carton contains. The numbers of defined quantities are also exact. By definition, 1 foot is exactly 12 inches, 1 inch is exactly 2.54 centimeters, and 1 gram is exactly 0.001 kilogram. Quantities derived from measurements other than counting, however, are uncertain to varying extents due to practical limitations of the measurement process used.

Significant Figures in Measurement

The numbers of measured quantities, unlike defined or directly counted quantities, are not exact. To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.

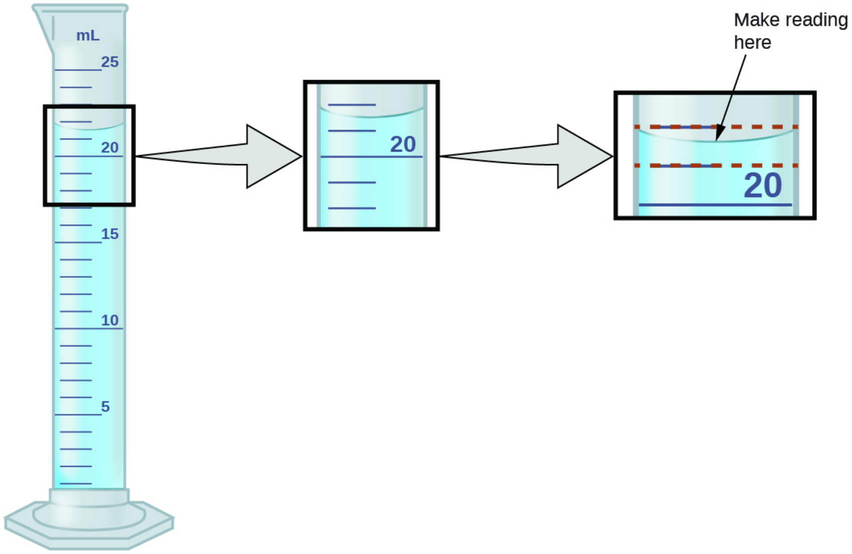


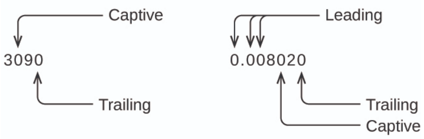
Figure $3.3.1$: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

A 25 millilter graduated cylinder filled with liquid. The markings on the cylinders is zoomed in to show the bottom of the meniscus between 21 and 22 milliliters.

Refer to the illustration in Figure $3.3.1$. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

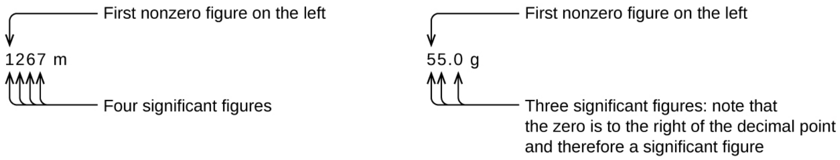
This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams.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

Whenever you make a measurement properly, all the digits in the result are significant. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought. We will use the terms "leading," "trailing," and "captive" for the zeros and will consider how to deal with them.



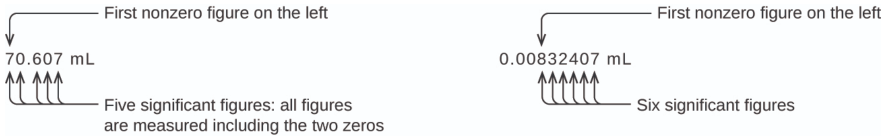
The left diagram uses the example of 3090. The zero in the hundreds place is labeled "captive" and the zero in the ones place is labeled trailing. The right diagram uses the example 0.008020. The three zeros in the ones, tenths, and hundredths places are labeled "leading." The zero in the ten-thousandths place is labeled "captive" and the zero in the millionths place is labeled "trailing."

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



The left diagram uses the example of 1267 meters. The number 1 is the first nonzero figure on the left. 1267 has 4 significant figures in total. The right diagram uses the example of 55.0 grams. The number 5 in the tens place is the first nonzero figure on the left. 55.0 has 3 significant figures. Note that the 0 is to the right of the decimal point and therefore is a significant figure.

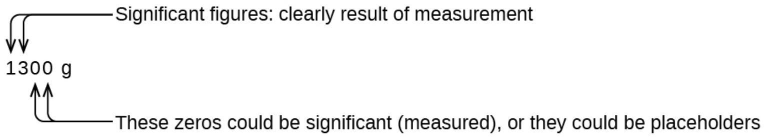
Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



The left diagram uses the example of 70.607 milliliters. The number 7 is the first nonzero figure on the left. 70.607 has 5 significant figures in total, as all figures are measured including the 2 zeros. The right diagram uses the example of 0.00832407 M L. The number 8 is the first nonzero figure on the left. 0.00832407 has 6 significant figures.

The leading zeros in this example are not significant. We could use exponential notation (as described in Appendix B) and express the number as 8.32407×10^{-3}; then the number 8.32407 contains all of the significant figures, and 10^{-3} locates the decimal point.

The number of significant figures is uncertain in a number that ends with a zero to the left of the decimal point location. The zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located. The ambiguity can be resolved with the use of exponential notation: 1.3×10^3 (two significant figures), 1.30×10^3 (three significant figures, if the tens place was measured), or 1.300×10^3 (four significant figures, if the ones place was also measured). In cases where only the decimal-formatted number is available, it is prudent to assume that all trailing zeros are not significant.



This figure uses the example of 1300 grams. The one and the 3 are significant figures as they are clearly the result of measurement. The 2 zeros could be significant if they were measured or they could be placeholders.

When determining significant figures, be sure to pay attention to reported values and think about the measurement and significant figures in terms of what is reasonable or likely—that is, whether the value makes sense. For example, the official January 2014 census reported the resident population of the US as 317,297,725. Do you think the US population was correctly determined to the reported nine significant figures, that is, to the exact number of people? People are constantly being born, dying, or moving into or out of the country, and assumptions are made to account for the large number of people who are not actually counted. Because of these uncertainties, it might be more reasonable to expect that we know the population to within perhaps a million or so, in which case the population should be reported as 317 million, or 3.17×10^8 people.

Significant Figures in Calculations

A second important principle of uncertainty is that results calculated from a measurement are at least as uncertain as the measurement itself. We must take the uncertainty in our measurements into account to avoid misrepresenting the uncertainty in calculated results. One way to do this is to report the result of a calculation with the correct number of significant figures, which is determined by the following three rules for rounding numbers:

1. When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (the least precise value in terms of addition and subtraction).
2. When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, we “round down” and leave the retained digit unchanged; if it is more than 5, we “round up” and increase the retained digit by 1; if the dropped digit *is* 5, we round up or down, whichever yields an even value for the retained digit. (The last part of this rule may strike you as a bit odd, but it’s based on reliable statistics and is aimed at avoiding any bias when dropping the digit “5,” since it is equally close to both possible values of the retained digit.)

The following examples illustrate the application of this rule in rounding a few different numbers to three significant figures:

- 0.028675 rounds “up” to 0.0287 (the dropped digit, 7, is greater than 5)
- 18.3384 rounds “down” to 18.3 (the dropped digit, 3, is less than 5)
- 6.8752 rounds “up” to 6.88 (the dropped digit is 5, and the retained digit is even)
- 92.85 rounds “down” to 92.8 (the dropped digit is 5, and the retained digit is even)

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

✓ Example 3.3.1: Rounding Numbers

Round the following to the indicated number of significant figures:

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

Solution

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

? Exercise 3.3.1

Round the following to the indicated number of significant figures:

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

Answer a

0.42

Answer b

0.00387

Answer c

421.2

Answer d

28,684

✓ Example 3.3.2: Addition and Subtraction with Significant Figures Rule:

When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (i.e., the least precise value in terms of addition and subtraction).

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

Solution

(a)

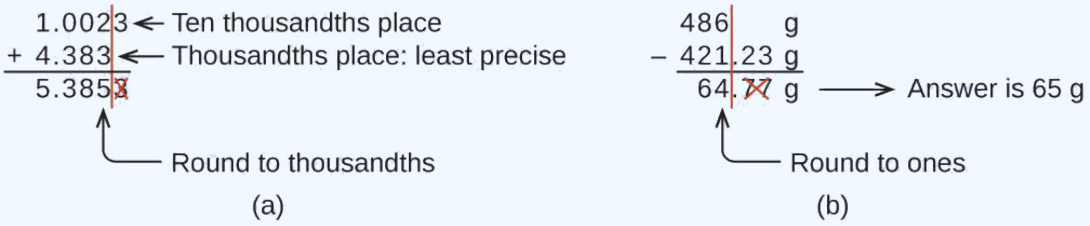
$$\begin{array}{r} 1.0023\text{ g} \\ +\ \underline{4.383\text{ g}} \\ 5.3853\text{ g} \end{array}$$

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

(b)

$$\begin{array}{r} 486\text{ g} \\ -\ \underline{421.23\text{ g}} \\ 64.77\text{ g} \end{array}$$

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



? Exercise 3.3.2

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

Answer a

2.64 mL

Answer b

0.658 m

✓ Example 3.3.3: Multiplication and Division with Significant Figures

Rule: When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).

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

Solution

(a)

$$0.6238 \text{ cm} \times 6.6 \text{ cm} = 4.11708 \text{ cm}^2 \rightarrow \text{result is } 4.1 \text{ cm}^2 \text{ (round to two significant figures)}$$

$$\text{four significant figures} \times \text{two significant figures} \rightarrow \text{two significant figures answer}$$

(b)

$$\frac{421.23 \text{ g}}{486 \text{ mL}} = 0.86728... \text{ g/mL} \rightarrow \text{result is } 0.867 \text{ g/mL (round to three significant figures)}$$

$$\frac{\text{five significant figures}}{\text{three significant figures}} \rightarrow \text{three significant figures answer}$$

? Exercise 3.3.3

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

Answer a

0.747 cm^2

Answer b

0.9884 m/s

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

✓ Example 3.3.4: Calculation with Significant Figures

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

Solution

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

? Exercise 3.3.4: Determination of Density Using Water Displacement

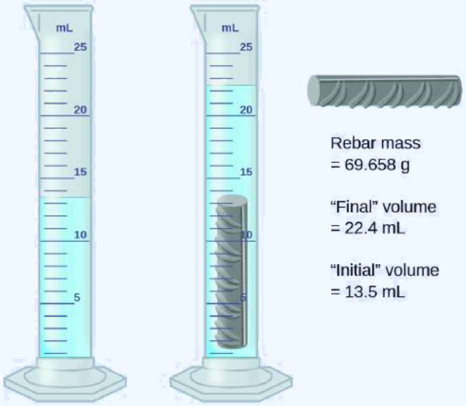
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer

1.034 g/mL

✓ Example 3.3.4

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



A graduated cylinder filled with liquid is shown. One shows the level before the rebar is added and the other shows the level with the rebar submerged in the liquid. Rebar mass is 69.658 grams, final volume is 22.4 milliliters, and initial volume is 13.5 milliliters.

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

Solution

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

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

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

The density is the mass-to-volume ratio:

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

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

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

? Exercise 3.3.4

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

A graduated cylinder filled with liquid is shown. One shows the level before the material is added and the other shows the level with the material submerged in the liquid. Mass is 51.842 grams, final volume is 19.8 milliliters, and initial volume is 17.1 milliliters.

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

Answer a

19 g/cm^3

Answer b

It is likely gold; it has the right appearance for gold and very close to the density given for gold.

Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the precision and the accuracy of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 3.3.2).

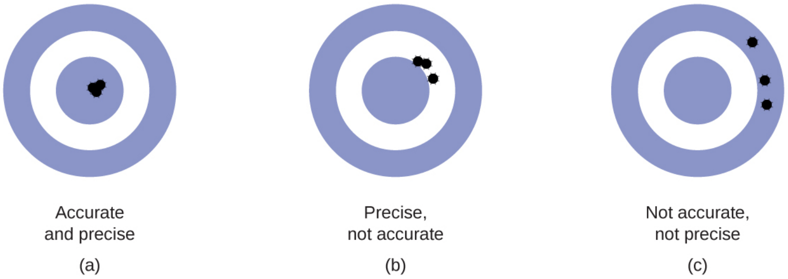


Figure 3.3.2: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in Table 3.3.2.

Table 3.3.2: Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers

Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1

Dispenser #1	Dispenser #2	Dispenser #3
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Considering these results, she will report that dispenser #1 is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low). Results for dispenser #2 represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL). Finally, she can report that dispenser #3 is working well, dispensing cough syrup both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

Summary

Quantities can be exact or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the measurement. The uncertainty of a calculated value depends on the uncertainties in the values used in the calculation and is reflected in how the value is rounded. Measured values can be accurate (close to the true value) and/or precise (showing little variation when measured repeatedly).

Glossary

uncertainty

estimate of amount by which measurement differs from true value

significant figures

(also, significant digits) all of the measured digits in a determination, including the uncertain last digit

rounding

procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

precision

how closely a measurement matches the same measurement when repeated

exact number

number derived by counting or by definition

accuracy

how closely a measurement aligns with a correct value

3.4: Significant Figures - Approximating Uncertainty

Learning Objectives

- Give an example of a measurement whose number of significant digits is clearly too great, and explain why.
- State the purpose of rounding off, and describe the information that must be known to do it properly.
- Round off a number to a specified number of significant digits.
- Explain how to round off a number whose second-most-significant digit is 9.
- Carry out a simple calculation that involves two or more observed quantities, and express the result in the appropriate number of significant figures.

The numerical values we deal with in science (and in many other aspects of life) represent measurements whose values are never known exactly. Our pocket-calculators or computers don't know this; they treat the numbers we punch into them as "pure" mathematical entities, with the result that the operations of arithmetic frequently yield answers that are physically ridiculous even though mathematically correct. The purpose of this unit is to help you understand why this happens, and to show you what to do about it.

Digits: Significant and otherwise

Consider the two statements shown below:

- **"The population of our city is 157,872."**
- **"The number of registered voters as of Jan 1 was 27,833.**

Which of these would you be justified in dismissing immediately? Certainly not the second one, because it probably comes from a database which contains one record for each voter, so the number is found simply by counting the number of records. The first statement cannot possibly be correct. Even if a city's population could be defined in a precise way (Permanent residents? Warm bodies?), how can we account for the minute-by minute changes that occur as people are born and die, or move in and move away?

What is the difference between the two population numbers stated above? The first one expresses a quantity that cannot be known exactly — that is, it carries with it a degree of uncertainty. It is quite possible that the last census yielded precisely 157,872 records, and that this might be the "population of the city" for legal purposes, but it is surely not the "true" population. To better reflect this fact, one might list the population (in an atlas, for example) as **157,900** or even **158,000**. These two quantities have been rounded off to four and three significant figures, respectively, and the have the following meanings:

- **157900** (the significant digits are underlined here) implies that the population is believed to be within the range of about 157850 to about 157950. In other words, the population is 157900±50. The "plus-or-minus 50" appended to this number means that we consider the absolute uncertainty of the population measurement to be 50 – (–50) = 100. We can also say that the relative uncertainty is 100/157900, which we can also express as 1 part in 1579, or 1/1579 = 0.000633, or about 0.06 percent.
- The value **158000** implies that the population is likely between about 157500 and 158500, or 158000±500. The absolute uncertainty of 1000 translates into a relative uncertainty of 1000/158000 or 1 part in 158, or about 0.6 percent.

Which of these two values we would report as "the population" will depend on the degree of confidence we have in the original census figure; if the census was completed last week, we might round to four significant digits, but if it was a year or so ago, rounding to three places might be a more prudent choice. In a case such as this, there is no really objective way of choosing between the two alternatives.

This illustrates an important point: the concept of *significant digits* has less to do with mathematics than with our confidence in a measurement. This confidence can often be expressed numerically (for example, the height of a liquid in a measuring tube can be read to ±0.05 cm), but when it cannot, as in our population example, we must depend on our personal experience and judgment.

So, what is a significant digit? According to the usual definition, it is all the numerals in a measured quantity (counting from the left) whose values are considered as known exactly, plus one more whose value could be one more or one less:

- In "157900" (four significant digits), the left most three digits are known exactly, but the fourth digit, "9" could well be "8" if the "true value" is within the implied range of 157850 to 157950.
- In "*158*000" (three significant digits), the left most two digits are known exactly, while the third digit could be either "7" or "8" if the true value is within the implied range of 157500 to 158500.

Although rounding off always leads to the loss of numeric information, what we are getting rid of can be considered to be “numeric noise” that does not contribute to the quality of the measurement. The purpose in rounding off is to avoid expressing a value to a greater degree of precision than is consistent with the uncertainty in the measurement.

Implied Uncertainty

If you know that a balance is accurate to within 0.1 mg, say, then the uncertainty in any measurement of mass carried out on this balance will be ±0.1 mg. Suppose, however, that you are simply told that an object has a length of 0.42 cm, with no indication of its precision. In this case, all you have to go on is the number of digits contained in the data. Thus the quantity “0.42 cm” is specified to 0.01 unit in 0 42, or one part in 42 . The implied relative uncertainty in this figure is 1/42, or about 2%. The precision of any numeric answer calculated from this value is therefore limited to about the same amount.

Rounding Error

It is important to understand that the number of significant digits in a value provides only a rough indication of its precision, and that information is lost when rounding off occurs. Suppose, for example, that we measure the weight of an object as 3.28 g on a balance believed to be accurate to within ±0.05 gram. The resulting value of 3.28±.05 gram tells us that the true weight of the object could be anywhere between 3.23 g and 3.33 g. The absolute uncertainty here is 0.1 g (±0.05 g), and the relative uncertainty is 1 part in 32.8, or about 3 percent.

How many significant digits should there be in the reported measurement? Since only the left most “3” in “3.28” is certain, you would probably elect to round the value to 3.3 g. So far, so good. But what is someone else supposed to make of this figure when they see it in your report? The value “3.3 g” suggests an *implied uncertainty* of 3.3±0.05 g, meaning that the true value is likely between 3.25 g and 3.35 g. This range is 0.02 g below that associated with the original measurement, and so rounding off has introduced a bias of this amount into the result. Since this is less than half of the ±0.05 g uncertainty in the weighing, it is not a very serious matter in itself. However, if several values that were rounded in this way are combined in a calculation, the rounding-off errors could become significant.

Rules for Rounding

The standard rules for rounding off are well known. Before we set them out, let us agree on what to call the various components of a numeric value.

- The *most significant digit* is the left most digit (not counting any leading zeros which function only as placeholders and are never significant digits.)
- If you are rounding off to ***n*** significant digits, then the *least significant digit* is the ***n***th digit from the most significant digit. The least significant digit can be a zero.
- The first non-significant digit is the ***n***+1th digit.

Rounding-off rules

- If the first non-significant digit is less than 5, then the least significant digit remains unchanged.
- If the first non-significant digit is greater than 5, the least significant digit is incremented by 1.
- If the first non-significant digit is 5, the least significant digit can either be incremented or left unchanged (*see below!*)
- All non-significant digits are removed.

Fantasies about fives

Students are sometimes told to increment the least significant digit by 1 if it is odd, and to leave it unchanged if it is even. One wonders if this reflects some idea that even numbers are somehow “better” than odd ones! (The ancient superstition is just the opposite, that only the odd numbers are "lucky".)

In fact, you could do it equally the other way around, incrementing only the even numbers. If you are only rounding a single number, it doesn't really matter what you do. However, when you are rounding a series of numbers that will be used in a calculation, if you treated each first nonsignificant 5 in the same way, you would be over- or understating the value of the rounded number, thus accumulating round-off error. Since there are equal numbers of even and odd digits, incrementing only the one kind will keep this kind of error from building up. You could do just as well, of course, by flipping a coin!

Table 3.4.1: Examples of rounding-off

number to round	number of significant digits	result	comment
34.216	3	34.2	First non-significant digit (1) is less than 5, so number is simply truncated.
2.252	2	2.2 or 2.3	First non-significant digit is 5, so least sig. digit can either remain unchanged or be incremented.
39.99	3	40.0	Crossing "decimal boundary", so all numbers change.
85,381	3	85,400	The two zeros are just placeholders
0.04597	3	0.0460	The two leading zeros are not significant digits.

Rounding up the Nines

Suppose that an object is found to have a weight of 3.98 ± 0.05 g. This would place its true weight somewhere in the range of **3.93** g to **4.03** g. In judging how to round this number, you count the number of digits in “3.98” that are known exactly, and you find none! Since the “4” is the left most digit whose value is uncertain, this would imply that the result should be rounded to one significant figure and reported simply as 4 g. An alternative would be to bend the rule and round off to two significant digits, yielding 4.0 g. How can you decide what to do? In a case such as this, you should look at the implied uncertainties in the two values, and compare them with the uncertainty associated with the original measurement.

Table 3.4.2

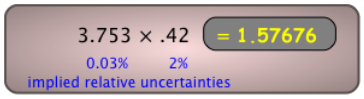
rounded value	implied max	implied min	absolute uncertainty	relative uncertainty
3.98 g	3.985 g	3.975 g	±.005 g or 0.01 g	1 in 400, or 0.25%
4 g	4.5 g	3.5 g	±.5 g or 1 g	1 in 4, 25%
4.0 g	**4.05 g**	**3.95 g**	**±.05 g or 0.1 g**	**1 in 40, 2.5%**

Clearly, rounding off to two digits is the only reasonable course in this example. Observed values should be rounded off to the number of digits that most accurately conveys the uncertainty in the measurement.

- Usually, this means rounding off to the number of significant digits in in the quantity; that is, the number of digits (counting from the left) that are known exactly, plus one more.
- When this cannot be applied (as in the example above when addition of subtraction of the absolute uncertainty bridges a power of ten), then we round in such a way that the relative implied uncertainty in the result is as close as possible to that of the observed value.

Rounding the Results of Calculations

When carrying out calculations that involve multiple steps, you should avoid doing any rounding until you obtain the final result. Suppose you use your calculator to work out the area of a rectangle:



rounded value	relative implied uncertainty
1.58	1 part in 158, or 0.6%
1.6	1 part in 16, or 6 %

Note

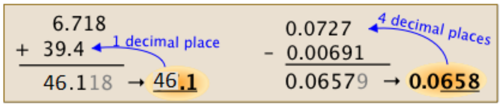
Your calculator is of course correct as far as the pure numbers go, but you would be wrong to write down "1.57676 cm^2" as the answer. Two possible options for rounding off the calculator answer are shown at the right.

It is clear that neither option is entirely satisfactory; rounding to 3 significant digits overstates the precision of the answer, whereas following the rule and rounding to the two digits in ".42" has the effect of throwing away some precision. In this case, it could be argued that rounding to three digits is justified because the implied relative uncertainty in the answer, 0.6%, is more consistent with those of the two factors.

> *The "rules" for rounding off are generally useful, convenient guidelines, but they do not always yield the most desirable result. When in doubt, it is better to rely on relative implied uncertainties.*

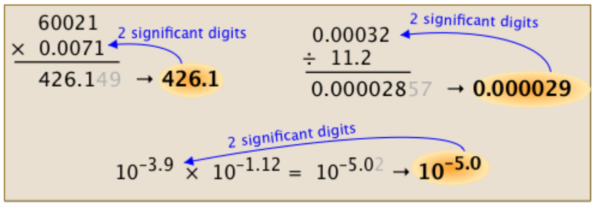
Addition and Subtraction

In operations involving significant figures, the answer is reported in such a way that it reflects the reliability of the **least precise** operation. An answer is no more precise that the least precise number used to get the answer. When adding or subtracting, we go by the number of *decimal places* (i.e., the number of digits on the right side of the decimal point) rather than by the number of significant digits. Identify the quantity having the smallest number of decimal places, and use this number to set the number of decimal places in the answer.



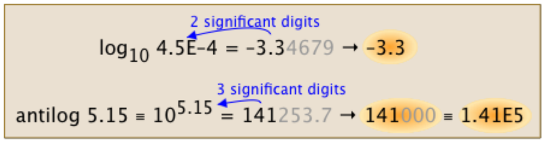
Multiplication and Division

The result must contain the same number of significant figures as in the value having the least number of significant figures.



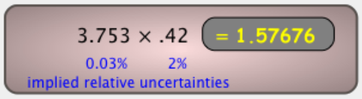
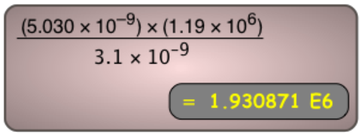
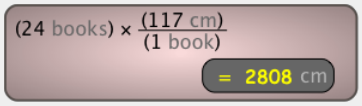
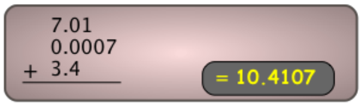
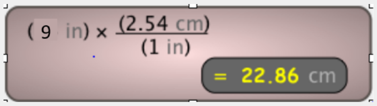
Logarithms and antilogarithms

If a number is expressed in the form $a \times 10^b$ ("scientific notation") with the additional restriction that the coefficient a is no less than 1 and less than 10, the number is in its *normalized* form. Express the base-10 logarithm of a value using the same number of significant figures as is present in the *normalized form* of that value. Similarly, for antilogarithms (numbers expressed as powers of 10), use the same number of significant figures as are in that power.

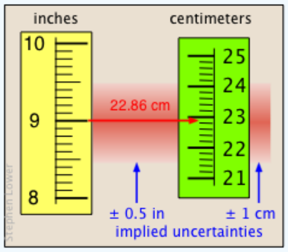


✓ Examples 3.4.1

The following examples will illustrate the most common problems you are likely to encounter in rounding off the results of calculations. They deserve your careful study!

calculator result	rounded	remarks
	1.6	Rounding to two significant figures yields an implied uncertainty of 1/16 or 6%, three times greater than that in the least-precisely known factor. This is a good illustration of how rounding can lead to the loss of information.
	1.9E6	The "3.1" factor is specified to 1 part in 31, or 3%. In the answer 1.9, the value is expressed to 1 part in 19, or 5%. These precisions are comparable, so the rounding-off rule has given us a reasonable result.
A certain book has a thickness of 117 mm; find the height of a stack of 24 identical books: 	2810 mm	The “24” and the “1” are exact, so the only uncertain value is the thickness of each book, given to 3 significant digits. The trailing zero in the answer is only a placeholder.
	10.4	In addition or subtraction, look for the term having the smallest number of decimal places, and round off the answer to the same number of places.
		
	23 cm	see below

The last of the examples shown above represents the very common operation of converting one unit into another. There is a certain amount of ambiguity here; if we take "9 in" to mean a distance in the range 8.5 to 9.5 inches, then the implied uncertainty is ±0.5 in, which is 1 part in 18, or about ± 6%. The relative uncertainty in the answer must be the same, since all the values are multiplied by the same factor, 2.54 cm/in. In this case we are justified in writing the answer to two significant digits, yielding an uncertainty of about ±1 cm; if we had used the answer "20 cm" (one significant digit), its implied uncertainty would be ±5 cm, or ±25%.



When the appropriate number of significant digits is in question, calculating the relative uncertainty can help you decide.

3.5: Solving Chemical Problems - Dimensional Analysis

Learning Objectives

- Explain the dimensional analysis (factor label) approach to mathematical calculations involving quantities.
- Describe how to use dimensional analysis to carry out unit conversions for a given property and computations involving two or more properties.
- Convert between the three main temperature units: Fahrenheit, Celsius, and Kelvin.

It is often the case that a quantity of interest may not be easy (or even possible) to measure directly but instead must be calculated from other directly measured properties and appropriate mathematical relationships. For example, consider measuring the average speed of an athlete running sprints. This is typically accomplished by measuring the *time* required for the athlete to run from the starting line to the finish line, and the *distance* between these two lines, and then computing *speed* from the equation that relates these three properties:

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

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

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

Note that this simple arithmetic involves dividing the numbers of each measured quantity to yield the number of the computed quantity (100/10 = 10) *and likewise* dividing the units of each measured quantity to yield the unit of the computed quantity (m/s = m/s). Now, consider using this same relation to predict the time required for a person running at this speed to travel a distance of 25 m. The same relation between the three properties is used, but in this case, the two quantities provided are a speed (10 m/s) and a distance (25 m). To yield the sought property, time, the equation must be rearranged appropriately:

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

The time can then be computed as:

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

Again, arithmetic on the numbers (25/10 = 2.5) was accompanied by the same arithmetic on the units (m/m/s = s) to yield the number and unit of the result, 2.5 s. Note that, just as for numbers, when a unit is divided by an identical unit (in this case, m/m), the result is “1”—or, as commonly phrased, the units “cancel.”

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

Conversion Factors and Dimensional Analysis

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

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

Several other commonly used conversion factors are given in Table $3.5.1$.

Table $3.5.1$: Common Conversion Factors

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

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

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

Since this simple arithmetic involves *quantities*, the premise of dimensional analysis requires that we multiply both *numbers and units*. The numbers of these two quantities are multiplied to yield the number of the product quantity, 86, whereas the units are multiplied to yield

$$\frac{\text{in.} \times \text{cm}}{\text{in.}}.$$

Just as for numbers, a ratio of identical units is also numerically equal to one,

$$\frac{\text{in.}}{\text{in.}} = 1$$

and the unit product thus simplifies to *cm*. (When identical units divide to yield a factor of 1, they are said to “cancel.”) Using dimensional analysis, we can determine that a unit conversion factor has been set up correctly by checking to confirm that the original unit will cancel, and the result will contain the sought (converted) unit.

Example $3.5.1$: Using a Unit Conversion Factor

The mass of a competition Frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g (Table $3.5.1$).

Solution

If we have the conversion factor, we can determine the mass in kilograms using an equation similar the one used for converting length from inches to centimeters.

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

We write the unit conversion factor in its two forms:

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

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

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

Exercise 3.5.1

Convert a volume of 9.345 qt to liters.

Answer

8.844 L

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

Example 3.5.2: Computing Quantities from Measurement Results

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

Solution

Since density $= \frac{\text{mass}}{\text{volume}}$, we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A $\times$ unit conversion factor. The necessary conversion factors are given in Table 1.7.1: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. We can convert mass from pounds to grams in one step:

$$9.26\ \cancel{\text{lb}} \times \frac{453.59\text{ g}}{1\ \cancel{\text{lb}}} = 4.20 \times 10^3\text{ g}$$

We need to use two steps to convert volume from quarts to milliliters.

1. *Convert quarts to liters.*

$$4.00\ \cancel{\text{qt}} \times \frac{1\text{ L}}{1.0567\ \cancel{\text{qt}}} = 3.78\text{ L}$$

2. *Convert liters to milliliters.*

$$3.78\ \cancel{\text{L}} \times \frac{1000\text{ mL}}{1\ \cancel{\text{L}}} = 3.78 \times 10^3\text{ mL}$$

Then,

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

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

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

Exercise 3.5.2

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

Answer

2.956×10^{-2} L

Example 3.5.3: Computing Quantities from Measurement Results

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

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

Solution

(a) We first convert distance from kilometers to miles:

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

and then convert volume from liters to gallons:

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

Then,

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

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

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

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

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

? Exercise 3.5.3

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

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

Answer a

51 mpg

Answer b

$62

Conversion of Temperature Units

We use the word temperature to refer to the hotness or coldness of a substance. One way we measure a change in temperature is to use the fact that most substances expand when their temperature increases and contract when their temperature decreases. The mercury or alcohol in a common glass thermometer changes its volume as the temperature changes. Because the volume of the liquid changes more than the volume of the glass, we can see the liquid expand when it gets warmer and contract when it gets cooler.

To mark a scale on a thermometer, we need a set of reference values: Two of the most commonly used are the freezing and boiling temperatures of water at a specified atmospheric pressure. On the Celsius scale, 0 °C is defined as the freezing temperature of water and 100 °C as the boiling temperature of water. The space between the two temperatures is divided into 100 equal intervals, which we call degrees. On the Fahrenheit scale, the freezing point of water is defined as 32 °F and the boiling temperature as 212 °F. The space between these two points on a Fahrenheit thermometer is divided into 180 equal parts (degrees).

Defining the Celsius and Fahrenheit temperature scales as described in the previous paragraph results in a slightly more complex relationship between temperature values on these two scales than for different units of measure for other properties. Most measurement units for a given property are directly proportional to one another (y = mx). Using familiar length units as one example:

$$\text{length in feet} = \left(\frac{1 \text{ ft}}{12 \text{ in.}}\right) \times \text{length in inches}$$

where

- y = length in feet,
- x = length in inches, and
- the proportionality constant, m, is the conversion factor.

The Celsius and Fahrenheit temperature scales, however, do not share a common zero point, and so the relationship between these two scales is a linear one rather than a proportional one ($y = mx + b$). Consequently, converting a temperature from one of these scales into the other requires more than simple multiplication by a conversion factor, m, it also must take into account differences in the scales' zero points (b).

The linear equation relating Celsius and Fahrenheit temperatures is easily derived from the two temperatures used to define each scale. Representing the Celsius temperature as x and the Fahrenheit temperature as y, the slope, m, is computed to be:

$$\begin{aligned} m &= \frac{\Delta y}{\Delta x} \\ &= \frac{212\ ^\circ\text{F} - 32\ ^\circ\text{F}}{100\ ^\circ\text{C} - 0\ ^\circ\text{C}} \\ &= \frac{180\ ^\circ\text{F}}{100\ ^\circ\text{C}} \\ &= \frac{9\ ^\circ\text{F}}{5\ ^\circ\text{C}} \end{aligned}$$

The y-intercept of the equation, *b*, is then calculated using either of the equivalent temperature pairs, (100 °C, 212 °F) or (0 °C, 32 °F), as:

$$\begin{aligned} b &= y - mx \\ &= 32\ ^\circ\text{F} - \frac{9\ ^\circ\text{F}}{5\ ^\circ\text{C}} \times 0\ ^\circ\text{C} \\ &= 32\ ^\circ\text{F} \end{aligned}$$

The equation relating the temperature scales is then:

$$T_{^\circ\text{F}} = \left(\frac{9\ ^\circ\text{F}}{5\ ^\circ\text{C}} \times T_{^\circ\text{C}}\right) + 32\ ^\circ\text{C}$$

An abbreviated form of this equation that omits the measurement units is:

$$T_{^\circ\text{F}} = \frac{9}{5} \times T_{^\circ\text{C}} + 32$$

Rearrangement of this equation yields the form useful for converting from Fahrenheit to Celsius:

$$T_{^\circ\text{C}} = \frac{5}{9}(T_{^\circ\text{F}} + 32)$$

As mentioned earlier in this chapter, the SI unit of temperature is the kelvin (K). Unlike the Celsius and Fahrenheit scales, the kelvin scale is an absolute temperature scale in which 0 (zero) K corresponds to the lowest temperature that can theoretically be achieved. The early 19th-century discovery of the relationship between a gas's volume and temperature suggested that the volume of a gas would be zero at −273.15 °C. In 1848, British physicist William Thompson, who later adopted the title of Lord Kelvin, proposed an absolute temperature scale based on this concept (further treatment of this topic is provided in this text's chapter on gases).

The freezing temperature of water on this scale is 273.15 K and its boiling temperature 373.15 K. Notice the numerical difference in these two reference temperatures is 100, the same as for the Celsius scale, and so the linear relation between these two temperature scales will exhibit a slope of 1 $\frac{\text{K}}{^\circ\text{C}}$. Following the same approach, the equations for converting between the kelvin and Celsius temperature scales are derived to be:

$$T_{\mathrm{K}} = T_{^\circ\mathrm{C}} + 273.15$$

$$T_{^\circ\mathrm{C}} = T_{\mathrm{K}} - 273.15$$

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure 3.5.1 shows the relationship among the three temperature scales. Recall that we do not use the degree sign with temperatures on the kelvin scale.

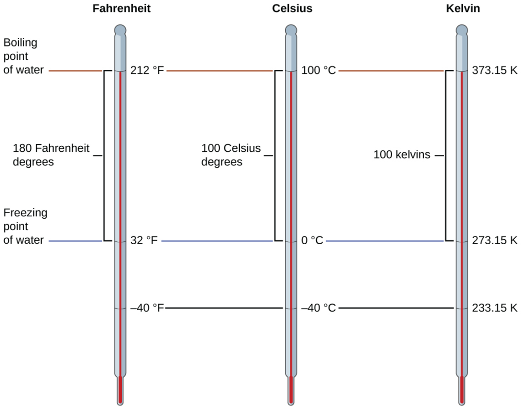


Figure 3.5.1: The Fahrenheit, Celsius, and kelvin temperature scales are compared.

Although the kelvin (absolute) temperature scale is the official SI temperature scale, Celsius is commonly used in many scientific contexts and is the scale of choice for nonscience contexts in almost all areas of the world. Very few countries (the U.S. and its territories, the Bahamas, Belize, Cayman Islands, and Palau) still use Fahrenheit for weather, medicine, and cooking.

✓ Example 3.5.4: Conversion from Celsius

Normal body temperature has been commonly accepted as 37.0 °C (although it varies depending on time of day and method of measurement, as well as among individuals). What is this temperature on the kelvin scale and on the Fahrenheit scale?

Solution

$$\mathrm{K} = {}^\circ\mathrm{C} + 273.15 = 37.0 + 273.2 = 310.2\ \mathrm{K}$$

$$^\circ\mathrm{F} = \frac{9}{5}\ {}^\circ\mathrm{C} + 32.0 = \left(\frac{9}{5} \times 37.0\right) + 32.0 = 66.6 + 32.0 = 98.6\ {}^\circ\mathrm{F}$$

? Exercise 3.5.4

Convert 80.92 °C to K and °F.

Answer

354.07 K, 177.7 °F

✓ Example 3.5.5: Conversion from Fahrenheit

Baking a ready-made pizza calls for an oven temperature of 450 °F. If you are in Europe, and your oven thermometer uses the Celsius scale, what is the setting? What is the kelvin temperature?

Solution

$$^\circ\mathrm{C} = \frac{5}{9}({}^\circ\mathrm{F} - 32) = \frac{5}{9}(450 - 32) = \frac{5}{9} \times 418 = 232^\circ\mathrm{C} \rightarrow \text{set oven to } 230^\circ\mathrm{C} \quad \text{(two significant figures)}$$

$$\mathrm{K} = {}^\circ\mathrm{C} + 273.15 = 230 + 273 = 503\ \mathrm{K} \rightarrow 5.0 \times 10^2\ \mathrm{K} \quad \text{(two significant figures)}$$

? Exercise 3.5.5

Convert 50 °F to °C and K.

Answer

10 °C, 280 K

Summary

Measurements are made using a variety of units. It is often useful or necessary to convert a measured quantity from one unit into another. These conversions are accomplished using unit conversion factors, which are derived by simple applications of a mathematical approach called the factor-label method or dimensional analysis. This strategy is also employed to calculate sought quantities using measured quantities and appropriate mathematical relations.

Key Equations

- $T_{^\circ\mathrm{C}} = \frac{5}{9} \times T_{^\circ\mathrm{F}} - 32$
- $T_{^\circ\mathrm{F}} = \frac{9}{5} \times T_{^\circ\mathrm{C}} + 32$
- $T_{\mathrm{K}} = {}^\circ\mathrm{C} + 273.15$
- $T_{^\circ\mathrm{C}} = \mathrm{K} - 273.15$

Glossary

dimensional analysis

(also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Fahrenheit

unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

unit conversion factor

ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

---

3.5.1: Metric and Imperial Unit Conversions

Learning Objectives

- The skill to convert a quantity into various units is important. **Unit conversion** and **dimensional analysis** are also scientific methods. There are many examples in Chemistry, and you will encounter them later.

In the field of science, the metric system is used in performing measurements. The metric system is actually easier to use than the English system, as you will see shortly. The metric system uses prefixes to indicate the magnitude of a measured quantity. The prefix itself gives the conversion factor. You should memorize some of the common prefixes, as you will be using them on a regular basis. Common prefixes are shown below:

Table 3.5.1.1

Prefix	Symbol	Power	Prefix	Symbol	Power
mega-	M	10^6	centi-	c	10^{-2}
kilo-	k	10^3	milli-	m	10^{-3}
hecto-	h	10^2	micro-		10^{-6}
deca-	D	10^1	nano-	n	10^{-9}
deci-	d	10^{-1}	pico-	p	10^{-12}

Metric - Metric Conversions

Suppose you wanted to convert the mass of a $250\ mg$ aspirin tablet to grams. Start with what you know and let the conversion factor units decide how to set up the problem. If a unit to be converted is in the numerator, that unit must be in the denominator of the conversion factor in order for it to cancel.

Notice how the units cancel to give grams. the conversion factor numerator is shown as 1×10^{-3} because on most calculators, it must be entered in this fashion, not as just 10^{-3}. If you don't know how to use the scientific notation on your calculator, try to find out as soon as possible. Look in your calculator's manual, or ask someone who knows. Also, notice how the unit, mg is assigned the value of 1, and the prefix, milli-, is applied to the gram unit. In other words, $1\ mg$ literally means $1 \times 10^{-3}\ g$.

Next, let's try a more involved conversion. Suppose you wanted to convert 250 mg to kg. You may or may not know a direct, one-step conversion. In fact, the better method (foolproof) to do the conversion would be to go to the base unit first, and then to the final unit you want. In other words, convert the milligrams to grams and then go to kilograms:

Example 3.5.1.1

The world's ocean is estimated to contain $1.4 \times 10^9\ \text{km}^3$ of water.

a. What is the volume in liters?
b. What is the weight if the specific density is 1.1?
c. How many moles of water are present if all the weight is due to water?
d. How many moles of H atoms (not H_2) are there in the ocean?
e. How many H atoms are present in the ocean?

Solution

$$\begin{aligned}
&1.4\text{e}9\left(\frac{1000\text{ m}}{1\text{ km}}\right)^3\left(\frac{10\text{ dm}}{1\text{ m}}\right)^3\\
&=1.4\text{e}21\text{ dm}^3\left(\frac{1\text{ L}}{1\text{ dm}^3}\right)\\
&=1.5\text{e}21\text{ L}\left(\frac{1.1\text{ kg}}{1\text{ L}}\right)\\
&=1.5\text{e}21\text{ kg}\left(\frac{1000\text{ g}}{1\text{ kg}}\right)\left(\frac{1\text{ mol}}{18\text{ g}}\right)\\
&=8.3\text{e}22\text{ mol H}_2\text{O}\left(\frac{2\text{ mol H atoms}}{1\text{ mol H}_2\text{O}}\right)\\
&=1.7\text{e}23\text{ mol H}\left(\frac{6.02\text{e}23\text{ atoms}}{1\text{ mol}}\right)\\
&=5.0\text{e}46\text{ H atoms}
\end{aligned}$$

In this example, a quantity has been converted from a unit for volume into other units of volume, weight, amount in moles, and number of atoms. Every factor used for the unit conversion is a unity. The numerator and denominator represent the same quantity in different ways.

Even in this simple example, several concepts such as the quantity in moles, Avogadro's number, and specific density (or specific gravity) have been applied in the conversion. If you have not learned these concepts, you may have difficulty in understanding some of the conversion processes. Identify what you do not know and find out in your text or from a resource.

✓ Example 3.5.1.2

A typical city speed for automobiles is 50 km/hr. Some years ago, most people believed that 10 seconds to dash a 100 meter race was the lowest limit. Which speed is faster, 50 km/hr or 10 m/s?

Solution

For comparison, the two speeds must be expressed in the same unit. Let's convert 50 km/hr to m/s.

$$50\ \frac{\cancel{\text{km}}}{\cancel{\text{hr}}}\left(\frac{1000\text{ m}}{1\ \ \cancel{\text{km}}}\right)\left(\frac{1\ \ \cancel{\text{hr}}}{60\ \ \cancel{\text{min}}}\right)\left(\frac{1\ \ \cancel{\text{min}}}{60\text{ s}}\right)=13.89\text{ m/s}$$

Thus, 50 km/hr is faster.

Note: a different unit can be selected for the comparison (e.g., miles/hour) but the result will be the same (test this out if interested).

? Exercise 3.5.1.1

The speed of a typhoon is reported to be 100 m/s. What is the speed in km/hr and in miles per hour?

English - Metric Conversions

These conversions are accomplished in the same way as metric - metric conversions. The only difference is the conversion factor used. It would be a good idea to memorize a few conversion factors involving converting mass, volume, length and temperature. Here are a few useful conversion factors.

- length: 2.54 cm = 1 inch (exact)
- mass: 454 g = 1 lb
- volume: 0.946 L = 1 qt
- temperature: ^{o}C = (^{o}F - 32)/1.8

All of the above conversions are to three significant figures, except length, which is an exact number. As before, let the units help you set up the conversion.

Suppose you wanted to convert mass of my $23\ lb$ cat to kilograms. One can quickly see that this conversion is not achieved in one step. The pound units will be converted to grams, and then from grams to kilograms. Let the units help you set up the problem:

$$\frac{23\ lb}{1} \times \frac{454\ g}{1\ lb} \times \frac{1\ kg}{1 \times 10^3\ g} = 10\ kg$$

Let's try a conversion which looks "intimidating", but actually uses the same basic concepts we have already examined. Suppose you wish to convert pressure of 14 lb/in^2 to g/cm^2. When setting up the conversion, worry about one unit at a time, for example, convert the pound units to gram units, first:

Next, convert in^2 to cm^2. Set up the conversion without the exponent first, using the conversion factor, 1 in = 2.54 cm. Since we need in^2 and cm^2, raise everything to the second power:

Notice how the units cancel to the units sought. Always check your units because they indicate whether or not the problem has been set up correctly.

✓ Example 3.5.1.2: Convert Quantities into SI units

Mr. Smart is ready for a T-bone steak. He went to market A and found the price to be 4.99 dollars per kilograms. He drove out of town to a roadside market, which sells at 2.29 per pound. Which price is better for Mr. Smart?

Solution

To help Mr. Smart, we have to know that 1.0 kg is equivalent to 2.206531 lb or 1 lb = 453.2 g. By the way, are these the same?

$$4.99\ \frac{\$}{\cancel{\text{kg}}}\left(\frac{1\ \ \cancel{\text{kg}}}{2.206532\ \text{lb}}\right) = 2.26468\ \frac{\$}{\text{lb}}$$

Of course, with the money system in Canada, there is no point quoting the price as detailed as it is given above. This brings about the significant digit issue, and the quantization. The price is therefore 2.26 \$/lb, better for Mr. Smart than the price of 2.29 \$/lb.

Exercises

1. 1.2e-4 kg

   Skill -
   Converting a quantity into SI units.

2. $(70 - 32) \times \frac{5}{9}\ ^\circ\text{C}$

   Skill -
   To convert temperature from one scale to another scale.

3. The price is Cdn\$0.60 / L

   Skill -
   Converting two quantities.

4. Canada at Cdn\$0.55 / L

   Skill -
   Determine the costs per unit common volume.

5. **A marathon race covers a distance of 26 miles and 385 yards. If**
   1.0 mile = 5280 ft, 1 ft = 12 in, and 1 in = 2.54 cm,
   express 26 miles in m.

   6486 m

Skill -
Convert quantities into SI units.

Contributors and Attributions

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3.5.2: Compound Unit Conversion Factors - Density

Learning Objectives

- Define density.
- Use density as a conversion factor.

Density (ρ) is a physical property found by dividing the mass of an object by its volume. Regardless of the sample size, density is always constant. For example, the density of a pure sample of tungsten is always 19.25 grams per cubic centimeter. This means that whether you have one gram or one kilogram of the sample, the density will never vary. The equation, as we already know, is as follows:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

or just

$$\rho = \frac{m}{V} \tag{3.5.2.1}$$

Based on this equation, it's clear that density can, and does, vary from element to element and substance to substance due to differences in the relationship of mass and volume. Pure water, for example, has a density of 0.998 g/cm^3 at 25° C. The average densities of some common substances are in Table $3.5.2.1$. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will “float.”

Table $3.5.2.1$: Densities of Common Substances

Substance	Density at 25°C (g/cm3)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

Density can be measured for all substances—solids, liquids and gases. For solids and liquids, density is often reported using the units of g/cm^3. Densities of gases, which are significantly lower than the densities of solids and liquids, are often given using units of g/L.

Example $3.5.2.1$: Ethyl Alcohol

Calculate the density of a 30.2 mL sample of ethyl alcohol with a mass of 23.71002 g

Solution

This is a direct application of Equation $3.5.2.1$:

$$\rho = \frac{23.71002\, g}{30.2\, mL} = 0.785\, g/mL$$

Exercise $3.5.2.1$

a. Find the density (in kg/L) of a sample that has a volume of 36.5 L and a mass of 10.0 kg.
b. If you have a 2.130 mL sample of acetic acid with mass 0.002234 kg, what is the density in kg/L?

Answer a

$0.274\, kg/L$

Answer b

$1.049\, kg/L$

Density as a Conversion Factor

Conversion factors can also be constructed for converting between different kinds of units. For example, density can be used to convert between the mass and the volume of a substance. Consider mercury, which is a liquid at room temperature and has a density of 13.6 g/mL. The density tells us that 13.6 g of mercury have a volume of 1 mL. We can write that relationship as follows:

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

$$\frac{13.6\ g}{1\ mL} = 1$$

and

$$\frac{1\ mL}{13.6\ g} = 1$$

Which one do we use? It depends, as usual, on the units we need to cancel and introduce. For example, suppose we want to know the mass of 2.0 mL of mercury. We would use the conversion factor that has milliliters on the bottom (so that the milliliter unit cancels) and grams on top, so that our final answer has a unit of mass:

$$2.0\ \cancel{\text{mL}} \times \frac{13.6\ \text{g}}{1\ \cancel{\text{mL}}} = 27.2\ \text{g} = 27\ \text{g}$$

In the last step, we limit our final answer to two significant figures because the volume quantity has only two significant figures; the 1 in the volume unit is considered an exact number, so it does not affect the number of significant figures. The other conversion factor would be useful if we were given a mass and asked to find volume, as the following example illustrates.

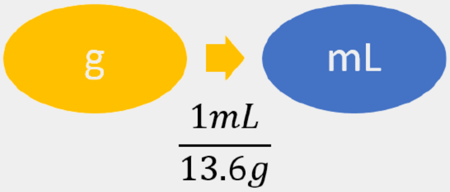
> *Density can be used as a conversion factor between mass and volume.*

✓ Example 3.5.2.2: Mercury Thermometer Steps for Problem Solving

A mercury thermometer for measuring a patient’s temperature contains 0.750 g of mercury. What is the volume of this mass of mercury?

Solution

Solution to Example 2.9.2

Steps for Problem Solving	**Unit Conversion**
Identify the "given" information and what the problem is asking you to "find."	Given: 0.750 g Find: mL
List other known quantities.	13.6 g/mL (density of mercury)
Prepare a concept map.	
Calculate.	$0.750\ \cancel{\text{g}} \times \frac{1\ \text{mL}}{13.6\ \cancel{\text{g}}} = 0.055147\ldots\ \text{mL} \approx 0.0551\ \text{mL}$ We have limited the final answer to three significant figures.

? Exercise 3.5.2.2

What is the volume of 100.0 g of air if its density is 1.3 g/L?

Answer

$77\ L$

Summary

- Density is defined as the mass of an object divided by its volume.
- Density can be used as a conversion factor between mass and volume.

Contributions & Attributions

3.5.3: Molar Mass and Avogadro's Number

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Define *Avogadro's number* and explain why it is important to know.
- Define the *mole*. Be able to calculate the number of moles in a given mass of a substance, or the mass corresponding to a given number of moles.
- Define *molecular weight*, *formula weight*, and *molar mass*; explain how the latter differs from the first two.
- Be able to find the number of atoms or molecules in a given weight of a substance.
- Find the *molar volume* of a solid or liquid, given its density and molar mass.
- Explain how the molar volume of a metallic solid can lead to an estimate of atomic diameter.

The chemical changes we observe always involve *discrete numbers of atoms* that rearrange themselves into new configurations. These numbers are HUGE— far too large in magnitude for us to count or even visualize, but they are still *numbers*, and we need to have a way to deal with them. We also need a bridge between these numbers, which we are unable to measure directly, and the weights of substances, which we do measure and observe. The *mole concept* provides this bridge, and is central to all of quantitative chemistry.

Counting Atoms: Avogadro's Number

Owing to their tiny size, atoms and molecules cannot be counted by direct observation. But much as we do when "counting" beans in a jar, we can estimate the number of particles in a sample of an element or compound if we have some idea of the volume occupied by each particle and the volume of the container. Once this has been done, we know the number of formula units (to use the most general term for any combination of atoms we wish to define) in any arbitrary weight of the substance. The number will of course depend both on the formula of the substance and on the weight of the sample. However, if we consider a weight of substance that is the same as its formula (molecular) weight expressed in grams, we have only one number to know: **Avogadro's number**.

Avogadro's number is known to ten significant digits:

$$N_A = 6.022141527 \times 10^{23}. \tag{3.5.3.1}$$

However, you only need to know it to three significant figures:

$$N_A \approx 6.02 \times 10^{23}. \tag{3.5.3.2}$$

So 6.02×10^{23} of *what*? Well, of anything you like: apples, stars in the sky, burritos. However, the only *practical* use for N_A is to have a more convenient way of expressing the huge numbers of the tiny particles such as atoms or molecules that we deal with in chemistry. Avogadro's number is a *collective number*, just like a dozen. Students can think of 6.02×10^{23} as the "chemist's dozen".

Before getting into the use of Avogadro's number in problems, take a moment to convince yourself of the reasoning embodied in the following examples.

✓ Example 3.5.3.1: Mass ratio from atomic weights

The atomic weights of oxygen and carbon are 16.0 and 12.0 atomic mass units (u), respectively. How much heavier is the oxygen atom in relation to carbon?

Solution

Atomic weights represent the relative masses of different kinds of atoms. This means that the atom of oxygen has a mass that is

$$\frac{16\ \cancel{u}}{12\ \cancel{u}} = \frac{4}{3} \approx 1.33$$

as great as the mass of a carbon atom.

✓ Example 3.5.3.2: Mass of a single atom

The absolute mass of a carbon atom is 12.0 unified atomic mass units (u). How many grams will a single oxygen atom weigh?

Solution

The absolute mass of a carbon atom is 12.0 u or

$$12\ \cancel{u} \times \frac{1.6605 \times 10^{-24}\, g}{1\ \cancel{u}} = 1.99 \times 10^{-23}\, g\, (\text{per carbon atom})$$

The mass of the oxygen atom will be 4/3 greater (from Example $3.5.3.1$):

$$\left(\frac{4}{3}\right) 1.99 \times 10^{-23}\, g = 2.66 \times 10^{-23}\, g\, (\text{per oxygen atom})$$

Alternatively we can do the calculation directly like with carbon:

$$16\ \cancel{u} \times \frac{1.6605 \times 10^{-24}\, g}{1\ \cancel{u}} = 2.66 \times 10^{-23}\, g\, (\text{per oxygen atom})$$

✓ Example 3.5.3.3: Relative masses from atomic weights

Suppose that we have N carbon atoms, where N is a number large enough to give us a pile of carbon atoms whose mass is 12.0 grams. How much would the same number, N, of oxygen atoms weigh?

Solution

We use the results from Example $3.5.3.1$again. The collection of N oxygen atoms would have a mass of

$$\frac{4}{3} \times 12\, g = 16.0\, g.$$

? Exercise 3.5.3.1

What is the numerical value of N in Example $3.5.3.3$?

Answer

Using the results of Examples $3.5.3.2$and $3.5.3.3$

$$N \times 1.99 \times 10^{-23}\, g\, (\text{per carbon atom}) = 12\, g$$

or

$$N = \frac{12\ \cancel{g}}{1.99 \times 10^{-23}\ \cancel{g}\ (\text{per carbon atom})} = 6.03 \times 10^{23} \text{atoms}$$

There are a lot of atoms in 12 g of carbon.

- It is a *number*, just as is "dozen", and thus is *dimensionless*.
- It is a *huge* number, far greater in magnitude than we can visualize
- Its practical use is limited to counting tiny things like atoms, molecules, "formula units", electrons, or photons.
- The value of N_A can be known only to the precision that the number of atoms in a measurable weight of a substance can be estimated. Because large numbers of atoms cannot be counted directly, a variety of ingenious indirect measurements have been made involving such things as Brownian motion and X-ray scattering.
- The current value was determined by measuring the distances between the atoms of silicon in an ultrapure crystal of this element that was shaped into a perfect sphere. (The measurement was made by X-ray scattering.) When combined with the

measured mass of this sphere, it yields Avogadro's number. However, there are two problems with this:

- The silicon sphere is an artifact, rather than being something that occurs in nature, and thus may not be perfectly reproducible.
- The standard of mass, the kilogram, is not precisely known, and its value appears to be changing. For these reasons, there are proposals to revise the definitions of both N_A and the kilogram.

Moles and their Uses

The *mole* (abbreviated mol) is the the SI measure of *quantity of a "chemical entity"*, which can be an atom, molecule, formula unit, electron or photon. One mole of anything is just Avogadro's number of that something. Or, if you think like a lawyer, you might prefer the official SI definition:

Definition: The Mole

The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12

Avogadro's number (Equation 3.5.3.2) like any pure number, is dimensionless. However, it also defines the mole, so we can also express N_A as 6.02×10^{23} mol^{-1}; in this form, it is properly known as ***Avogadro's constant***. This construction emphasizes the role of Avogadro's number as a *conversion factor* between number of moles and number of "entities".

Example 3.5.3.4: number of moles in N particles

How many moles of nickel atoms are there in 80 nickel atoms?

Solution

$$\frac{80\ atoms}{6.02 \times 10^{23}\ atoms\ mol^{-1}} = 1.33 \times 10^{-22} mol$$

Is this answer reasonable? Yes, because 80 is an extremely small fraction of N_A.

Molar Mass

The atomic weight, molecular weight, or formula weight of one mole of the fundamental units (atoms, molecules, or groups of atoms that correspond to the formula of a pure substance) is the ratio of its mass to 1/12 the mass of one mole of C^{12} atoms, and being a ratio, is dimensionless. But at the same time, this *molar mass* (as many now prefer to call it) is also the observable mass of one mole (N_A) of the substance, so we frequently emphasize this by stating it explicitly as so many grams (or kilograms) per mole: g mol^{-1}.

> *It is important always to bear in mind that the mole is a number and not a mass. But each individual particle has a mass of its own, so a mole of any specific substance will always correspond to a certain mass of that substance.*

Example 3.5.3.5: Boron content of borax

Borax is the common name of sodium tetraborate, $Na_2B_4O_7$.

a. how many moles of boron are present in 20.0 g of borax?
b. how many grams of boron are present in 20.0 g of borax?

Solution

The formula weight of $Na_2B_4O_7$ so the molecular weight is:

$$(2 \times 23.0) + (4 \times 10.8) + (7 \times 16.0) = 201.2$$

a. 20 g of borax contains (20.0 g) ÷ (201 g mol^{-1}) = 0.10 mol of borax, and thus **0.40 mol** of B.
b. 0.40 mol of boron has a mass of (0.40 mol) × (10.8 g mol^{-1}) = **4.3 g**.

✓ Example 3.5.3.6: Magnesium in chlorophyll

The plant photosynthetic pigment chlorophyll contains 2.68 percent magnesium by weight. How many atoms of Mg will there be in 1.00 g of chlorophyll?

Solution

Each gram of chlorophyll contains 0.0268 g of Mg, atomic weight 24.3.

- Number of moles in this weight of Mg: (.0268 g) / (24.2 g mol^{-1}) = 0.00110 mol
- Number of atoms: (0.00110 mol) × (6.02E23 mol^{-1}) = 6.64×10^{20}

Is this answer reasonable? (Always be suspicious of huge-number answers!) Yes, because we would expect to have huge numbers of atoms in any observable quantity of a substance.

Molar Volume

This is the volume occupied by one mole of a pure substance. Molar volume depends on the density of a substance and, like density, varies with temperature owing to thermal expansion, and also with the pressure. For solids and liquids, these variables ordinarily have little practical effect, so the values quoted for 1 atm pressure and 25°C are generally useful over a fairly wide range of conditions. This is definitely **not** the case with gases, whose molar volumes must be calculated for a specific temperature and pressure.

✓ Example 3.5.3.7: Molar Volume of a Liquid

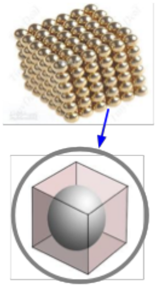
Methanol, CH_3OH, is a liquid having a density of 0.79 g per milliliter. Calculate the molar volume of methanol.

Solution

The molar volume will be the volume occupied by one molar mass (32 g) of the liquid. Expressing the density in liters instead of mL, we have

$$V_M = \frac{32\ g\ mol^{-1}}{790\ g\ L^{-1}} = 0.0405\ L\ mol^{-1}$$

The molar volume of a metallic element allows one to estimate the size of the atom. The idea is to mentally divide a piece of the metal into as many little cubic boxes as there are atoms, and then calculate the length of each box. Assuming that an atom sits in the center of each box and that each atom is in direct contact with its six neighbors (two along each dimension), this gives the diameter of the atom. The manner in which atoms pack together in actual metallic crystals is usually more complicated than this and it varies from metal to metal, so this calculation only provides an approximate value.



✓ Example 3.5.3.8: Radius of a Strontium Atom

The density of metallic strontium is 2.60 g cm^{-3}. Use this value to estimate the radius of the atom of Sr, whose atomic weight is 87.6.

Solution

The molar volume of Sr is:

$$\frac{87.6\ g\ mol^{-1}}{2.60\ g\ cm^{-3}} = 33.7\ cm^3\ mol^{-1} \tag{3.5.3.3}$$

The volume of each "box" is"

$$\frac{33.7\ cm^3 mol^{-1}}{6.02 \times 10^{23}\ mol^{-1}} = 5.48 \times 10^{-23}\ cm^3 \tag{3.5.3.4}$$

The side length of each box will be the cube root of this value, $3.79 \times 10^{-8}\ cm$. The atomic radius will be half this value, or

$$1.9 \times 10^{-8}\ cm = 1.9 \times 10^{-10}\ m = 190 pm \tag{3.5.3.5}$$

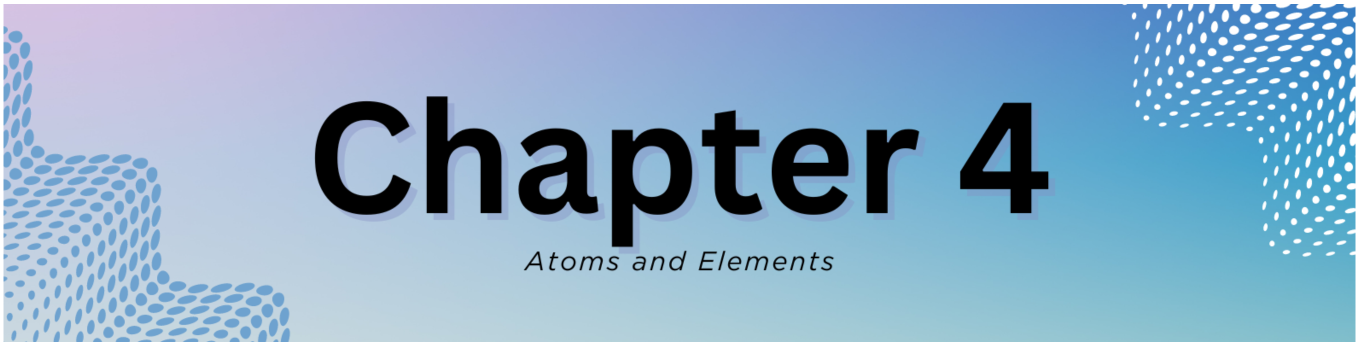
Note: Your calculator probably has no cube root button, but you *are* expected to be able to find cube roots; you can usually use the x^y button with y=0.333. You should also be able estimate the magnitude of this value for checking. The easiest way is to express the number so that the exponent is a multiple of 3. Take 54×10^{-24}, for example. Since 3^3=27 and 4^3 = 64, you know that the cube root of 55 will be between 3 and 4, so the cube root should be a bit less than 4 × 10^{-8}.

So how good is our atomic radius? Standard tables give the atomic radius of strontium is in the range 192-220 pm.

- **4.2: Avogadro's Number and the Mole** by Stephen Lower is licensed CC BY 3.0. Original source: http://www.chem1.com/acad/webtext/virtualtextbook.html.

CHAPTER OVERVIEW

4: Atoms and Elements



Take some aluminum foil. Cut it in half. Now there are two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil. It should be obvious that the pieces are still aluminum foil; they are just becoming smaller and smaller. But how far can this exercise be taken, at least in theory? Can one continue cutting the aluminum foil into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of aluminum foil? Thought experiments like this—and the conclusions based on them—were debated as far back as the fifth century BC by Democritus and other ancient Greek philosophers (Figure 4.1).

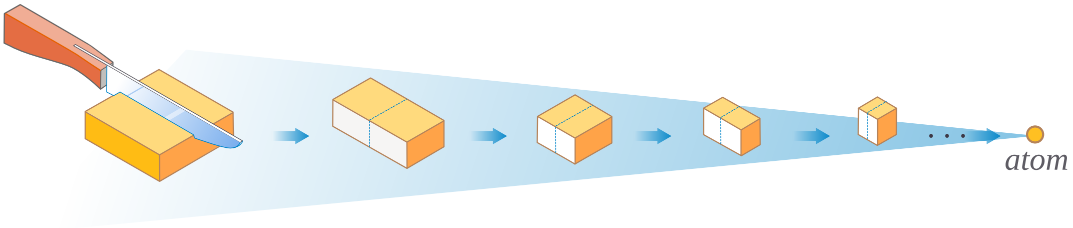


Figure 4.1: Democritus argued that matter, like an aluminum block, cannot be repeatedly cut in half perpetually. At some point, a limit is reached before the substance can no longer be called "aluminum"; this is the atomic limit. (CC BY-NC; Ümit Kaya via LibreTexts)

Most elements in their pure form exist as individual atoms. For example, a macroscopic chunk of iron metal is composed, microscopically, of individual atoms. Some elements, however, exist as groups of atoms called molecules. Several important elements exist as two-atom combinations and are called diatomic molecules. In representing a diatomic molecule, we use the symbol of the element and include the subscript 2 to indicate that two atoms of that element are joined together. The elements that exist as diatomic molecules are hydrogen (H_2), oxygen (O_2), nitrogen (N_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).

Chapter Sections

4.1: Evidence for Atoms - Brownian Motion

Learning Objectives

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

- Describe the basic structure of the atom, the substructure of all matter.

How do we know that atoms are really there if we cannot see them with our eyes? A brief account of the progression from the proposal of atoms by the Greeks to the first direct evidence of their existence follows.

People have long speculated about the structure of matter and the existence of atoms. The earliest significant ideas to survive are due to the ancient Greeks in the fifth century BCE, especially those of the philosophers Leucippus and Democritus. (There is some evidence that philosophers in both India and China made similar speculations, at about the same time.) They considered the question of whether a substance can be divided without limit into ever smaller pieces. There are only a few possible answers to this question. One is that infinitesimally small subdivision is possible. Another is what Democritus in particular believed—that there is a smallest unit that cannot be further subdivided. Democritus called this the atom. We now know that atoms themselves can be subdivided, but their identity is destroyed in the process, so the Greeks were correct in a respect. The Greeks also felt that atoms were in constant motion, another correct notion.

The Greeks and others speculated about the properties of atoms, proposing that only a few types existed and that all matter was formed as various combinations of these types. The famous proposal that the basic elements were earth, air, fire, and water was brilliant, but incorrect. The Greeks had identified the most common examples of the four states of matter (solid, gas, plasma, and liquid), rather than the basic elements. More than 2000 years passed before observations could be made with equipment capable of revealing the true nature of atoms.

Over the centuries, discoveries were made regarding the properties of substances and their chemical reactions. Certain systematic features were recognized, but similarities between common and rare elements resulted in efforts to transmute them (lead into gold, in particular) for financial gain. Secrecy was endemic. Alchemists discovered and rediscovered many facts but did not make them broadly available. As the Middle Ages ended, alchemy gradually faded, and the science of chemistry arose. It was no longer possible, nor considered desirable, to keep discoveries secret. Collective knowledge grew, and by the beginning of the 19th century, an important fact was well established—the masses of reactants in specific chemical reactions always have a particular mass ratio. This is very strong indirect evidence that there are basic units (atoms and molecules) that have these same mass ratios. The English chemist John Dalton (1766–1844) did much of this work, with significant contributions by the Italian physicist Amedeo Avogadro (1776–1856). It was Avogadro who developed the idea of a fixed number of atoms and molecules in a mole, and this special number is called Avogadro’s number in his honor. The Austrian physicist Johann Josef Loschmidt was the first to measure the value of the constant in 1865 using the kinetic theory of gases.

PATTERNS AND SYSTEMATICS

The recognition and appreciation of patterns has enabled us to make many discoveries. The periodic table of elements was proposed as an organized summary of the known elements long before all elements had been discovered, and it led to many other discoveries. We shall see in later chapters that patterns in the properties of subatomic particles led to the proposal of quarks as their underlying structure, an idea that is still bearing fruit.

Knowledge of the properties of elements and compounds grew, culminating in the mid-19th-century development of the periodic table of the elements by Dmitri Mendeleev (1834–1907), the great Russian chemist. Mendeleev proposed an ingenious array that highlighted the periodic nature of the properties of elements. Believing in the systematics of the periodic table, he also predicted the existence of then-unknown elements to complete it. Once these elements were discovered and determined to have properties predicted by Mendeleev, his periodic table became universally accepted.

Also during the 19th century, the kinetic theory of gases was developed. Kinetic theory is based on the existence of atoms and molecules in random thermal motion and provides a microscopic explanation of the gas laws, heat transfer, and thermodynamics. Kinetic theory works so well that it is another strong indication of the existence of atoms. But it is still indirect evidence—individual atoms and molecules had not been observed. There were heated debates about the validity of kinetic theory until direct evidence of atoms was obtained.

The first truly direct evidence of atoms is credited to Robert Brown, a Scottish botanist. In 1827, he noticed that tiny pollen grains suspended in still water moved about in complex paths. This can be observed with a microscope for any small particles in a fluid. The motion is caused by the random thermal motions of fluid molecules colliding with particles in the fluid, and it is now called **Brownian motion** (Figure $4.1.1$). Statistical fluctuations in the numbers of molecules striking the sides of a visible particle cause it to move first this way, then that. Although the molecules cannot be directly observed, their effects on the particle can be. By examining Brownian motion, the size of molecules can be calculated. The smaller and more numerous they are, the smaller the fluctuations in the numbers striking different sides.

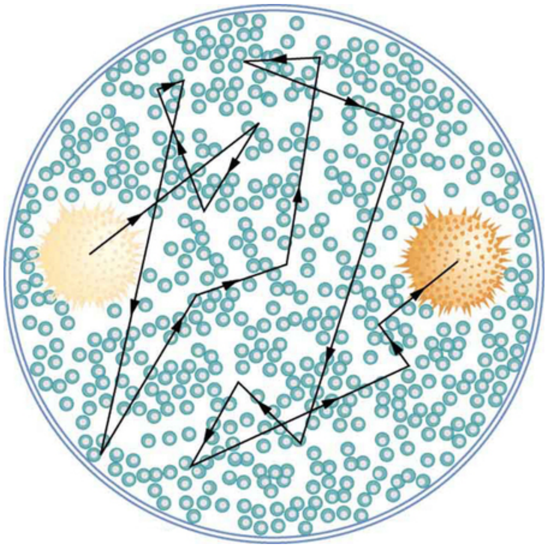


Figure $4.1.1$: The position of a pollen grain in water, measured every few seconds under a microscope, exhibits Brownian motion. Brownian motion is due to fluctuations in the number of atoms and molecules colliding with a small mass, causing it to move about in complex paths. This is nearly direct evidence for the existence of atoms, providing a satisfactory alternative explanation cannot be found.

It was Albert Einstein who, starting in his epochal year of 1905, published several papers that explained precisely how Brownian motion could be used to measure the size of atoms and molecules. (In 1905 Einstein created special relativity, proposed photons as quanta of EM radiation, and produced a theory of Brownian motion that allowed the size of atoms to be determined. All of this was done in his spare time, since he worked days as a patent examiner. Any one of these very basic works could have been the crowning achievement of an entire career—yet Einstein did even more in later years.) Their sizes were only approximately known to be $10^{-10}\,m$, based on a comparison of latent heat of vaporization and surface tension made in about 1805 by Thomas Young of double-slit fame and the famous astronomer and mathematician Simon Laplace.

Using Einstein's ideas, the French physicist Jean-Baptiste Perrin (1870–1942) carefully observed Brownian motion; not only did he confirm Einstein's theory, he also produced accurate sizes for atoms and molecules. Since molecular weights and densities of materials were well established, knowing atomic and molecular sizes allowed a precise value for Avogadro's number to be obtained. (If we know how big an atom is, we know how many fit into a certain volume.) Perrin also used these ideas to explain atomic and molecular agitation effects in sedimentation, and he received the 1926 Nobel Prize for his achievements. Most scientists were already convinced of the existence of atoms, but the accurate observation and analysis of Brownian motion was conclusive—it was the first truly direct evidence.

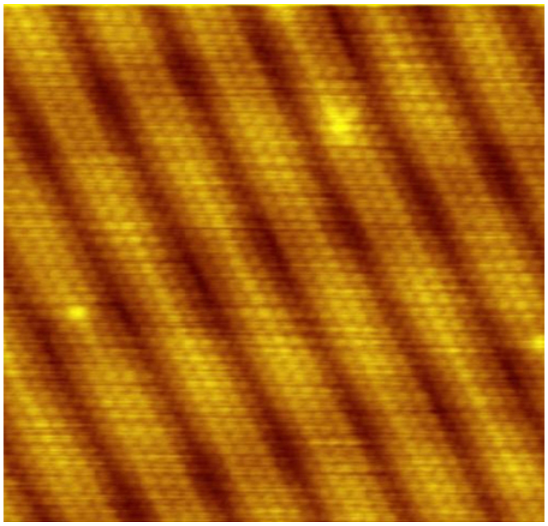


Figure $4.1.2$ Individual atoms can be detected with devices such as the scanning tunneling electron microscope that produced this image of individual gold atoms on a graphite substrate. (credit: Erwin Rossen, Eindhoven University of Technology, via Wikimedia Commons)

A huge array of direct and indirect evidence for the existence of atoms now exists. For example, it has become possible to accelerate ions (much as electrons are accelerated in cathode-ray tubes) and to detect them individually as well as measure their masses (see More Applications of Magnetism for a discussion of mass spectrometers). Other devices that observe individual atoms, such as the scanning tunneling electron microscope, will be discussed elsewhere (Figure $4.1.2$). All of our understanding of the properties of matter is based on and consistent with the atom. The atom's substructures, such as electron shells and the nucleus, are both interesting and important. The nucleus in turn has a substructure, as do the particles of which it is composed. These topics, and the question of whether there is a smallest basic structure to matter, will be explored in later parts of the text.

Summary

- Atoms are the smallest unit of elements; atoms combine to form molecules, the smallest unit of compounds.
- The first direct observation of atoms was in Brownian motion.
- Analysis of Brownian motion gave accurate sizes for atoms ($10^{-10}\ m$ on average) and a precise value for Avogadro's number.

Glossary

atom

basic unit of matter, which consists of a central, positively charged nucleus surrounded by negatively charged electrons

Brownian motion

the continuous random movement of particles of matter suspended in a liquid or gas

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4.2: Early Ideas About the Building Blocks of Matter

Chemistry is the study of the material world. What are different materials made of? How is their composition and structure related to their properties? How does one material become transformed into another? These are the sorts of questions that have driven the development of chemistry. People have been using chemistry for a very long time. Medicines were obtained from plants in early societies all over the world. People made dyes for clothing and paints for houses. Metallurgy was practiced in India and the Sahel, in Africa, before 1000 BC.

The Greek philosopher, Democritus, is often cited as the earliest person to formulate an idea of atoms, although similar ideas were recorded in India around the same time. Democritus thought that all things were made of atoms. Atoms were very small, he thought. They were also indivisible. Although you could cut a piece of wood in half, and cut each of those pieces in half, at some point you would reach the stage at which the wood could not be cut any longer, because you had a slice that was one atom thick.

Figure 2.2.1: *Democritus.*

There were an infinite variety of atoms, Democritus thought, making up an infinite variety of materials in the world. The properties of those atoms were directly responsible for the properties of materials. Water was made of water atoms, and water atoms were slippery. Iron was made of iron atoms, and iron atoms were strong and hard.

> *All of the materials in the world around us are made from atoms.*

A more practical aspect of chemistry has its roots in the Islamic Golden Age. Practitioners such as Jabir Ibn Hayyan developed laboratory apparatus and experimental methods to recrystallize and distill compounds from natural sources. Like Democritus, these early chemists wanted to know what the world is made of, but they were also trying to make improvements in practical applications such as tanning leather, making glass or rust-proofing iron.

The translation of Arabic texts into Latin helped spur the European Renaissance. Practical observations from the Islamic period, such as the fact that matter could be converted into different forms but did not disappear, gave rise to some of the most fundamental ideas of modern chemistry.

> *Conservation of mass: matter can be converted from one form to another, but it does not disappear.*

As is usually true in science, new developments in chemistry built on earlier work as well as the work of contemporary colleagues, continually improving our understanding of nature in small steps. In the 1600's, Robert Boyle adopted the Islamic emphasis on experimental work. Among his experiments, he was able to isolate the hydrogen gas formed by reacting metals with acids, as other scientists were doing at that time. In the 1700's, Joseph Priestley isolated several different "airs" or gases, including oxygen. Henry Cavendish showed that hydrogen combined with oxygen to form water. Antoine Lavoisier argued that oxygen and nitrogen, the other major component of air, are elements. The free exchange of ideas allowed people to rapidly advance our understanding of the material world.

Lavoisier, in particular, was important in bringing a number of important ideas together. He clearly stated that elements were the basic unit of matter, that could not be obtained from other materials. Compounds were made by combining different elements. His careful use of a balance to weigh reactants and products of an experiment clearly confirmed the idea of conservation of mass: the total mass of products after a reaction equals the total mass of reactants. These conclusions were more sophisticated versions of earlier ideas, and Lavoisier was able to present them in a way that eventually gained wide acceptance.

- A compound is a mixture of different elements bonded together.
- Conservation of mass, revised: the total mass of products after a reaction equals the total mass of reactants.

In the 1800's one of the principle proponents of the developing atomic theory was John Dalton. He advanced the idea that all atoms of a particular element are identical (as far as he could tell at that time). An element is a fundamental atomic building block from which other materials are made. Dalton performed analyses to try to deduce the atomic weights of different elements. Taking these ideas together, he showed that a particular compound always contained the same elements in the same ratio.

- An element is a fundamental atomic building block from which other materials are made.
- A compound is a mixture of different elements bonded together in a specific ratio.
- A compound may have a specific number of atoms of one type combined with a specific number of atoms of another type.
- Because all atoms have weight, we can also think of a compound as a specific weight of one kind of element combined with a specific weight of another element.

For example, water is a compound made from hydrogen and oxygen. It is crucial for life, of course. Water is about 1/9th hydrogen by weight; the other 8/9^{ths} are oxygen. However, a different compound, hydrogen peroxide, is a rocket fuel. Hydrogen peroxide is only about 1/19th hydrogen by weight. Those specific ratios of hydrogen to oxygen are inherent qualities of each compound.

Furthermore, Dalton found that he could make compounds through different methods. For example, he could make cupric oxide (CuO) by heating copper in air, or he could make it through various reactions involving copper and acids. It didn't matter how he made the cupric oxide; the ratio of copper to oxygen was always the same in the product.

There is one other compound containing copper and oxygen in a different ratio; it is called cuprous oxide, and it has the formula Cu_2O. However, it is very different from cupric oxide. The most obvious difference is that cuprous oxide is red whereas cupric oxide is black. Once again, when elements are combined in different ratios, different materials are produced, and they have properties that differ from each other and from they elements of which they are comprised.

Contributors and Attributions

- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

4.2.1: Dalton's Atomic Theory

Learning Objectives

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

- State the postulates of Dalton's atomic theory
- Use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions

The language used in chemistry is seen and heard in many disciplines, ranging from medicine to engineering to forensics to art. The language of chemistry includes its own vocabulary as well as its own form of shorthand. Chemical symbols are used to represent atoms and elements. Chemical formulas depict molecules as well as the composition of compounds. Chemical equations provide information about the quality and quantity of the changes associated with chemical reactions.

This chapter will lay the foundation for our study of the language of chemistry. The concepts of this foundation include the atomic theory, the composition and mass of an atom, the variability of the composition of isotopes, ion formation, chemical bonds in ionic and covalent compounds, the types of chemical reactions, and the naming of compounds. We will also introduce one of the most powerful tools for organizing chemical knowledge: the periodic table.

Atomic Theory through the Nineteenth Century

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for "indivisible." They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four "elements"—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and "elements" as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained using an atomic theory. First published in 1807, many of Dalton's hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of Dalton's atomic theory.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure $4.2.1.1$). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

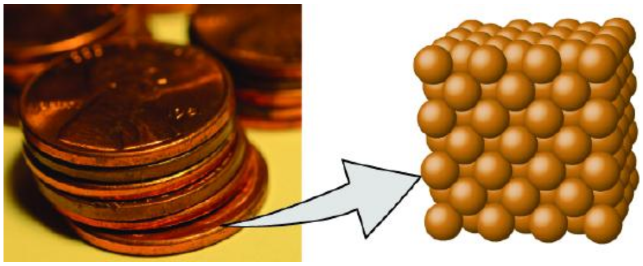


Figure 4.2.1.1: A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

The left image shows a photograph of a stack of pennies. The right image calls out an area of one of the pennies, which is made up of many sphere-shaped copper atoms. The atoms are densely organized.

3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (Figure $4.2.1.2$).

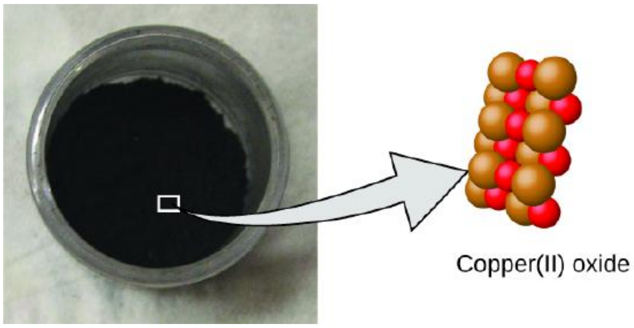


Figure 4.2.1.2: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by “Chemicalinterest”/Wikimedia Commons)

The left image shows a container with a black, powdery compound. The right image calls out the molecular structure of the powder which contains copper atoms that are clustered together with an equal number of oxygen atoms.

5. *Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (Figure 4.2.1.3).*

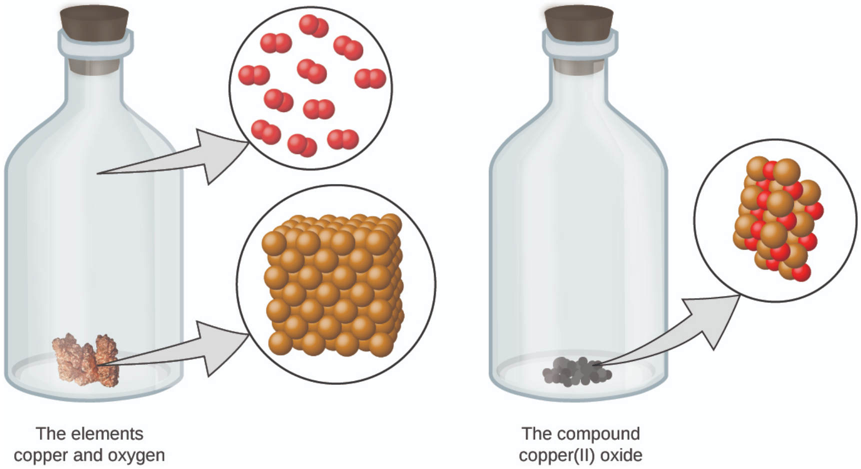


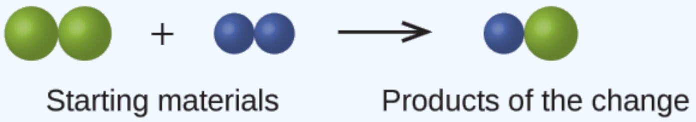
Figure 4.2.1.3: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by Copper [images-of-elements.com]).

The left stoppered bottle contains copper and oxygen. There is a callout which shows that copper is made up of many sphere-shaped atoms. The atoms are densely organized. The open space of the bottle contains oxygen gas, which is made up of bonded pairs of oxygen atoms that are evenly spaced. The right stoppered bottle shows the compound copper two oxide. A callout from the powder shows a molecule of copper two oxide, which contains copper atoms that are clustered together with an equal number of oxygen atoms.

Dalton’s atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you’ve learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes from one type to another will remain constant (the law of conservation of matter).

✓ Example 4.2.1.1: Testing Dalton’s Atomic Theory

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton’s atomic theory? If so, which one?



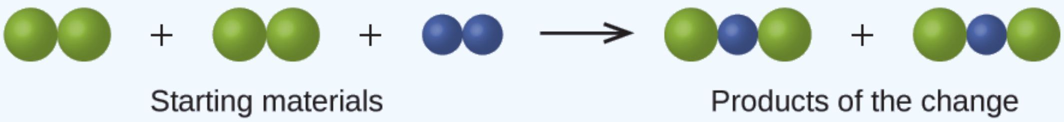
This equation shows that the starting materials of the reaction are two bonded, green spheres, which are being combined with two smaller, bonded purple spheres. The product of the change is one purple sphere that is bonded to one green sphere.

Solution

The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

? Exercise 4.2.1.1

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one



This equation shows that the starting materials of the reaction are two sets of bonded, green spheres which are each being combined with two smaller, bonded purple spheres. The products of the change are two molecules that each contain one purple sphere bonded between two green spheres.

Answer

The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the law of definite proportions or the law of constant composition. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table $4.2.1.1$.

Table $4.2.1.1$: Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82\text{ g carbon}}{2.78\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$
B	22.33 g	4.19 g	$\frac{22.33\text{ g carbon}}{4.19\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$
C	19.40 g	3.64 g	$\frac{19.40\text{ g carbon}}{3.63\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The law of multiple proportions states that *when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small, whole numbers*. For example, copper and chlorine can form a green, crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.

$$\frac{\frac{1.116 \text{ g Cl}}{1 \text{ g Cu}}}{\frac{0.558 \text{ g Cl}}{1 \text{ g Cu}}} = \frac{2}{1}$$

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound.

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (Figure 4.2.1.4).

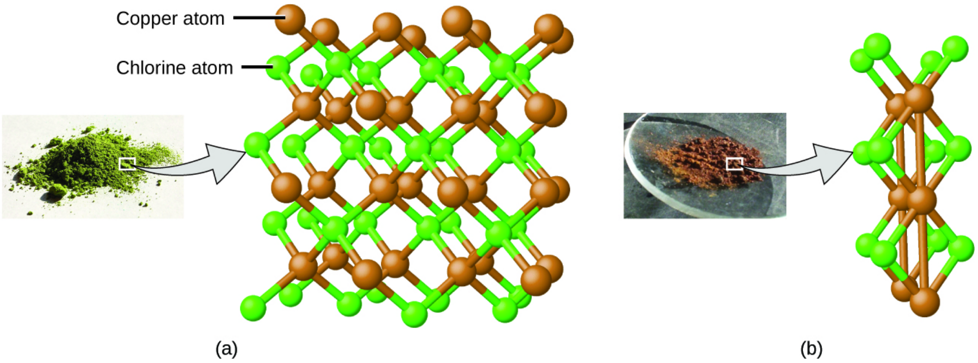


Figure 4.2.1.4: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by “Benjah-bmm27”/Wikimedia Commons; credit b: modification of work by “Walkerma”/Wikimedia Commons)

Figure A shows a pile of green powder. A callout shows that the green powder is made up of a lattice of copper atoms interspersed with chlorine atoms. The atoms are color coded brown for copper and green for chlorine. The number of copper atoms is equal to the number of chlorine atoms in the molecule. Figure B shows a pile of brown powder. A callout shows that the brown powder is also made up of copper and chlorine atoms similar to the molecule shown in figure A.

✓ Example 4.2.1.2: Laws of Definite and Multiple Proportions

A sample of compound A (a clear, colorless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colorless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

Solution

In compound A, the mass ratio of carbon to oxygen is:

$$\frac{1.33 \text{ g O}}{1 \text{ g C}}$$

In compound B, the mass ratio of carbon to oxygen is:

$$\frac{2.67 \text{ g O}}{1 \text{ g C}}$$

The ratio of these ratios is:

$$\frac{\frac{1.33 \text{ g O}}{1 \text{ g C}}}{\frac{2.67 \text{ g O}}{1 \text{ g C}}} = \frac{1}{2}$$

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much carbon per amount of oxygen (or twice as much oxygen per amount of carbon) as B. A possible pair of compounds that would fit this relationship would be A = CO_2 and B = CO.

? Exercise 4.2.1.1

A sample of compound X (a clear, colorless, combustible liquid with a noticeable odor) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colorless, combustible liquid with a noticeable odor that is slightly different from X's odor) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

Answer

In compound X, the mass ratio of carbon to hydrogen is $\frac{14.13\text{ g C}}{2.96\text{ g H}}$.

In compound Y, the mass ratio of carbon to oxygen is $\frac{19.91\text{ g C}}{3.34\text{ g H}}$.

The ratio of these ratios is

$$\frac{\frac{14.13\text{ g C}}{2.96\text{ g H}}}{\frac{19.91\text{ g C}}{3.34\text{ g H}}} = \frac{4.77\text{ g C/g H}}{5.96\text{ g C/g H}} = 0.800 = \frac{4}{5}.$$

This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

Summary

The ancient Greeks proposed that matter consists of extremely small particles called atoms. Dalton postulated that each element has a characteristic type of atom that differs in properties from atoms of all other elements, and that atoms of different elements can combine in fixed, small, whole-number ratios to form compounds. Samples of a particular compound all have the same elemental proportions by mass. When two elements form different compounds, a given mass of one element will combine with masses of the other element in a small, whole-number ratio. During any chemical change, atoms are neither created nor destroyed.

Glossary

Dalton's atomic theory

set of postulates that established the fundamental properties of atoms

law of constant composition

(also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

law of multiple proportions

when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

law of definite proportions

(also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

- 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

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4.3: The Discovery of The Electron - The Plum Pudding Atomic Model

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 4.3.1). 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.

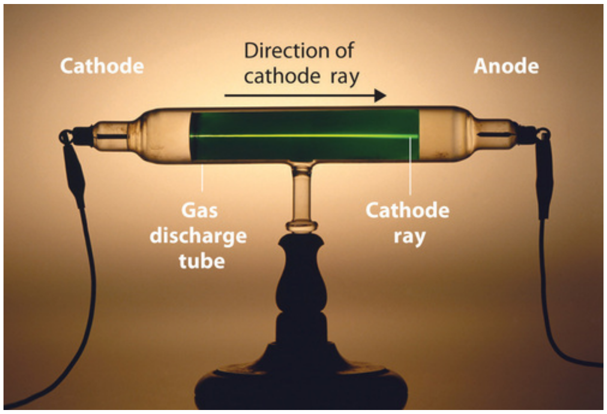


Figure 4.3.1: A Gas Discharge Tube Producing Cathode Rays. When a high voltage is applied to a gas contained at low pressure in a gas discharge tube, electricity flows through the gas, and energy is emitted in the form of light. Image used with Permission (CC BY-SA-NC).

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 4.3.2). 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.

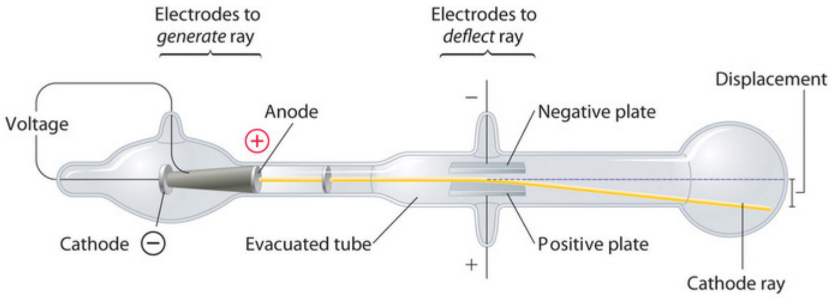


Figure 4.3.2: Deflection of Cathode Rays by an Electric Field. As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged. Image used with Permission (CC BY-SA-NC).

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

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

It was at this point that two separate lines of investigation began to converge, both aimed at determining how and why matter emits energy. The video below shows how JJ Thompson used such a tube to measure the ratio of charge over the 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 4.3.3: 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.

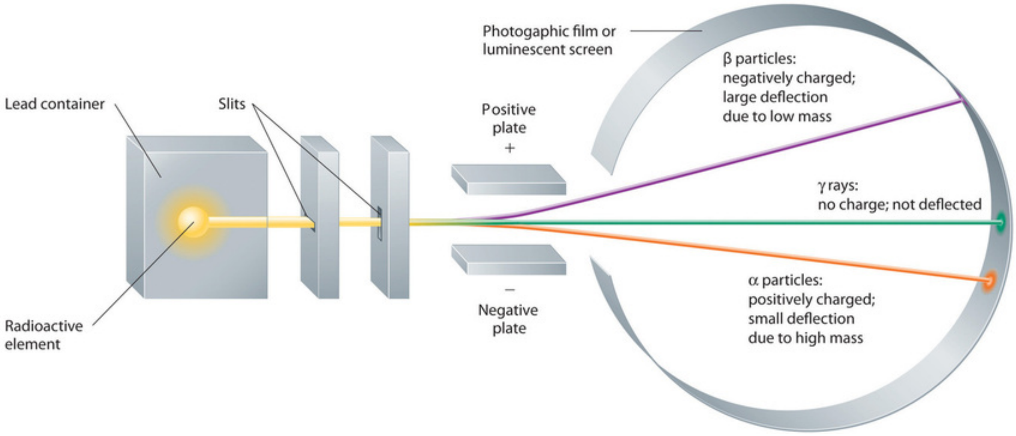


Figure 4.3.4: Effect of an Electric Field on α Particles, β Particles, and γ Rays. A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown to scale.) Image used with Permission (CC BY-SA-NC).

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 4.3.3 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 4.3.5 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.

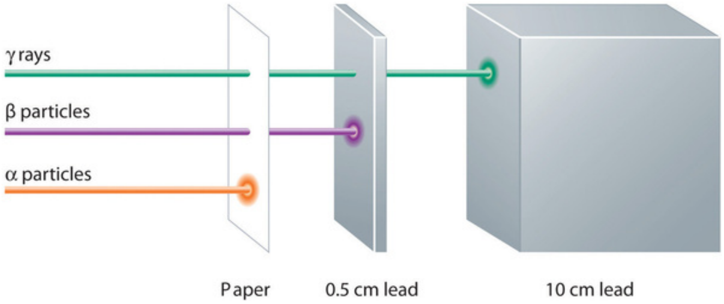


Figure 4.3.5: Relative Penetrating Power of the Three Types of Radiation. A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead or concrete is needed to absorb them. Image used with Permission (CC BY-SA-NC).

4.4: Discovery of the Proton - The Nuclear Atomic Model

Learning Objectives

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

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 $4.4.6$).

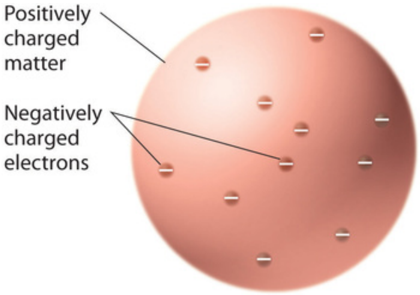
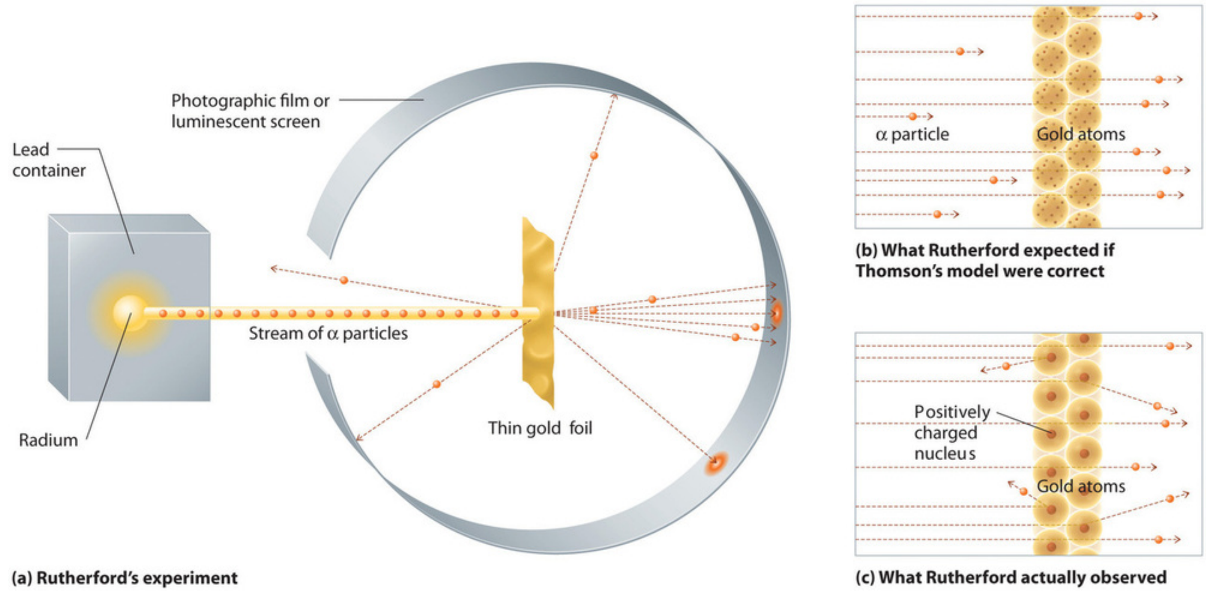


Figure $4.4.6$: Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom. In this model, the electrons are embedded in a uniform sphere of positive charge. Image used with Permission (CC BY-SA-NC).

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 $4.4.7a$) 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 $4.4.7b$). 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 $4.4.7c$). 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."



(a) Rutherford's experiment

(b) What Rutherford expected if Thomson's model were correct

(c) What Rutherford actually observed

Figure 4.4.7: 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).

The Nuclear Atom: https://youtu.be/eqoyZuv1tWA

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."

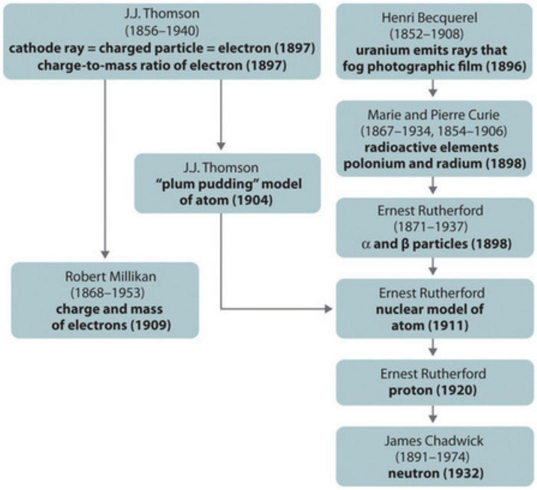


Figure 4.4.8: A Summary of the Historical Development of Models of the Components and Structure of the Atom. The dates in parentheses are the years in which the key experiments were performed. Image used with Permission (CC BY-SA-NC).

The historical development of the different models of the atom's structure is summarized in Figure 4.4.8. 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.

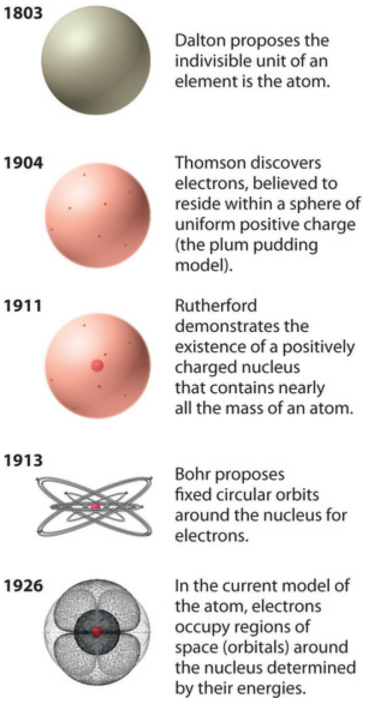


Figure 4.4.9: The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom. Bohr's model and the current model are described in Chapter 6, "The Structure of Atoms." Image used with Permission (CC BY-SA-NC).

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 4.4.9 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).

4.5: The Subatomic Particles and Isotopes

Learning Objectives

- Describe the locations, charges, and masses of the three main subatomic particles.
- Determine the number of protons and electrons in an atom.
- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion.
- Define the atomic mass unit and average atomic mass

Dalton's Atomic Theory explained a lot about matter, chemicals, and chemical reactions. Nevertheless, it was not entirely accurate, because contrary to what Dalton believed, atoms can, in fact, be broken apart into smaller subunits or subatomic particles. We have been talking about the electron in great detail, but there are two other particles of interest to us: protons and neutrons. We already learned that J. J. Thomson discovered a negatively charged particle, called the **electron**. Rutherford proposed that these electrons orbit a positive nucleus. In subsequent experiments, he found that there is a smaller positively charged particle in the nucleus, called a **proton**. There is also a third subatomic particle, known as a neutron.

Electrons

Electrons are one of three main types of particles that make up atoms. Unlike protons and neutrons, which consist of smaller, simpler particles, electrons are fundamental particles that do not consist of smaller particles. They are a type of fundamental particle called leptons. All leptons have an electric charge of -1 or 0. Electrons are extremely small. The mass of an electron is only about 1/2000 the mass of a proton or neutron, so electrons contribute virtually nothing to the total mass of an atom. Electrons have an electric charge of -1, which is equal but opposite to the charge of a proton, which is $+1$. All atoms have the same number of electrons as protons, so the positive and negative charges "cancel out", making atoms electrically neutral.

Unlike protons and neutrons, which are located inside the nucleus at the center of the atom, electrons are found outside the nucleus. Because opposite electric charges attract one another, negative electrons are attracted to the positive nucleus. This force of attraction keeps electrons constantly moving through the otherwise empty space around the nucleus. The figure below is a common way to represent the structure of an atom. It shows the electron as a particle orbiting the nucleus, similar to the way that planets orbit the sun. However, this is an incorrect perspective, as quantum mechanics demonstrates that electrons are more complicated.

Figure $4.5.1$: Electrons are much smaller than protons or neutrons. If an electron was the mass of a penny, a proton or a neutron would have the mass of a large bowling ball!

Protons

A proton is one of three main particles that make up the atom. Protons are found in the nucleus of the atom. This is a tiny, dense region at the center of the atom. Protons have a positive electrical charge of one $(+1)$ and a mass of 1 atomic mass unit (amu), which is about 1.67×10^{-27} kilograms. Together with neutrons, they make up virtually all of the mass of an atom.

Neutrons

Atoms of all elements—except for most atoms of hydrogen—have neutrons in their nucleus. Unlike protons and electrons, which are electrically charged, neutrons have no charge—they are electrically neutral. That's why the neutrons in the diagram above are labeled n^0. The zero stands for "zero charge". The mass of a neutron is slightly greater than the mass of a proton, which is 1 atomic mass unit (amu). (An atomic mass unit equals about 1.67×10^{-27} kilograms.) A neutron also has about the same diameter as a proton, or 1.7×10^{-15} meters.

As you might have already guessed from its name, the neutron is neutral. In other words, it has no charge whatsoever and is therefore neither attracted to nor repelled from other objects. Neutrons are in every atom (with one exception), and they are bound together with other neutrons and protons in the atomic nucleus.

Before we move on, we must discuss how the different types of subatomic particles interact with each other. When it comes to neutrons, the answer is obvious. Since neutrons are neither attracted to nor repelled from objects, they don't really interact with protons or electrons (beyond being bound into the nucleus with the protons).

Even though electrons, protons, and neutrons are all types of subatomic particles, they are not all the same size. When you compare the masses of electrons, protons, and neutrons, what you find is that electrons have an extremely small mass, compared to either protons or neutrons. On the other hand, the masses of protons and neutrons are fairly similar, although technically, the mass of a neutron is slightly larger than the mass of a proton. Because protons and neutrons are so much more massive than electrons, almost all of the mass of any atom comes from the nucleus, which contains all of the neutrons and protons.

Table $4.5.1$: Properties of Subatomic Particles

Particle	Symbol	Mass (amu)	Relative Mass (proton = 1)	Relative Charge	Location
proton	p^+	1	1	+1	inside the nucleus
electron	e^-	5.45×10^{-4}	0.00055	−1	outside the nucleus
neutron	n^0	1	1	0	inside the nucleus

Table $4.5.1$ gives the properties and locations of electrons, protons, and neutrons. The third column shows the masses of the three subatomic particles in "atomic mass units." An **atomic mass unit (amu)** is defined as one-twelfth of the mass of a carbon-12 atom. Atomic mass units (amu) are useful, because, as you can see, the mass of a proton and the mass of a neutron are almost exactly 1 in this unit system.

Negative and positive charges of equal magnitude cancel each other out. This means that the negative charge on an electron perfectly balances the positive charge on the proton. In other words, a neutral atom must have exactly one electron for every proton. If a neutral atom has 1 proton, it must have 1 electron. If a neutral atom has 2 protons, it must have 2 electrons. If a neutral atom has 10 protons, it must have 10 electrons. You get the idea. In order to be neutral, an atom must have the same number of electrons and protons.

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the atomic mass unit (amu) and the fundamental unit of charge (e). The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as “carbon-12” as will be discussed later in this module.) Thus, one amu is exactly $1/12$ of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The Dalton (Da) and the unified atomic mass unit (u) are alternative units that are equivalent to the amu.)

Atomic Number

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

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

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

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

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

✓ Example 4.5.1: Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 4.5.2).

Figure 4.5.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by “Almazi”/Wikimedia Commons; credit b: modification of work by Mike Mozart)

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

Solution

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

? Exercise 4.5.1

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

Answer

78 protons; 117 neutrons; charge is 4+

Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure 4.5.3). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).

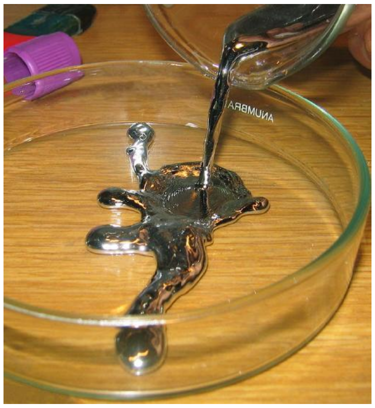


Figure 4.5.3: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. from Wikipedia (user: Materialscientist).

The symbols for several common elements and their atoms are listed in Table 4.5.2. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Symbols have one or two letters, for example, H for hydrogen and Cl for chlorine. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table.

Table 4.5.2: Some Common Elements and Their Symbols

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists or locations; for example, element 106 is now known as *seaborgium* (Sg) in honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements.

Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure 4.5.4). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ${}^{24}\text{Mg}$, ${}^{25}\text{Mg}$, and ${}^{26}\text{Mg}$. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ${}^{24}\text{Mg}$ is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ${}^{25}\text{Mg}$ is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ${}^{24}\text{Mg}$ atom has 12 neutrons in its nucleus, a ${}^{25}\text{Mg}$ atom has 13 neutrons, and a ${}^{26}\text{Mg}$ has 14 neutrons.

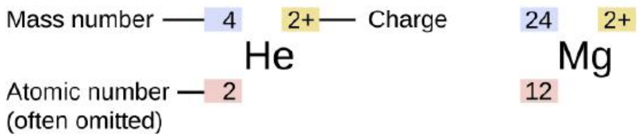


Figure 4.5.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 4.5.2. Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ${}^{2}\text{H}$, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ${}^{3}\text{H}$, is also called tritium and sometimes symbolized T.

Table 4.5.2: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	${}^{1}_{1}\text{H}$ (protium)	1	1	0	1.0078	99.989
	${}^{2}_{1}\text{H}$ (deuterium)	1	1	1	2.0141	0.0115
	${}^{3}_{1}\text{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	${}^{3}_{2}\text{He}$	2	2	1	3.01603	0.00013
	${}^{4}_{2}\text{He}$	2	2	2	4.0026	100
lithium	${}^{6}_{3}\text{Li}$	3	3	3	6.0151	7.59
	${}^{7}_{3}\text{Li}$	3	3	4	7.0160	92.41
beryllium	${}^{9}_{4}\text{Be}$	4	4	5	9.0122	100
boron	${}^{10}_{5}\text{B}$	5	5	5	10.0129	19.9
	${}^{11}_{5}\text{B}$	5	5	6	11.0093	80.1
carbon	${}^{12}_{6}\text{C}$	6	6	6	12.0000	98.89
	${}^{13}_{6}\text{C}$	6	6	7	13.0034	1.11
	${}^{14}_{6}\text{C}$	6	6	8	14.0032	— (trace)
nitrogen	${}^{14}_{7}\text{N}$	7	7	7	14.0031	99.63
	${}^{15}_{7}\text{N}$	7	7	8	15.0001	0.37
oxygen	${}^{16}_{8}\text{O}$	8	8	8	15.9949	99.757
	${}^{17}_{8}\text{O}$	8	8	9	16.9991	0.038
	${}^{18}_{8}\text{O}$	8	8	10	17.9992	0.205
fluorine	${}^{19}_{9}\text{F}$	9	9	10	18.9984	100

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
neon	${}^{20}_{10}\text{Ne}$	10	10	10	19.9924	90.48
	${}^{21}_{10}\text{Ne}$	10	10	11	20.9938	0.27
	${}^{22}_{10}\text{Ne}$	10	10	12	21.9914	9.25

Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the atomic mass of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

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

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

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

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

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

✓ Example 4.5.2: Calculation of Average Atomic Mass

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

Solution

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

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

? Exercise 4.5.2

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

Answer

24.31 amu

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

Example 4.5.3: Calculation of Percent Abundance

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

Solution

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

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

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

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

Substituting this into the average mass equation, we have:

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

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

Exercise 4.5.3

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

Answer

69.15% Cu-63 and 30.85% Cu-65

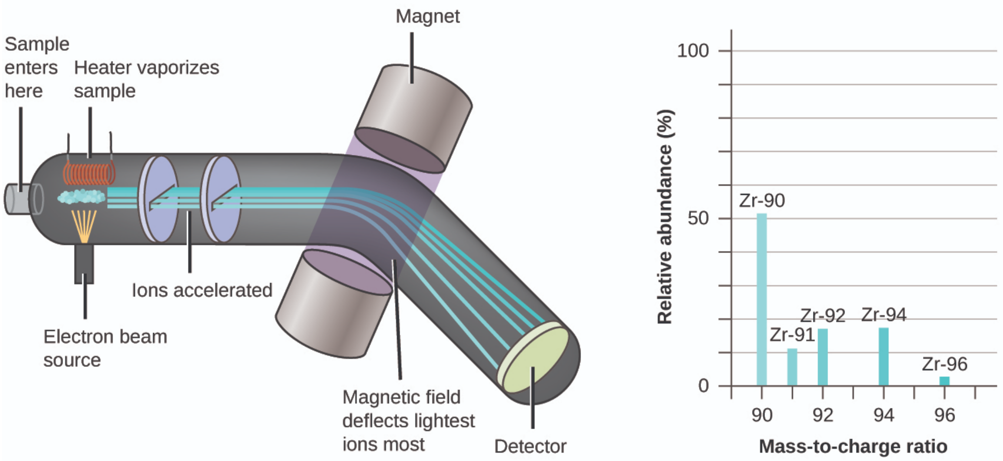


Figure 4.5.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure 4.5.5), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation’s path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent that that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.

***Video* $4.5.1$**: *Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.*

Summary

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly $1/12$ of the mass of a carbon-12 atom and is equal to 1.6605×10^{-24} g.

Protons are relatively heavy particles with a charge of 1+ and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of 1− and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom’s elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom. An atom is neutral when it contains equal numbers of electrons and protons.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

Key Equations

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

Glossary

anion

negatively charged atom or molecule (contains more electrons than protons)

atomic mass

average mass of atoms of an element, expressed in amu

atomic mass unit (amu)

(also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a ^{12}C atom

atomic number (Z)

number of protons in the nucleus of an atom

cation
positively charged atom or molecule (contains fewer electrons than protons)

chemical symbol
one-, two-, or three-letter abbreviation used to represent an element or its atoms

Dalton (Da)
alternative unit equivalent to the atomic mass unit

fundamental unit of charge
(also called the elementary charge) equals the magnitude of the charge of an electron (e) with $e = 1.602 \times 10^{-19}$ C

ion
electrically charged atom or molecule (contains unequal numbers of protons and electrons)

mass number (A)
sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)
alternative unit equivalent to the atomic mass unit

4.5.1: Ions - Differences in Electrons

Learning Objectives

- Distinguish the difference between the two types of ions.
- Describe ion formation using electron configurations.
- Predict ionic charge.

Ions

As seen in prior sections, atoms contain a nucleus with neutrons and positively charged protons, surrounded by negatively charged electrons. In an atom, the total number of electrons, negative charge, *equals* the total number of protons, positive charge, and therefore, atoms are electrically neutral or uncharged. If an atom loses or gains electrons, it will become a positively or negatively charged particle, called an **ion**. The *loss* of one or more electrons results in more protons than electrons and an overall positively charged ion, called a **cation**. For example, a sodium atom with one less electron is a cation, Na^+, with a +1 charge (Figure $4.5.1.1$).

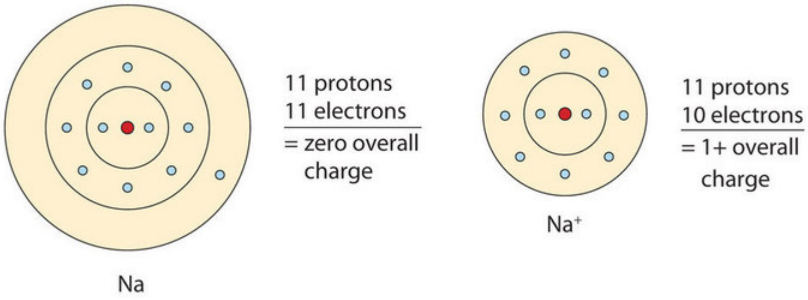


Figure $4.5.1.1$: On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

When an atom *gains* one or more electrons, it becomes a negatively charged **anion**, because there are more electrons than protons. When chlorine gains one electron it forms a chloride ion, Cl^-, with a –1 charge (Figures $4.5.1.2$)

> The names for positive and negative ions are pronounced CAT-eye-ons (cations) and ANN-eye-ons (anions), respectively.

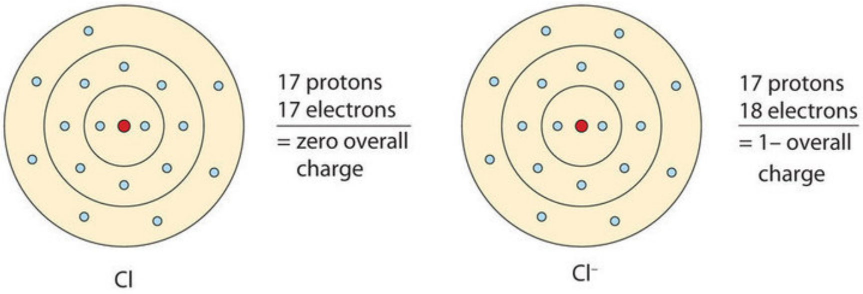


Figure $4.5.1.2$: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

Key Takeaways

- Ions can be positively charged or negatively charged.
- Ionic charge relates to valence electrons and valence shells.

Exercises

1. What are the two types of ions?
2. When the following atoms become ions, what charges do they acquire?

a. Li
b. S

c. Ca
d. F

4. Identify each as a cation, an anion, or neither.

a. H^+
b. $Cl^−$
c. O_2
d. Ba^{2+}
e. CH_4
f. CS_2

5. Identify each as a cation, an anion, or neither.

a. NH_3
b. $Br^−$
c. $H^−$
d. Hg^{2+}
e. CCl_4
f. SO_3

Answers

1. Cations (positive charged) and anions (negative charged)
2.
   a. 1+
   b. 2−
   c. 2+
   d. 1−

4.

a. cation
b. anion
c. neither
d. cation
e. neither
f. neither

5.

a. neither
b. anion
c. anion
d. cation
e. neither
f. neither

Contributors

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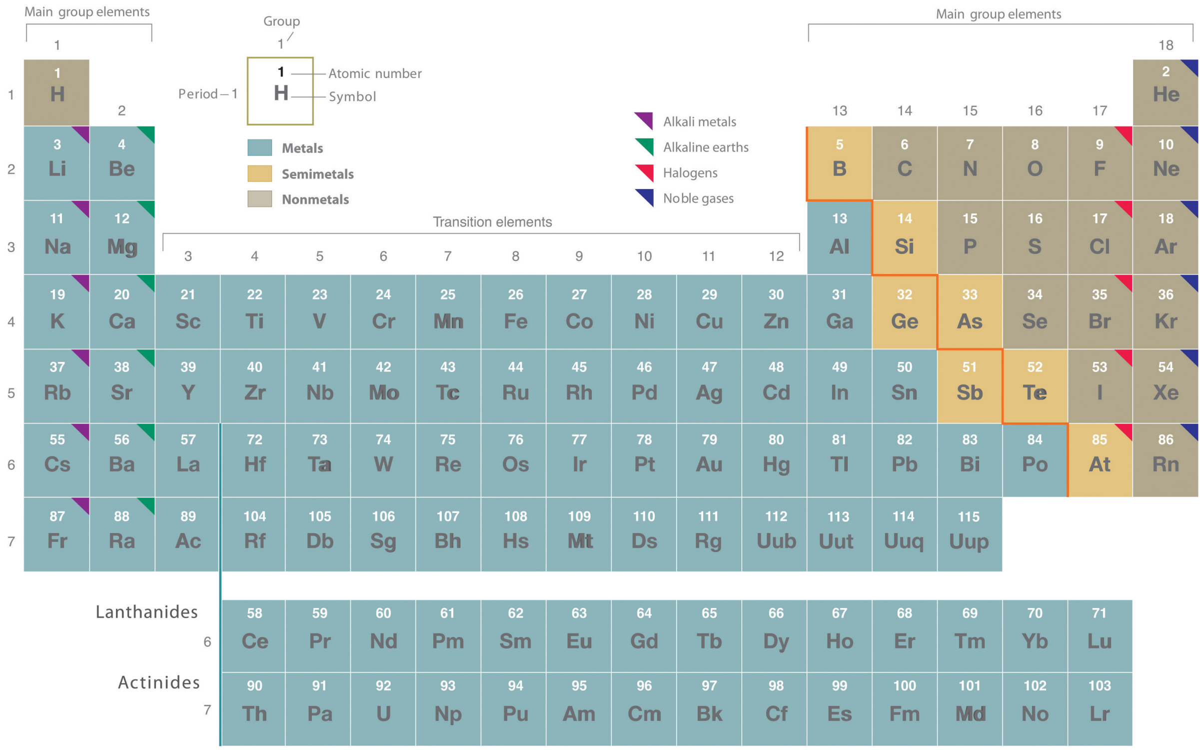
4.6: The Periodic Table of the Elements

Learning Objectives

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

Rutherford’s nuclear model of the atom helped explain why atoms of different elements exhibit different chemical behavior. The identity of an element is defined by its *atomic number (Z)*, the number of protons in the nucleus of an atom of the element. The atomic number is therefore different for each element. The known elements are arranged in order of increasing Z in the *periodic table* (Figure 4.6.1). The rationale for the peculiar format of the periodic table is explained later. Each element is assigned a unique one-, two-, or three-letter symbol. The names of the elements are listed in the periodic table, along with their symbols, atomic numbers, and atomic masses. The chemistry of each element is determined by its number of protons and electrons. In a neutral atom, the number of electrons equals the number of protons.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup			

Lanthanides	6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 4.6.1: The Periodic Table Showing the Elements in Order of Increasing Z. The metals are on the bottom left in the periodic table, and the nonmetals are at the top right. The semimetals lie along a diagonal line separating the metals and nonmetals. An interactive Periodic table can be found Periodic Table of the Elements, LibreTexts. (CC-BY-SA-NC 3.0; Anonymous via LibreTexts)

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

Metals, Nonmetals, and Semimetals

The heavy orange zigzag line running diagonally from the upper left to the lower right through groups 13–16 in Figure 4.6.1 divides the elements into metals (in blue, below and to the left of the line) and nonmetals (in bronze, above and to the right of the line). Gold-colored lements that lie along the diagonal line exhibit properties intermediate between metals and nonmetals; they are called semimetals.

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

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

✓ Example $4.6.1$: Classifying Elements

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

Given: element

Asked for: classification

Strategy:

Find selenium in the periodic table shown in Figure $4.6.1$ and then classify the element according to its location.

Solution:

The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure $4.6.1$, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

? Exercise $4.6.1$

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

Answer

metal

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

Group 1: The Alkali Metals

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

Group 2: The Alkaline Earth Metals

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

Group 17: The Halogens

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

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

Group 18: The Noble Gases

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

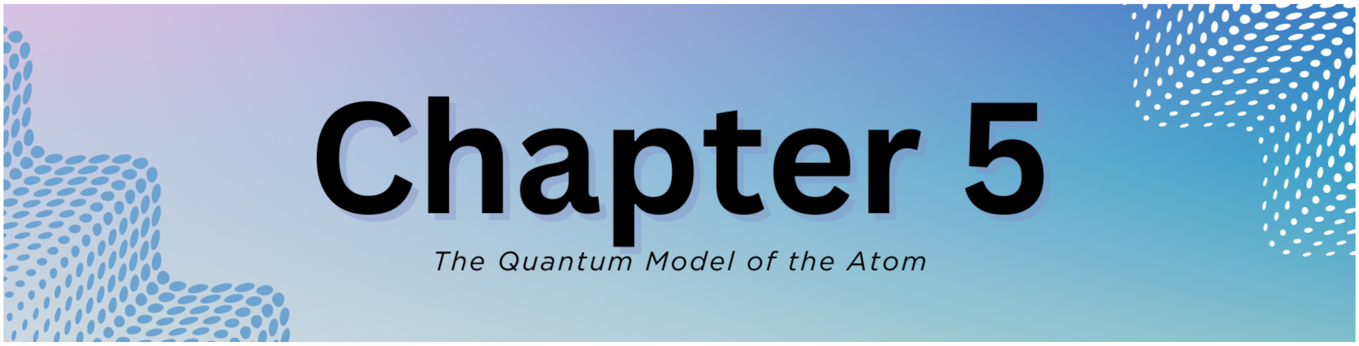
> *The noble gases are unreactive at room temperature and pressure.*

Summary

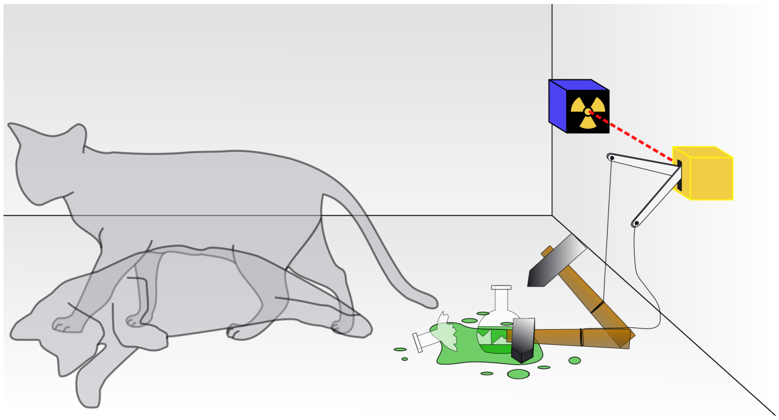
The periodic table is used as a predictive tool. It arranges of the elements in order of increasing atomic number. Elements that exhibit similar chemistry appear in vertical columns called groups (numbered 1–18 from left to right); the seven horizontal rows are called periods. Some of the groups have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

CHAPTER OVERVIEW

5: The Quantum Model of the Atom



In the early 1930's Erwin Schrödinger published a way of thinking about the circumstance of radioactive decay that is still useful. We imagine an apparatus containing just one Nitrogen-13 atom and a detector that will respond when the atom decays. Connected to the detector is a relay connected to a hammer, and when the atom decays the relay releases the hammer which then falls on a glass vial containing poison gas. We take the entire apparatus and put it in a box. We also place a cat in the box, close the lid, and wait 10 minutes.



Schrödinger's cat: a cat, a flask of poison, and a radioactive source are placed in a sealed box. If an internal monitor detects radioactivity (i.e., a single atom decaying), the flask is shattered, releasing the poison, which kills the cat. The Copenhagen interpretation of quantum mechanics implies that after a while, the cat is simultaneously alive and dead. Yet, when one looks in the box, one sees the cat either alive or dead, not both alive and dead. This poses the question of when exactly quantum superposition ends and reality collapses into one possibility or the other. (CC BY-SA 3.0; Dhatfield).

A diagram of a box which has the superposition of both states. The diagram of both the dead and alive cat are present, along with the intact and broken flask, as well as the released and unreleased hammer attached to the radioactive sensor.

We then ask: Is the cat alive or dead? The answer according to quantum mechanics is that it is 50% dead and 50% alive.

Quantum Mechanics describes the world in terms of a *wave function*. DeWitt wrote about the cat that "at the end of [one half-life] the total wave function for the system will have a form in which the living cat and dead cat are mixed in equal portions." (Reference: B.S. DeWitt and N. Graham, eds., **The Many-Worlds Interpretation of Quantum Mechanics** (Princeton, 1973), pg. 156.) When we open the box, we "collapse the wave function" or "collapse the state" and have either a live cat or a dead cat.

Of course, this is just a thought experiment. So far as I know nobody has actually every done this experiment. In a sense the cat is a "red herring" [sorry!]. The paradox is just an illuminating way of thinking about the consequences of radioactive decay being totally random. Imagine we have a friend waiting outside when we open the box. For us the wave function collapses and we have, say, a live cat. But our friend's wave function does not collapse until he comes into the room. This leads to a strong solipsism, since our friend can they say that we owe our objective existence to his kind intervention in coming into the room and collapsing our state.

As Heisenberg said, then, "The wave function represents partly a fact and partly our knowledge of a fact." Our friend needn't have come into the room to collapse his wave function: if we have a cell phone we can call him and tell him the result of the experiment. Of course, this assumes that we don't lie to him and tell him the cat is dead when it is alive. Unexplained but apparently true is the fact that when a state collapses, it collapses into the same state for everybody. If we see a live cat everybody sees a live cat (unless they or us are hallucinating).

Chapter Sections

5.1: The Nature of Light and Electromagnetic Radiation

Learning Objectives

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

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

Figure 5.1.1: 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 5.1.1). 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.

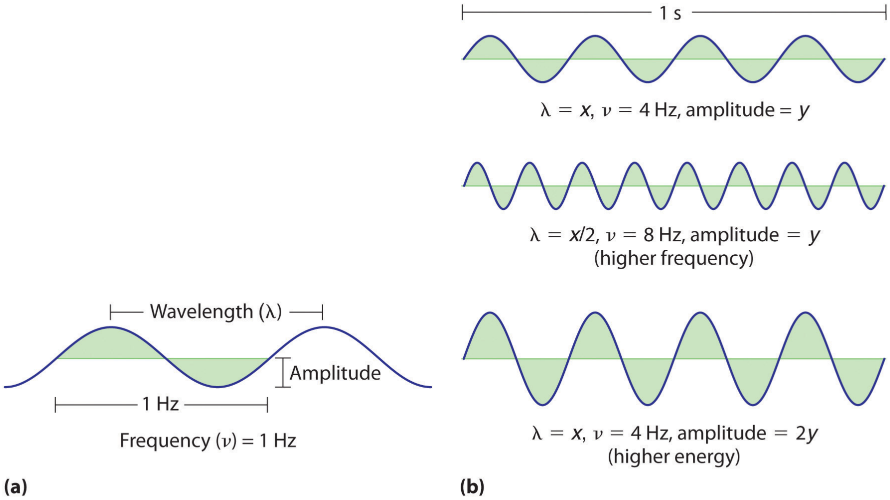


Figure 5.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 5.1.2). As you may have noticed in Figure 5.1.1, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the wavelength (λ), distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs. λ is the lowercase Greek lambda, and ν is the lowercase Greek nu. Wavelengths are described by a unit of distance, typically meters. The frequency (ν), the number of oscillations (i.e., of a wave) that pass a particular point in a given period of time. of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations persecond (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894),a pioneer in the field of electromagnetic radiation. The amplitude (the vertical height of a wave, which is defined as half the peak-to-trough height), or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 5.1.2, two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), the distance traveled by a wave per unit time, which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

(wavelength)(frequency) = speed

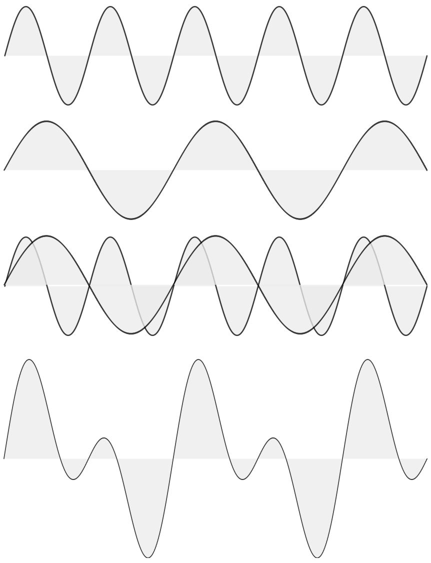
$$\lambda\nu = v \tag{5.1.1}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{wave}}{second}\right) = \frac{meters}{second} \tag{5.1.2}$$

Be careful not to confuse the symbols for the speed, v, with the frequency, ν. 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.

Wave Interference

When waves interact with each other or overlap, they interfere with one another such that theit amplitudes are changed. The best way to see what this means is to watch: try watching the video on the Double Slit experiment to see waves interacting. Basically, to find the total wave made of several different waves, you just add the amplitude at each point. For instance, if the high part (amplitude 1, say) of one wave overlaps the low part of another (-2, say, this wave is bigger), the result is a smaller wave (-1, here), called **destructive interference**. If the 2 peaks (high parts) overlap, then the wave get bigger, called **constructive interference**. In the graph below, the sum wave has big peaks in regions of constructive interference, and small peaks in regions of destructive interference.



Two sine waves, plotted separately (top), on the same axes (middle), and summed to show the total wave with regions of constructive and destructive interference (bottom).

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as electromagnetic radiation, which is energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure 5.1.3). Some forms of electromagnetic radiation are shown in Figure 5.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which is the speed with which all forms of electromagnetic radiation travel in a vacuum, a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (which is about 3.00 ×10^8 m/s or 1.86 × 10^5 mi/s). This is about a million times faster than the speed of sound.

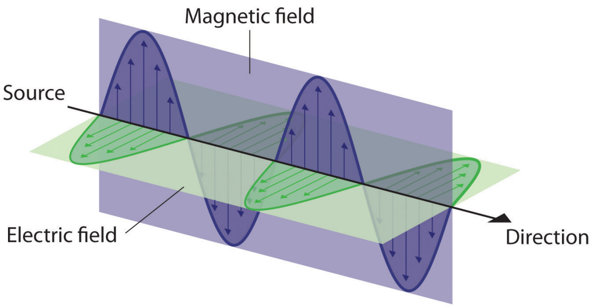


Figure 5.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 5.1.4 and Table 5.1.1, 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 5.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$\begin{aligned} c &= \lambda\nu \\ \nu &= \frac{c}{\lambda} \end{aligned} \tag{5.1.3}$$

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

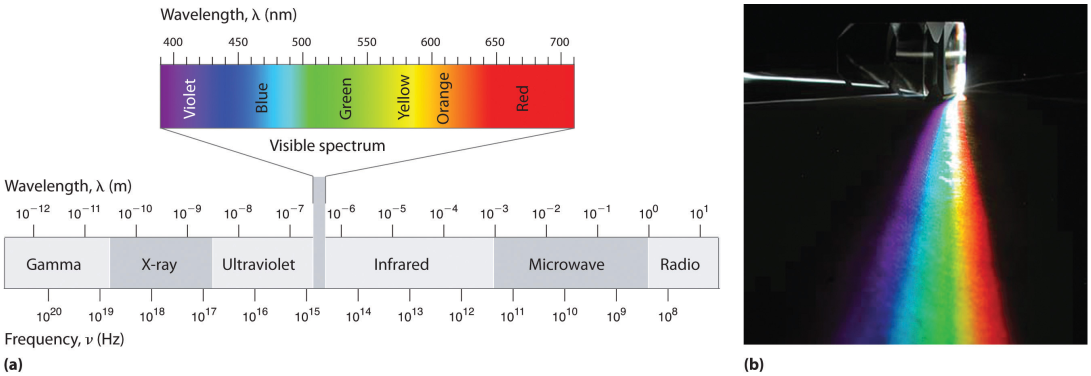


Figure 5.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Within this visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 5.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 5.1.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray

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

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

$$E \propto \nu \tag{5.1.4}$$

$$E \propto \frac{1}{\lambda} \tag{5.1.5}$$

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

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

✓ Example 5.1.1: 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 5.1.3 to calculate the wavelength in meters.

Solution:

From Equation 5.1.3, we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998 × 10^8 m/s:

$$\lambda\nu = c = 2.998 \times 10^8 m/s \tag{5.1.6}$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{\nu} = \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \cancel{MHz}}\right)\left(\frac{1\ \cancel{MHz}}{10^6\ \cancel{s^{-1}}}\right) = 2.965\ m \tag{5.1.7}$$

? Exercise 5.1.1

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

Contributors and Attributions

- Khan Academy: Introduction to Waves (13 min)
- Amplitude, Period, Frequency, and Wavelength of Periodic Waves (14 min)
- Brightstorm: Wave Interference (8 min)
- Veritasium: The Original Double Slit Experiment (8 min)
- Brightstorm: Standing Waves (10 min)
- Emily V Eames (City College of San Francisco)
- Modified by Joshua Halpern (Howard University)

5.2: The Photoelectric Effect - Light as a Particle

Learning Objectives

- To be familiar with the photoelectron effect for bulk materials
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light wavelength
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light intensity
- Describe what a workfunction is and relate it to ionization energy
- Describe the photoelectric effect with Einstein's quantized photon model of light

Nature, it seemed, was quantized (non-continuous, or discrete). If this was so, how could Maxwell's equations correctly predict the result of the blackbody radiator? Planck spent a good deal of time attempting to reconcile the behavior of electromagnetic waves with the discrete nature of the blackbody radiation, to no avail. It was not until 1905, with yet another paper published by Albert Einstein, that the wave nature of light was expanded to include the particle interpretation of light which adequately explained Planck's equation.

The photoelectric effect was first documented in 1887 by the German physicist Heinrich Hertz and is therefore sometimes referred to as the Hertz effect. While working with a spark-gap transmitter (a primitive radio-broadcasting device), Hertz discovered that upon absorption of certain frequencies of light, substances would give off a visible spark. In 1899, this spark was identified as light-excited electrons (called **photoelectrons**) leaving the metal's surface by J.J. Thomson (Figure 1.3.1).

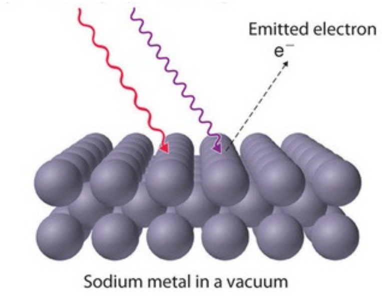


Figure 1.3.1 : The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

The classical picture underlying the photoelectron effect was that the atoms in the metal contained electrons, that were shaken and caused to vibrate by the oscillating electric field of the incident radiation. Eventually some of them would be shaken loose, and would be ejected from the cathode. It is worthwhile considering carefully how the *number* and *speed* of electrons emitted would be expected to vary with the *intensity* and *color* of the incident radiation along with the time needed to observe the photoelectrons.

- Increasing the intensity of radiation would shake the electrons more violently, so one would expect more to be emitted, and they would shoot out at greater speed, on average.
- Increasing the frequency of the radiation would shake the electrons faster, so it might cause the electrons to come out faster. For very dim light, it would take some time for an electron to work up to a sufficient amplitude of vibration to shake loose.

Lenard's Experimental Results (Intensity Dependence)

In 1902, Hertz's student, Philipp Lenard, studied how the energy of the emitted photoelectrons varied with the intensity of the light. He used a carbon arc light and could increase the intensity a thousand-fold. The ejected electrons hit another metal plate, the collector, which was connected to the cathode by a wire with a sensitive ammeter, to measure the current produced by the illumination (Figure 1.3.2). To measure the energy of the ejected electrons, Lenard charged the collector plate negatively, to repel the electrons coming towards it. Thus, only electrons ejected with enough kinetic energy to get up this potential hill would contribute to the current.

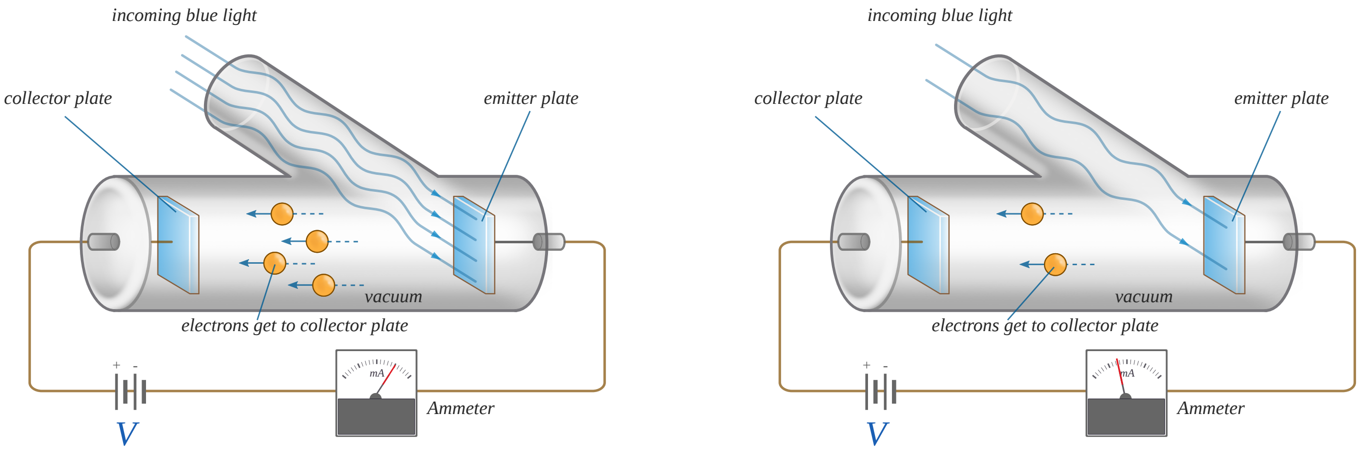


Figure 5.2.2: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Lenard discovered that there was a well defined minimum voltage that stopped any electrons getting through (V_{stop}). To Lenard's surprise, he found that V_{stop} did not depend at all on the intensity of the light! Doubling the light intensity doubled the *number* of electrons emitted, but did not affect the *kinetic energies* of the emitted electrons. The more powerful oscillating field ejected more electrons, but the maximum individual energy of the ejected electrons was the same as for the weaker field (Figure 1.3.2).

Millikan's Experimental Results (Wavelength Dependence)

The American experimental physicist Robert Millikan followed up on Lenard's experiments and using a powerful arc lamp, he was able to generate sufficient light intensity to separate out the colors and check the photoelectric effect using light of different colors. He found that the maximum energy of the ejected electrons *did* depend on the color - the shorter wavelength, higher frequency light eject photoelectrons with greater kinetic energy (Figures 1.3.3).

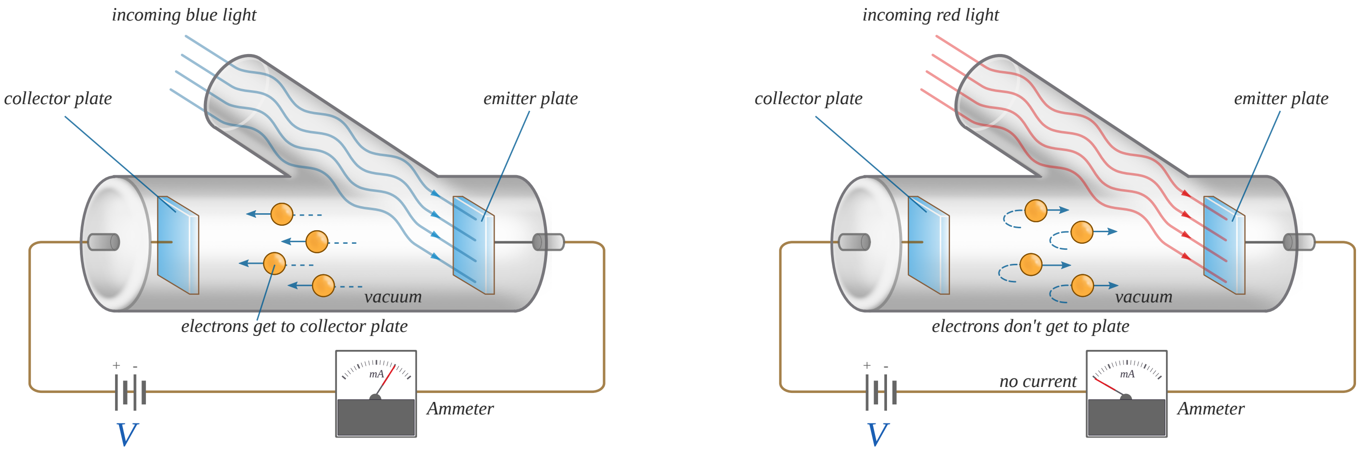


Figure 1.3.3 : Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector plate, the potential supplied by the battery is less than V_{stop}, for blue light. (right) Indicent low-energy red light. Since the electrons ejected by the red light are not getting to the collector plate, the potential supplied by the battery exceeds V_{stop} for red light. (CC BY-NC; Ümit Kaya via LibreTexts)

As shown in Figure 1.3.4 , just the opposite behavior from classical is observed from Lenard's and Millikan's experiments. The intensity affects the number of electrons, and the frequency affects the kinetic energy of the emitted electrons. From these sketches, we see that

- the kinetic energy of the electrons is linearly proportional to the frequency of the incident radiation above a threshold value of ν_0 (no current is observed below ν_0), and the kinetic energy is independent of the intensity of the radiation, and
- the number of electrons (i.e. the electric current) is proportional to the intensity and independent of the frequency of the incident radiation above the threshold value of ν_0 (i.e., no current is observed below ν_0).

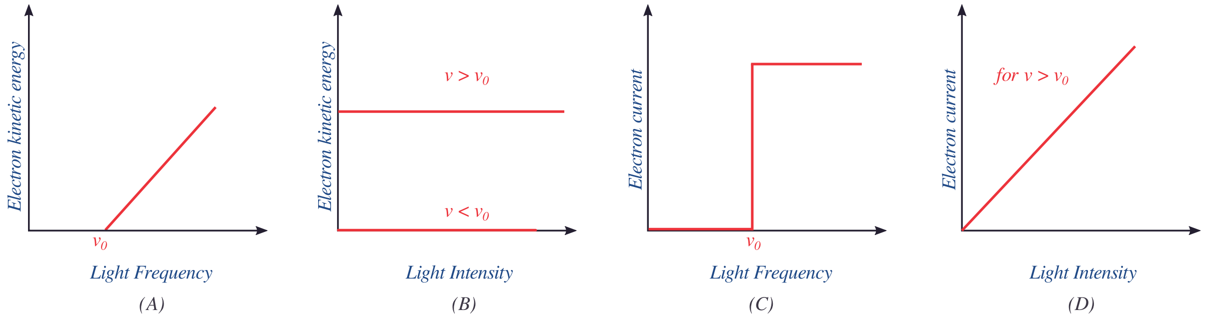


Figure 1.3.4 : Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the light intensity above the threshold frequency and zero below. (C) The number of electrons emitted per second (i.e. the electric current) is independent of light frequency above the threshhold frequency and zero below. (D) The number of electrons increases linearly with the light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Classical Theory does not Describe Experiment

Classical theory predicts that energy carried by light is proportional to its amplitude independent of its frequency, and this fails to correctly explain the observed wavelength dependence in Lenard's and Millikan's observations.

As with most of the experimental results we discuss in this text, the behavior described above is a simplification of the true experimental results observed in the laboratory. A more complex description involves a greater introduction of more complex physics and instrumentation, which will be ignored for now.

Einstein's Quantum Picture

In 1905 Einstein gave a very simple interpretation of Lenard's results and borrowed Planck's hypothesis about the quantized energy from his blackbody research and assumed that the incoming radiation should be thought of as quanta of energy $h\nu$, with ν the frequency. In photoemission, one such quantum is absorbed by one electron. If the electron is some distance into the material of the cathode, some energy will be lost as it moves towards the surface. There will always be some electrostatic cost as the electron leaves the surface, which is the workfunction, Φ. The most energetic electrons emitted will be those very close to the surface, and they will leave the cathode with kinetic energy

$$KE = h\nu - \Phi \tag{5.2.1}$$

On cranking up the negative voltage on the collector plate until the current just stops, that is, to V_{stop}, the highest kinetic energy electrons (KE_e) must have had energy eV_{stop} upon leaving the cathode. Thus,

$$eV_{stop} = h\nu - \Phi \tag{5.2.2}$$

Thus, Einstein's theory makes a very definite quantitative prediction: if the frequency of the incident light is varied, and V_{stop} plotted as a function of frequency, the slope of the line should be $\frac{h}{e}$ (Figure $5.2.4A$). It is also clear that there is a minimum light frequency for a given metal ν_o, that for which the quantum of energy is equal to Φ (Equation 5.2.1). Light below that frequency, no matter how bright, will not eject electrons.

> *According to both Planck and Einstein, the energy of light is proportional to its frequency rather than its amplitude, there will be a minimum frequency ν_0 needed to eject an electron with no residual energy.*

Since every photon of sufficient energy excites only one electron, increasing the light's intensity (i.e. the number of photons/sec) only increases the *number* of released electrons and not their kinetic energy. In addition, no time is necessary for the atom to be heated to a critical temperature and therefore the release of the electron is nearly instantaneous upon absorption of the light. Finally, because the photons must be above a certain energy to satisfy the workfunction, a threshold frequency exists below which no photoelectrons are observed. This frequency is measured in units of Hertz (1/second) in honor of the discoverer of the photoelectric effect.

Einstein's Equation 5.2.1 explains the properties of the photoelectric effect quantitatively. A strange implication of this experiment is that light can behave as a kind of massless "particle" now known as a *photon* whose energy $E = h\nu$ can be transferred to an actual particle (an electron), imparting kinetic energy to it, just as in an elastic collision between to massive particles such as billiard balls.

> Robert Millikan initially did not accept Einstein's theory, which he saw as an attack on the wave theory of light, and worked for ten years until 1916, on the photoelectric effect. He even devised techniques for scraping clean the metal surfaces inside the vacuum tube. For all his efforts he found disappointing results: he confirmed Einstein's theory after ten years. In what he writes in his paper, Millikan is still desperately struggling to avoid this conclusion. However, by the time of his Nobel Prize acceptance speech, he has changed his mind rather drastically!

Einstein's simple explanation (Equation 5.2.1) completely accounted for the observed phenomena in Lenard's and Millikan's experiments (Figure 1.3.4) and began an investigation into the field we now call *quantum mechanics*. This new field seeks to provide a quantum explanation for classical mechanics and create a more unified theory of physics and thermodynamics. The study of the photoelectric effect has also lead to the creation of new field of photoelectron spectroscopy. Einstein's theory of the photoelectron presented a completely different way to measure Planck's constant than from black-body radiation.

The Workfunction (Φ)

The **workfunction** is an intrinsic property of the metal. While the workfunctions and ionization energies appear as similar concepts, they are independent. The workfunction of a metal is the minimum amount of energy (E) necessary to remove an electron from the surface of the bulk (*solid*) metal (sometimes referred to as **binding energy**).

$$\mathrm{M(s)} + \Phi \rightarrow \mathrm{M^+(s)} + \mathrm{e^-}\,(\text{free with no kinetic energy})$$

The workfunction is qualitatively similar to ionization energy (IE), which is the amount of energy required to remove an electron from an atom or molecule in the *gaseous* state.

$$\mathrm{M(g)} + \mathrm{IE} \rightarrow \mathrm{M^+(g)} + \mathrm{e^-}\,(\text{free with no kinetic energy})$$

However, these two energies differ in magnitude (Table 1.3.1). For instance, copper has a workfunction of about 4.7 eV, but has a higher ionization energy of 7.7 eV. Generally, the ionization energies for metals are greater than the corresponding workfunctions (i.e., the electrons are less tightly bound in bulk metal).

Table 1.3.1 : Workfunctions and Ionization Energies of Select Elements

Element	Workfunction Φ (eV)	Ionization Energy (eV)
Lithium (Li)	2.93	5.39
Beryllium (Be)	4.98	9.32
Boron (B)	4.45	8.298
Carbon (C)	5.0	11.26
Sodium (Na)	2.36	5.13
Aluminum (Al)	4.20	5.98
Silicon (Si)	4.85	8.15
Potassium (K)	2.3	4.34
Iron (Fe)	4.67	7.87
Cobalt (Co)	4.89	7.88
Copper (Cu)	4.7	7.7
Gallium (Ga)	4.32	5.99

Element	Workfunction Φ (eV)	Ionization Energy (eV)
Germanium (Ge)	5.0	7.89
Arsenic (As)	3.75	9.81
Selenium (Se)	5.9	9.75
Silver (Ag)	4.72	7.57
Tin (Sn)	4.42	7.34
Cesium (Cs)	1.95	3.89
Gold (Au)	5.17	9.22
Mercury $(Hg)_{liquid}$	4.47	10.43
Bismuth (Bi)	4.34	7.29

✓ Example 1.3.1 : Calcium

a. What is the energy in joules and electron volts of a photon of 420-nm violet light?
b. What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the workfunction for calcium metal is 2.71 eV?

Strategy

To solve part (a), note that the energy of a photon is given by $E = h\nu$. For part (b), once the energy of the photon is calculated, it is a straightforward application of Equation 5.2.1 to find the ejected electron’s maximum kinetic energy, since Φ is given.

Solution for (a)

Photon energy is given by

$$E = h\nu$$

Since we are given the wavelength rather than the frequency, we solve the familiar relationship $c = \nu\lambda$ for the frequency, yielding

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

Combining these two equations gives the useful relationship

$$E = \frac{hc}{\lambda}$$

Now substituting known values yields

$$\begin{aligned} E &= \frac{(6.63 \times 10^{-34}\ J \cdot s)(3.00 \times 10^{8} m/s)}{420 \times 10^{-9}\ m} \\ &= 4.74 \times 10^{-19}\ J \end{aligned}$$

Converting to eV, the energy of the photon is

$$\begin{aligned} E &= (4.74 \times 10^{-19}\ J)\left(\frac{1\ eV}{1.6 \times 10^{-19}\ J}\right) \\ &= 2.96\ eV. \end{aligned}$$

Solution for (b)

Finding the kinetic energy of the ejected electron is now a simple application of Equation 5.2.1. Substituting the photon energy and binding energy yields

$$\begin{aligned} KE_e &= h\nu - \Phi \\ &= 2.96\ eV - 2.71\ eV \\ &= 0.246\ eV. \end{aligned}$$

Discussion

The energy of this 420-nm photon of violet light is a tiny fraction of a joule, and so it is no wonder that a single photon would be difficult for us to sense directly—humans are more attuned to energies on the order of joules. But looking at the energy in electron volts, we can see that this photon has enough energy to affect atoms and molecules. A DNA molecule can be broken with about 1 eV of energy, for example, and typical atomic and molecular energies are on the order of eV, so that the UV photon in this example could have biological effects.

The ejected electron (called a photoelectron) has a rather low energy, and it would not travel far, except in a vacuum. The electron would be stopped by a retarding potential of 0.26 eV. In fact, if the photon wavelength were longer and its energy less than 2.71 eV, then the formula would give a negative kinetic energy, an impossibility. This simply means that the 420-nm photons with their 2.96-eV energy are not much above the frequency threshold. You can show for yourself that the threshold wavelength is 459 nm (blue light). This means that if calcium metal is used in a light meter, the meter will be insensitive to wavelengths longer than those of blue light. Such a light meter would be insensitive to red light, for example.

? Exercise 1.3.1 : Silver

What is the longest-wavelength electromagnetic radiation that can eject a photoelectron from silver? Is this in the visible range?

Answer

Given that the workfunction is 4.72 eV from Table 1.3.1 , then only photons with wavelengths lower than 263 nm will induce photoelectrons (calculated via $E = h\nu$). This is ultraviolet and not in the visible range.

? Exercise 1.3.2

Why is the workfunction of an element generally lower than the ionization energy of that element?

Answer

The workfunction of a metal refers to the minimum energy required to extract an electron from the surface of a (**bulk**) metal by the absorption a photon of light. The workfunction will vary from metal to metal. In contrast, ionization energy is the energy needed to detach electrons from **atoms** and also varies with each particular atom, with the valence electrons require less energy to extract than core electrons (i.e., from lower shells) that are more closely bound to the nuclei. The electrons in the metal lattice there less bound (i.e., free to move within the metal) and removing one of these electrons is much easier than removing an electron from an atom because the metallic bonds of the bulk metal reduces their binding energy. As we will show in subsequent chapters, the more delocalized a particle is, the lower its energy.

Summary

Although Hertz discovered the photoelectron in 1887, it was not until 1905 that a theory was proposed that explained the effect completely. The theory was proposed by Einstein and it made the claim that electromagnetic radiation had to be thought of as a series of particles, called photons, which collide with the electrons on the surface and emit them. This theory ran contrary to the belief that electromagnetic radiation was a wave and thus it was not recognized as correct until 1916 when Robert Millikan experimentally confirmed the theory

The photoelectric effect is the process in which electromagnetic radiation ejects electrons from a material. Einstein proposed photons to be quanta of electromagnetic radiation having energy $E = h\nu$ is the frequency of the radiation. All electromagnetic radiation is composed of photons. As Einstein explained, all characteristics of the photoelectric effect are due to the interaction of individual photons with individual electrons. The maximum kinetic energy KE_e of ejected electrons (photoelectrons) is given by

$KE_e = h\nu - \Phi$, where $h\nu$ is the photon energy and Φ is the workfunction (or binding energy) of the electron to the particular material.

Conceptual Questions

1. Is visible light the only type of electromagnetic radiation that can cause the photoelectric effect?
2. Which aspects of the photoelectric effect cannot be explained without photons? Which can be explained without photons? Are the latter inconsistent with the existence of photons?
3. Is the photoelectric effect a direct consequence of the wave character of electromagnetic radiation or of the particle character of electromagnetic radiation? Explain briefly.
4. Insulators (nonmetals) have a higher Φ than metals, and it is more difficult for photons to eject electrons from insulators. Discuss how this relates to the free charges in metals that make them good conductors.
5. If you pick up and shake a piece of metal that has electrons in it free to move as a current, no electrons fall out. Yet if you heat the metal, electrons can be boiled off. Explain both of these facts as they relate to the amount and distribution of energy involved with shaking the object as compared with heating it.

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5.3: Blackbody Radiation and The UV Catastrophe - Evidence of Quantization

Learning Objectives

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation. Objectives for this section include

- Be familiar with black-body radiators
- Understand the Rayleigh-Jeans Law and how it fails to properly model black-body radiation
- How classical assumptions about blackbody emitters showed increasing need for a quantum treatment of light

All normal matter at temperatures above absolute zero emits electromagnetic radiation, which represents a conversion of a body's internal thermal energy into electromagnetic energy, and is therefore called *thermal radiation*. Conversely, all normal matter *absorbs* electromagnetic radiation to some degree. An object that absorbs ALL radiation falling on it, at all wavelengths, is called a blackbody. When a blackbody is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. This emission is called *blackbody radiation*.

A room temperature blackbody appears black, as most of the energy it radiates is infra-red and cannot be perceived by the human eye. Because the human eye cannot perceive light waves at lower frequencies, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears grey, even though its objective physical spectrum peaks in the infrared range. When it becomes a little hotter, it appears dull red. As its temperature increases further it becomes yellow, white, and ultimately blue-white.

Figure 5.3.1 : Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

Blackbody radiation has a characteristic, continuous frequency spectrum that experimentally depends only on the body's temperature. In fact, we can be much more precise:

> *A body emits radiation at a given temperature and frequency exactly as well as it absorbs the same radiation.*

This statement was proved by Gustav Kirchhoff: the essential point is that if we *instead* suppose a particular body can absorb better than it emits, then in a room full of objects all at the same temperature, it will absorb radiation from the other bodies better than it radiates energy back to them. This means it will get hotter, and the rest of the room will grow colder, contradicting the second law of thermodynamics. *Thus, a body must emit radiation exactly as well as it absorbs the same radiation at a given temperature and frequency in order to not violate the second law of thermodynamics.*

Any body at any temperature above absolute zero **will** radiate to some extent, the intensity and frequency distribution of the radiation depending on the detailed structure of the body. To begin analyzing heat radiation, we need to be specific about the body doing the radiating: *the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a perfect emitter.* So how do we construct a perfect absorber in the laboratory? In 1859 Kirchhoff had a good idea: a small hole in the side of a large box is an excellent absorber, since any radiation that goes through the hole bounces around inside, a lot getting absorbed on each bounce, and has little chance of ever getting out again. So, we can do this *in reverse*: have an oven with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a perfect emitter as we're going to find (Figure 5.3.2).

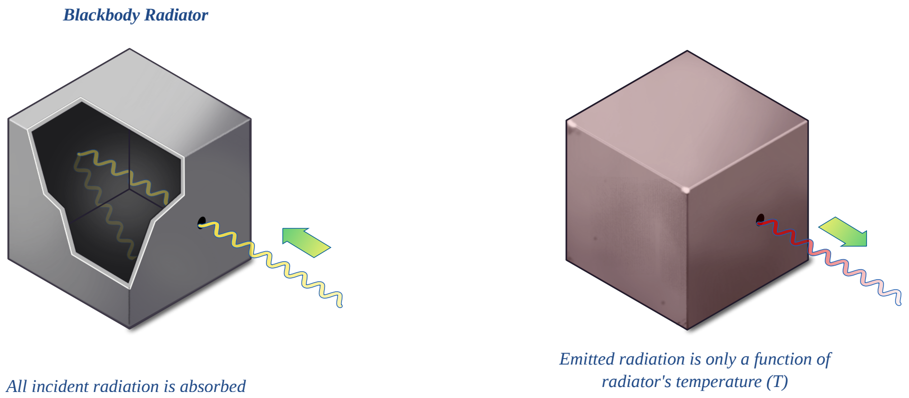

Figure 5.3.2 : Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation. (CC BY-NC; Ümit Kaya via LibreTexts)

By the 1890's, experimental techniques had improved sufficiently that it was possible to make fairly precise measurements of the energy distribution of blackbody radiation. In 1895, at the University of Berlin, Wien and Lummer punched a small hole in the side of an otherwise completely closed oven, and began to measure the radiation coming out. The beam coming out of the hole was passed through a diffraction grating, which sent the different wavelengths/frequencies in different directions, all towards a screen. A detector was moved up and down along the screen to find how much radiant energy was being emitted in each frequency range. They found a radiation intensity/frequency curve close to the distributions in Figure 5.3.3 .

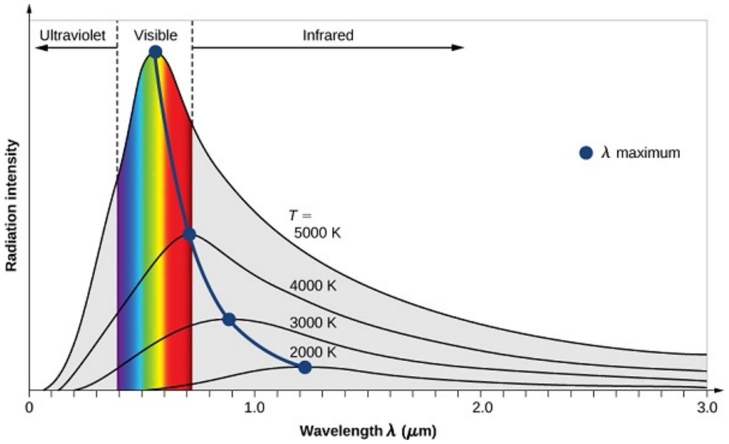

Figure 5.3.3 : Graphic representation of spectral distribution of blackbody radiation at different temperatures. (CC-BY 4.0; OpenStax)

5.3.1: The Ultraviolet Catastrophe

Lord Rayleigh and J. H. Jeans developed an equation which explained blackbody radiation at low frequencies. The equation which seemed to express blackbody radiation was built upon all the known assumptions of physics at the time. *The big assumption which Rayleigh and Jean implied was that infinitesimal amounts of energy were continuously added to the system when the frequency was increased*. Classical physics assumed that energy emitted by atomic oscillations could have any continuous value. This was true for anything that had been studied up until that point, including things like acceleration, position, or energy.

Experimental data performed on the black box showed slightly different results than what was expected by the Rayleigh-Jeans law (Figure 5.3.5). The law had been studied and widely accepted by many physicists of the day, but the experimental results did not lie, something was different between what was theorized and what actually happens. The experimental results showed a bell type of curve, but according to the Rayleigh-Jeans law the frequency diverged as it neared the ultraviolet region (Equation ???). Ehrenfest later dubbed this the "ultraviolet catastrophe".

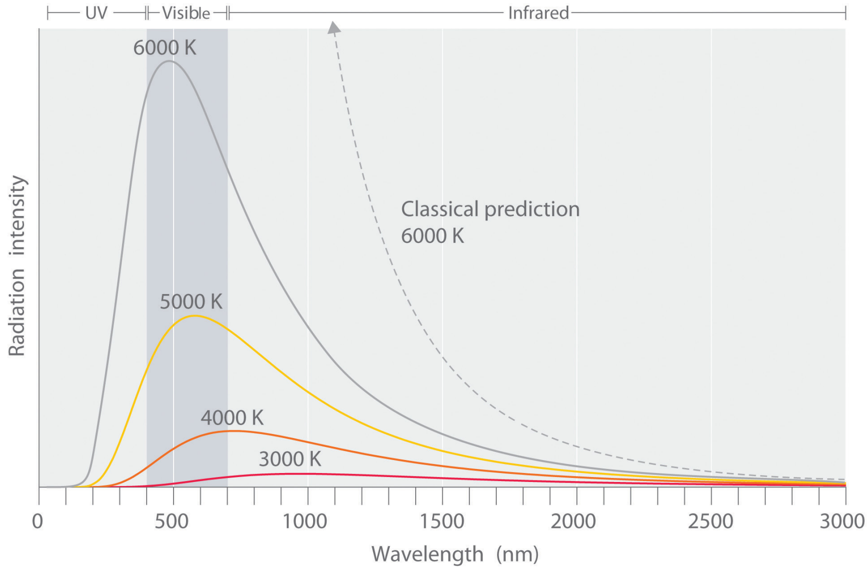

Figure 5.3.5 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure 5.3.5 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. (CC BY-SA-NC; anonymous)

5.3.2: Implications

The ultraviolet catastrophe was a perplexing issue in physics during the late 1800s. Scientists, using classical physics, predicted that the intensity of radiation emitted by a black body would skyrocket to infinity as the frequency of the radiation increased, particularly in the ultraviolet range.

This prediction, however, clashed with actual experimental observations. The solution to this puzzle emerged with the advent of quantum theory, notably through the work of Max Planck. Planck suggested that energy comes in discrete units or "quanta." This concept effectively explained the observed spectrum of black-body radiation and resolved the problem of the ultraviolet catastrophe.

In simpler terms, the lessons learned from the ultraviolet catastrophe led to the acceptance of quantum theory. This groundbreaking shift in understanding how matter and energy behave at the tiniest scales laid the foundation for much of modern physics and marked a crucial step from classical to quantum mechanics.

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5.4: The Bohr Model of The Atom

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 H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines of particular wavelengths, called a **line spectrum**, are observed rather than a continuous range of wavelengths (Figure $5.4.1$). 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.

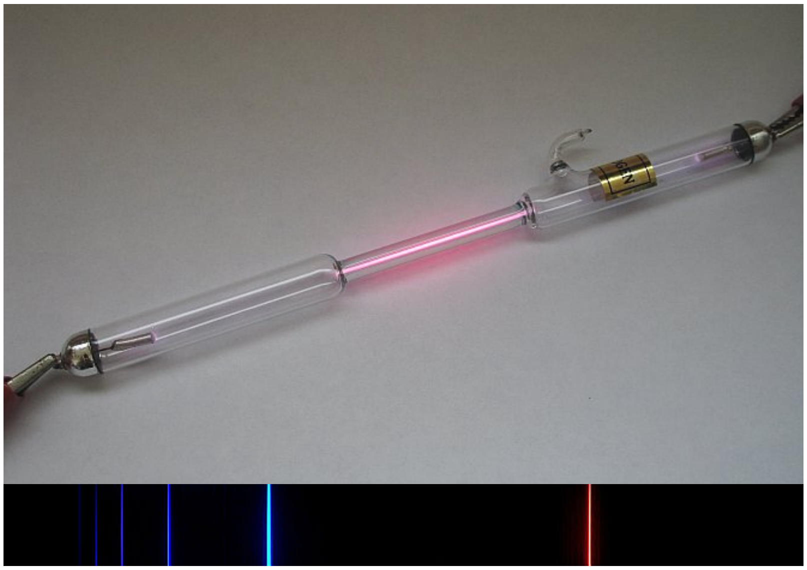


Figure $5.4.1$: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (CC BY-SA 3.0 Unported; Science Made Alive via Wikipedia) (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, 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:

$$u = constant \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \tag{5.4.1}$$

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

$$\frac{1}{\lambda} = \Re \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{5.4.2}$$

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

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 $n_1 = 2$, $n_2 = 3, 4, 5,\ldots$). 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 ($n_1 = 1$, $n_2 = 2, 3, 4,\ldots$) 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.

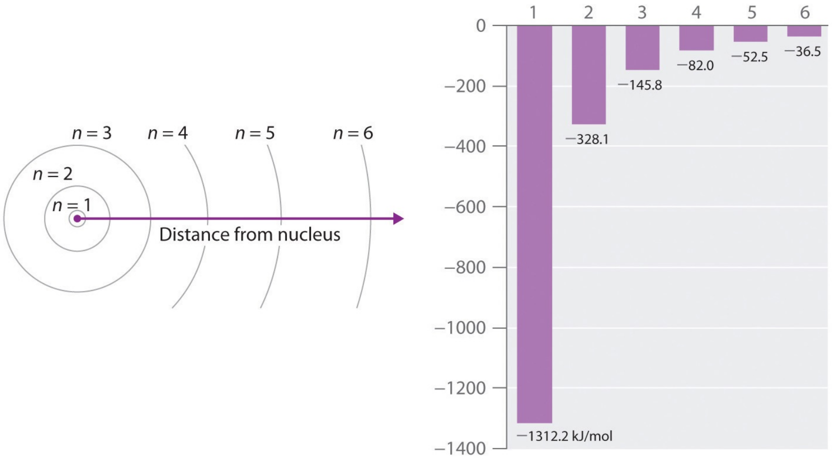
Bohr's Model

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

$$E_n = \frac{-\Re hc}{n^2} \tag{5.4.3}$$

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



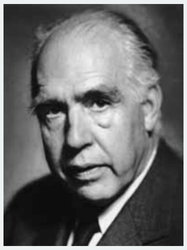
(a) Hydrogen orbits (Bohr model). Orbits are not drawn to scale.

(b) Hydrogen orbit energy (kJ/mol) vs. *n*

Figure 5.4.2: The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing *n*. (b) The energy of the orbit becomes increasingly less negative with increasing *n*.

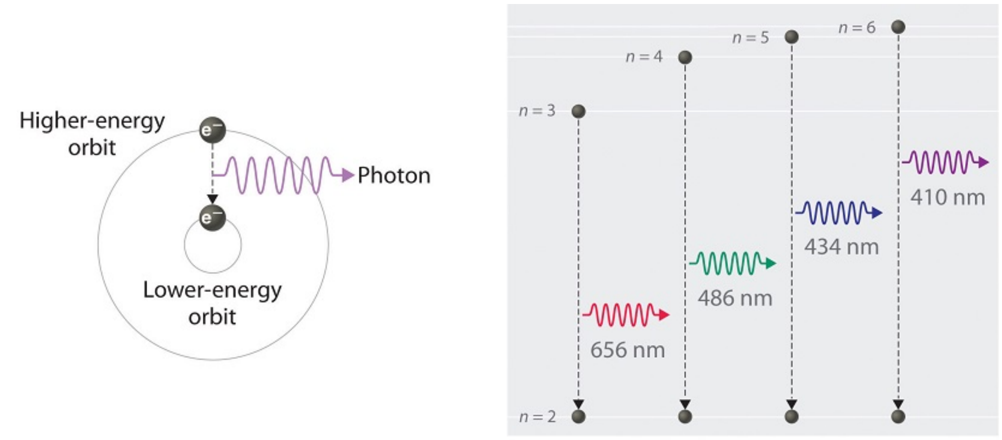
Niels Bohr (1885–1962)

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



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

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative, the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with n = 1 is the lowest lying and most tightly bound. The negative sign in Equation 5.4.3 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 5.4.2*a*). 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 5.4.1).



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

Figure 5.4.3: The Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of *n* (at a higher energy) to an orbit with a lower value of *n* (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with *n* ≥ 3 to the orbit with *n* = 2. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.

So the difference in energy (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 5.4.3) for each energy value gives

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= -\frac{\Re hc}{n_2^2} - \left(-\frac{\Re hc}{n_1^2}\right) \\ &= -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)\end{aligned}$$

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 5.4.3. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{5.4.4}$$

Canceling hc on both sides gives

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{5.4.5}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equations 5.4.4 and 5.4.5 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 $\Re$ from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of 1.0974 × 10^7 m^{-1}, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen ($5.4.3b$); 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 $5.4.3a$). 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 ≥ 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 $5.4.1a$). 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 $5.4.4$

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

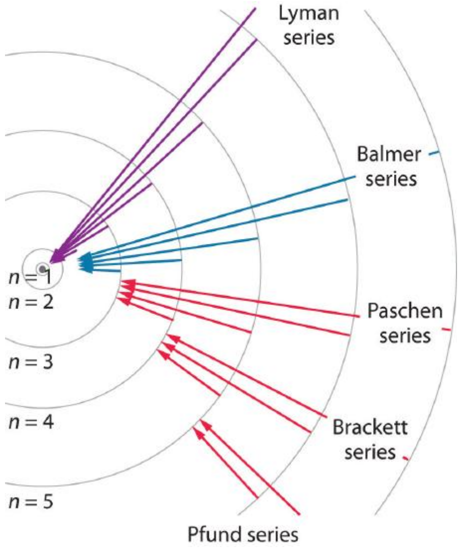


Figure $5.4.4$: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit ($n = 1$); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with $n = 3$, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)

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 5.4.1: The Lyman Series

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

Given: lowest-energy orbit in the Lyman series

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

Strategy:

A. Substitute the appropriate values into Equation 5.4.2 (the Rydberg equation) and solve for λ.
B. 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:

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

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.

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

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}.

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

and

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

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 5.4.1: The Pfund Series

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

Answer

4.65×10^3 nm; infrared

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

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 5.4.5). In fact, Bohr’s model worked only for species that contained just one electron: H, He^+, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

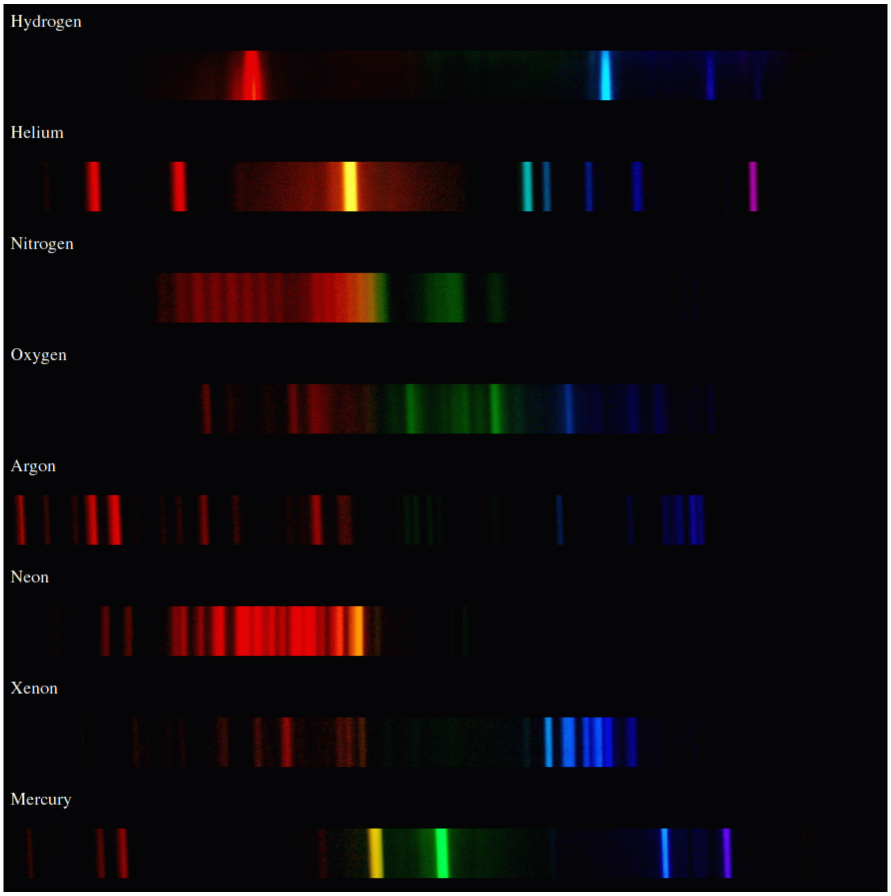


Figure 5.4.5: The atomic emission spectra for various elements. Each thin band in each spectrum corresponds to a single, unique transition between energy levels in an atom. Astronomical spectra image(opens in new window) from the Rochester Institute of Technology, CC BY-NC-SA 2.0(opens in new window).

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.

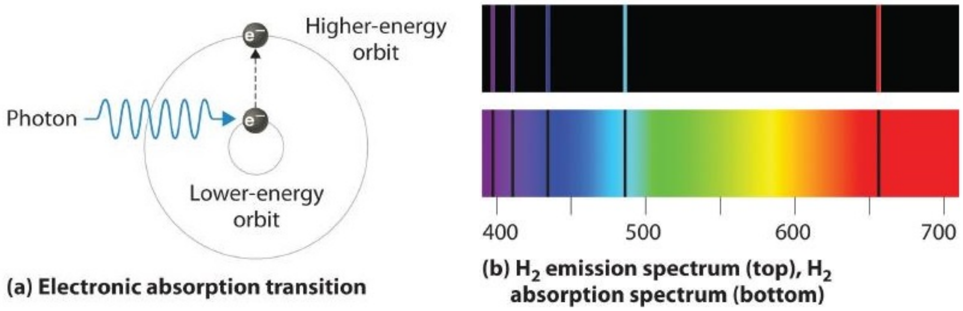


Figure 5.4.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here. (CC 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 5.4.7 Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning “sun.” Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium pick up electrons from the rocks to form helium atoms.

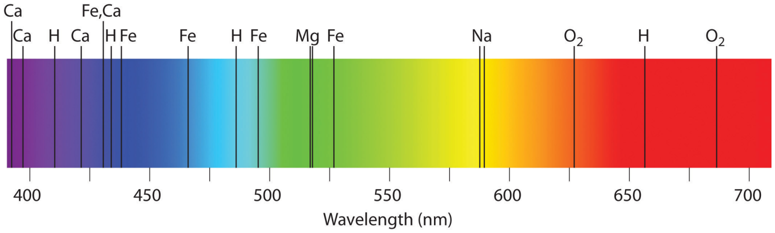
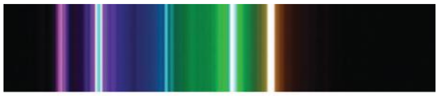
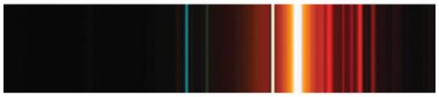


Figure 5.4.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun’s atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth’s atmosphere. (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 5.4.5. Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure 5.4.5). 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 5.4.8: The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is cause by absorption of light in the cooler outer part of the lamp.

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.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

5.5: Wave-Particle Duality of Matter

So far we have seen that to fully understand some experimental results with light we cannot simply treat them as *waves* but sometimes we have to consider that they also have properties of *particles* (photons). It turns out that for particles like the electrons, there are some experimental results whose results can only be understood if we treat those particles as waves.

Light Waves

Many of the properties of light (e.g., surface of water or acoustics) including **reflection, refraction, diffraction, and interference** can be explained, both qualitatively and quantitatively, in terms of light viewed as a wave.

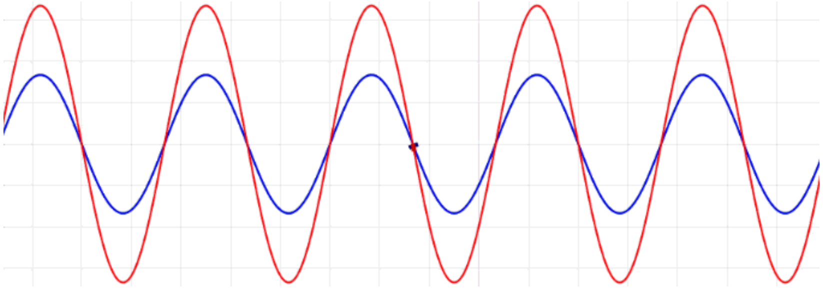


Figure: Linear Interference: The phenomenon of interference between waves is based on this idea. When two or more waves traverse the same space, the net amplitude at each point is the sum of the amplitudes of the individual waves. In some cases, such as in noise-cancelling headphones, the summed variation has a smaller amplitude than the component variations; this is called destructive interference. In other cases, such as in Line Array, the summed variation will have a bigger amplitude than any of the components individually; this is called constructive interference. (CC BY-SA 4.0 Internation; Lookangmany via Wikipedia)

The amplitudes of waves add. **Constructive interference** is obtained when identical waves are in phase and **destructive interference** occurs when identical waves are exactly out of phase, or shifted by half a wavelength.

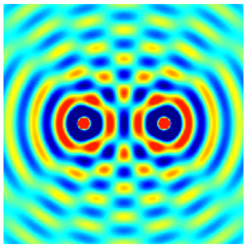


Figure: 2-D Interference: Interference of waves from two point sources. Image use with permission (Public Domain; Oleg Alexandrov)

Quantum Matter Waves

Continuing with our analysis of experiments that lead to the new quantum theory, we now look at the phenomenon of electron diffraction. It is well-known that *light* has the ability to diffract around objects in its path, leading to an interference pattern that is particular to the object. This is, in fact, how holography works (the interference pattern is created by allowing the diffracted light to interfere with the original beam so that the hologram can be viewed by shining the original beam on the image). A simple illustration of diffraction is the Young double slit experiment pictured below:

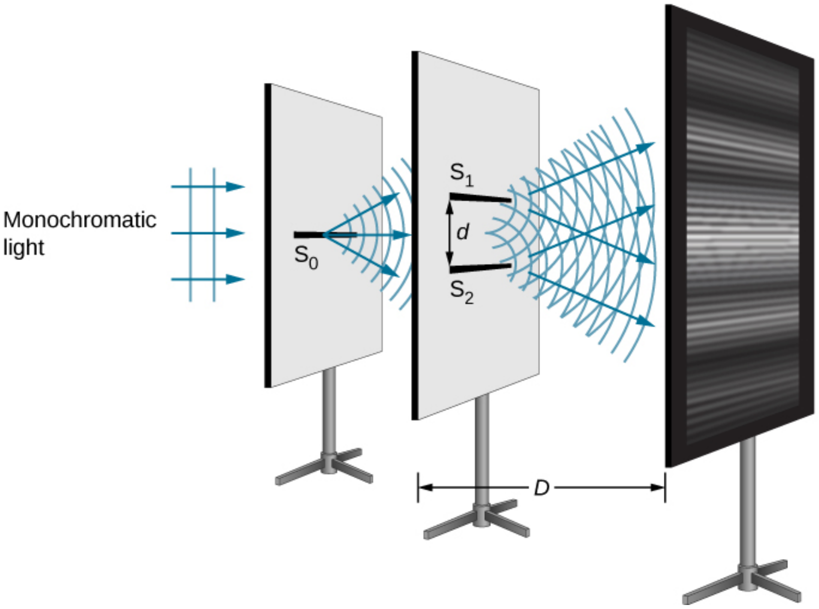


Figure: The double-slit interference experiment using monochromatic light and narrow slits. Fringes produced by interfering Huygens wavelets from slits S_1 and S_2 are observed on the screen. (CC-BY-SA; OpenStax).

Amazingly, if electrons are used instead of light in the double-slit experiment, and a fluorescent screen is used, one finds the same kind of interference pattern! This is shown in the electron double-slit diffraction pattern below:

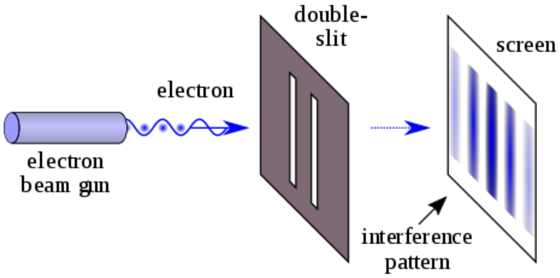


Figure: Particles of matter (like an electron) produce a wave pattern when two slits are used. (Public domain; NekoJaNekoJa).

Obviously, classical mechanics is not able to predict such a result. If the electrons are treated as classical particles, one would predict an intensity pattern corresponding to particles that can pass through one slit or the other, landing on the screen directly opposite the slit (i.e., no intensity maximum at the center of the screen):

Video: De Broglie's Theory can be seen in Young's Double Slit Experiment. https://youtu.be/O55XiriEaQI

Through such experiments, the idea that electrons can behave as waves, creating interference patterns normally associated with light, is now well-established. The fact that particles can behave as waves but also as particles, depending on which experiment you perform on them, is known as the *particle-wave duality*.

Deriving the De Broglie Wavelength

De Broglie derived his equation using well established theories through the following series of substitutions:

1. De Broglie first used Einstein's famous equation relating matter and energy:

$$E = mc^2 \tag{5.5.1}$$

with

- E = energy,
- m = mass,
- c = speed of light

2. Using Planck's theory which states every quantum of a wave has a discrete amount of energy given by Planck's equation:

$$E = h\nu \tag{5.5.2}$$

with

- E = energy,
- h = Plank's constant (6.62607 x 10^{-34} J s),
- ν= frequency

3. Since de Broglie believed particles and wave have the same traits, he hypothesized that the two energies would be equal:

$$mc^2 = h\nu \tag{5.5.3}$$

4. Because real particles do not travel at the speed of light, De Broglie submitted velocity (v) for the speed of light (c).

$$mv^2 = h\nu \tag{5.5.4}$$

5. Since the speed of a wave relates its frequency to its wavelength, de Broglie substituted v/λ for ν and arrived at the final expression that relates wavelength and particle with speed.

$$mv^2 = \frac{hv}{\lambda} \tag{5.5.5}$$

Hence:

$$\lambda = \frac{hv}{mv^2} = \frac{h}{mv} = \frac{h}{p} \tag{5.5.6}$$

At this stage, a majority of Wave-Particle Duality problems are simply "plug and chug" using Equation 5.5.6 with some variation of canceling out units

✓ Example 5.5.1: 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:

A. Convert the speed of the baseball to the appropriate SI units: meters per second.
B. Substitute values into Equation 5.5.6 and solve for the wavelength.

Solution:

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

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

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

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} = \frac{6.626 \times 10^{-34}\ \ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}^{\cancel{-2}} \cdot \cancel{s}}{\left(0.149\ \ \cancel{kg}\right)\left(44.69\ \ \cancel{m} \cdot\ \cancel{s^{-1}}\right)} = 9.95 \times 10^{-35}\ m \tag{5.5.7}$$

(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.

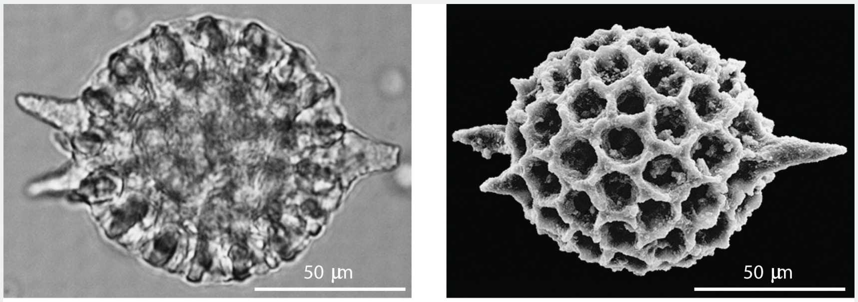
✓ Example 5.5.2: Wavelength of an Electron in Motion

Find the de Broglie wavelength for an electron moving at the speed of $5.0 \times 10^6\ m/s$ (mass of an electron is $9.1 \times 10^{-31}\ kg$).

Size matters in Quantum Mechanics

As you calculated in Example $5.5.1$, objects such as a baseball 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 (Example $5.5.2$), exhibit the properties of both particles *and* waves.To effectively diffract a wave, the wavelength of the wave must be comparable to the dimensions of the diffraction device!

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:



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

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. (CC BY-SA-NC; Anonymous by request).

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 $5.5.3$). If the length of the string is L, then the lowest-energy vibration (the fundamental) has wavelength

$$\begin{gathered}\frac{\lambda}{2} = L \\ \lambda = 2L\end{gathered} \tag{5.5.9}$$

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

$$\lambda = \frac{2L}{n} \tag{5.5.10}$$

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 $5.5.3$ 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.

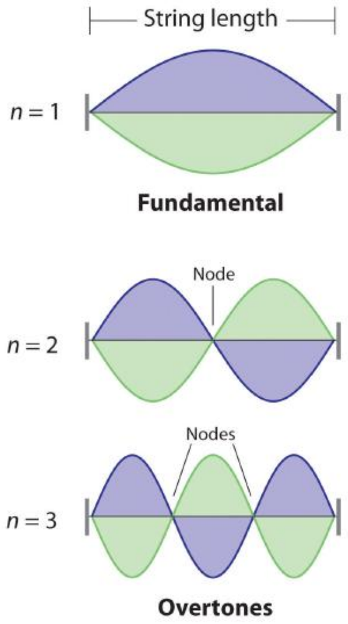


Figure $5.5.3$: Standing Waves on a Vibrating String. The vibration with \(*n* = 1\) is the fundamental and contains no nodes. Vibrations with higher values of *n* are called overtones; they contain \(*n* − 1\) nodes.

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

$$2\pi r = n\lambda \tag{5.5.11}$$

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 $5.5.4$). The standing wave could exist only if the circumference of the circle was an integral multiple of the wavelength such that the propagated waves were all in phase, thereby increasing the net amplitudes and causing *constructive interference*. Otherwise, the propagated waves would be out of phase, resulting in a net decrease in amplitude and causing *destructive interference*. The 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 5.5.11, one complete wavelength would close the circle. Higher energy levels would have successively higher values of *n* with a corresponding number of nodes.

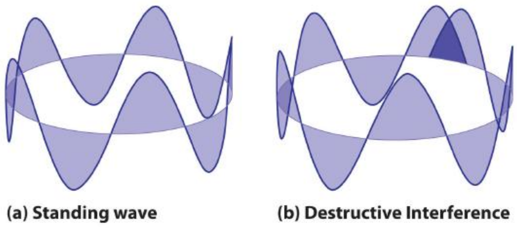


Figure $5.5.4$: Standing Circular Wave and Destructive Interference. (a) In a standing circular wave with \(*n* = 5\), the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of the circle is not equal to an integral multiple of wavelengths, then the wave does not overlap exactly with itself, and the resulting destructive interference will result in cancellation of the wave. Consequently, a standing wave cannot exist under these conditions.

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* at the same distance from the nucleus.

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.

5.6: The Wavefunction and Schrödinger's Equation

Estimated Time to Read: 6 min

Quantum Mechanics

Electrons and other subatomic particles behave as both particles and waves. An individual particle like an electron has mass, but it is spread out, not located in one position, and it has a wavelength. The wavelike nature of electrons and other subatomic particles, as well as the paradox described by Heisenberg's uncertainty principle, 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 and its allowed energies. Schrödinger's wave equation allowed scientists to make predictions about the electronic structure of atoms. Where are the electrons found? What is their energy?

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.

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.

Wavefunctions

A wavefunction (Ψ) is a mathematical function that relates the location of an electron and the energy of the electron. A wavefunction uses three variables to describe the position of an electron in space (as with the Cartesian coordinates *x*, *y*, and *z*). A fourth variable specifies the time at which the electron is at the specified location.

By analogy, 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 $5.6.1$). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

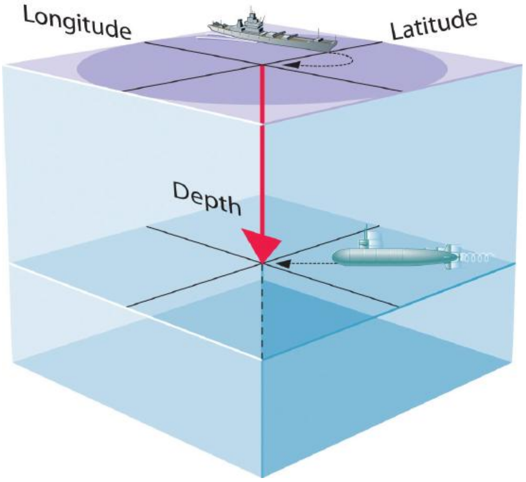


Figure $5.6.1$: The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object

The magnitude of the wavefunction at a particular point in space is proportional to the amplitude of the wavefunction at that point. Many wavefunctions are complex functions, which means 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 in space is proportional to the probability of finding an electron at that point in space. (The square of the wavefunction (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$]) 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. One way of graphically representing the probability distribution is demonstrated in Figure $5.6.2$ for a hydrogen atom. The probability of finding an electron is indicated by the density of colored dots.

Schrödinger's approach treats electrons as three-dimensional standing waves. It is a requirement of standing waves that they be in phase with one another to avoid cancellation; this results in a limited number of solutions (wavefunctions), each of which 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, which are specified by the quantum numbers. Quantum numbers define solutions to the Schrödinger equation. 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.

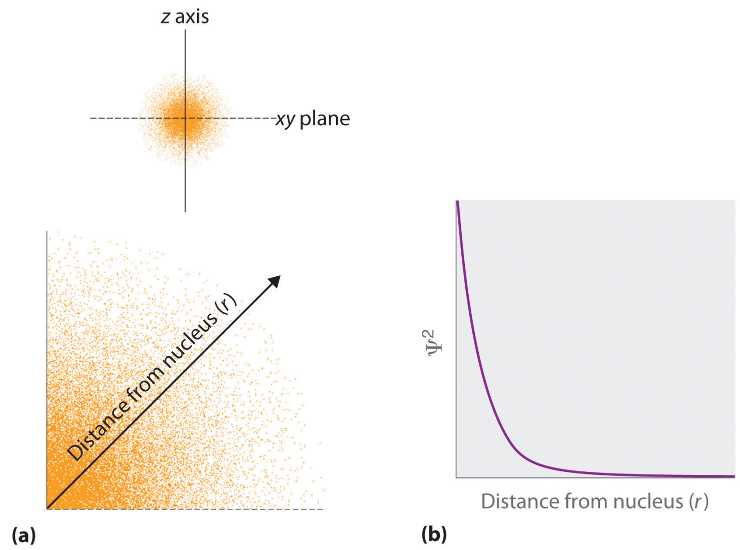
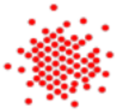


Figure $5.6.2$: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus *r* for the ground state of the hydrogen atom, the electron probability density is greatest at *r* = 0 (the nucleus) and falls off with increasing *r*. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of *r* is very small but *not* zero.

The *wavefunction* is a mathematical expression that describes the electron. It can be plotted as a three-dimensionional graph. The three-dimensional plot of the wavefunction is sometimes called an *orbital*. Often, chemists find it useful to look at pictures of orbitals in order to gain some sense of where electrons may be and how they may behave. In another sense, orbitals are probability maps that reveal the probability of an electron being located at a particular position in space.

Suppose you could take a series of photos of an electron and superimpose all of those pictures, like time-lapse photography. The result might look something like the drawing in Figure $5.6.2$, in which every dot represents where the electron showed up in one of the photos. It's impossible to predict exactly where the electron would show up in the next photo, but it would be a pretty good guess that it would show up somewhere in the same rough circle as it did all of the other times.



1s

Figure 5.6.3: Probability map, or orbital, of a wavefunction. Each dots represents the probability of an electron being located at that point in space at a moment in time. (https://employees.csbsju.edu/cschall...tomnumbers.htm; Chris Schaller)

In three-dimensional space, the probability map, or ***orbital*** (named in reference to the Bohr Model*)* shown in Figure 5.6.3 would be a sphere instead of a circle. The probability map shown can be interpreted as a thin slice through the middle of the probability sphere. The orbital shown is specifically an s orbital. In the very center of the sphere, is the nucleus of the atom. The electron is found within a certain distance of the nucleus, but it can be found in any direction. Other electrons will have different distributions about the nucleus of the atom, resulting in other orbital shapes in three-dimensional space. Quantum numbers will be used to describe the various orbitals, the probability of finding an electron at a point in space and roughly how much energy the electron has.

5.7: Atomic Orbitals and Quantum Numbers

Learning Objectives

- Understand the general idea of the quantum mechanical description of electrons in an atom, and that it uses the notion of three-dimensional wave functions, or orbitals, that define the distribution of probability to find an electron in a particular part of space
- List and describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom

Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding to these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an *n* value, where *n* = 1, 2, 3, …. Generally speaking, the energy of an electron in an atom is greater for greater values of *n*. This number, *n*, is referred to as the **principal quantum number**.

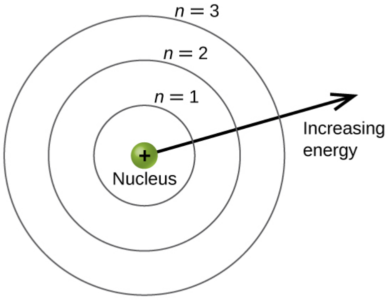


Figure 5.7.1: Different energy levels are numbered by principal quantum numbers *n*.

The principal quantum number is one of three quantum numbers used to characterize an orbital. Recall that an atomic orbital, which is distinct from an *orbit*, is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

Another quantum number is ***l***, the **angular momentum quantum number**. It is an integer that defines the shape of the orbital, and takes on the values, *l* = 0, 1, 2, …, *n* – 1. This means that an orbital with *n* = 1 can have only one value of *l*, *l* = 0, whereas *n* = 2 permits *l* = 0 and *l* = 1, and so on. The principal quantum number defines the general size and energy of the orbital. The *l* value specifies the shape of the orbital. Orbitals with the same value of *l* form a subshell. In addition, the greater the angular momentum quantum number, the greater is the angular momentum of an electron at this orbital.

Orbitals with *l* = 0 are called *s* orbitals, which are spherically shaped probability densities. The value *l* = 1 corresponds to the *p* orbitals, of which there are three unique 3D orientations. The orbitals with *l* = 2 are called the *d* orbitals, followed by the *f-, g-, and h*-orbitals for *l* = 3, 4, 5, and there are higher values we will not consider.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction ψ is zero at this distance for this orbital. Such a value of radius *r* is called a radial node. The number of radial nodes in an orbital is *n* – *l* – 1.

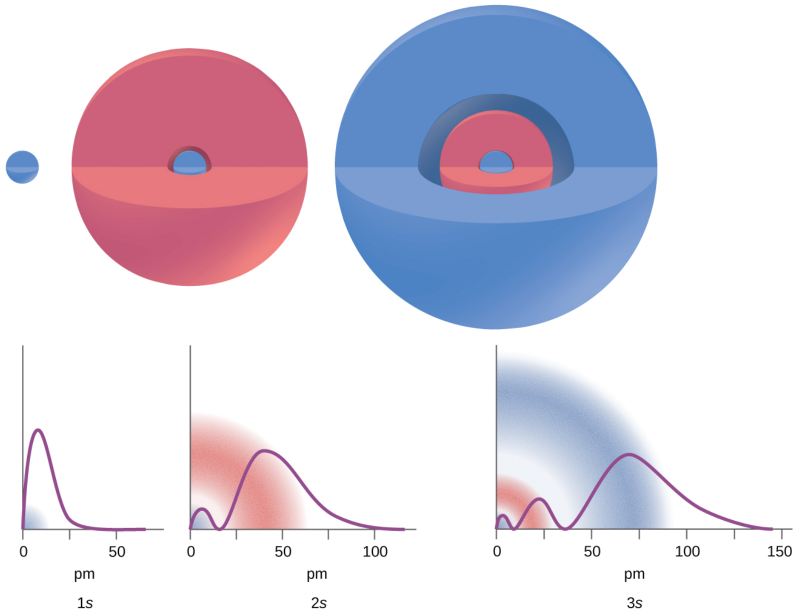


Figure 5.7.2: The graphs show the probability (y axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus.

Consider the examples in Figure 5.7.2. The orbitals depicted are of the *s* type, thus *l* = 0 for all of them. It can be seen from the graphs of the probability densities that there are 1 – 0 – 1 = 0 places where the density is zero (nodes) for 1*s* (*n* = 1), 2 – 0 – 1 = 1 node for 2*s*, and 3 – 0 – 1 = 2 nodes for the 3*s* orbitals.

The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.

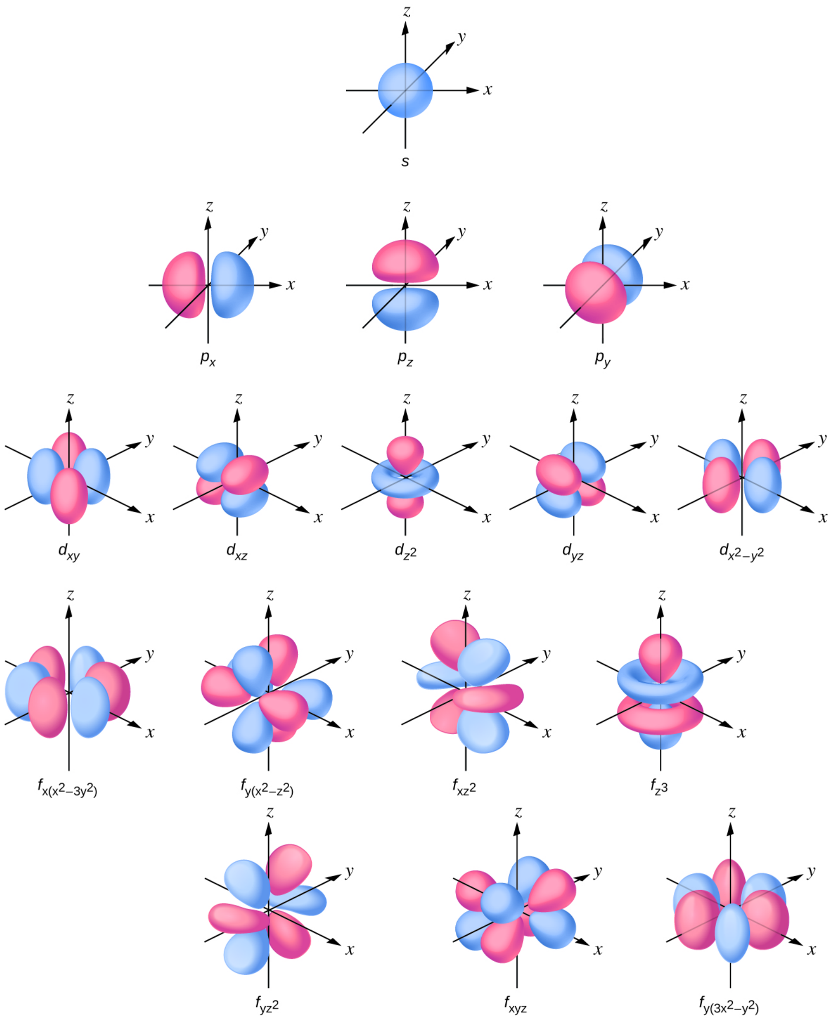


Figure 5.7.3: Shapes of s, p, d, and f orbitals.

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

If an electron has an angular momentum ($l \neq 0$), then this vector can point in different directions. In addition, the *z* component of the angular momentum can have more than one value. This means that if a magnetic field is applied in the *z* direction, orbitals with different values of the *z* component of the angular momentum will have different energies resulting from interacting with the field. The magnetic quantum number, called m_l, specifies the *z* component of the angular momentum for a particular orbital. For example, for an *s* orbital, $l = 0$, and the only value of m_l is zero. For *p* orbitals, $l = 1$, and m_l can be equal to –1, 0, or +1. Generally speaking, m_l can be equal to $–l, –(l – 1), \ldots, –1, 0, +1, \ldots, (l – 1), l$. The total number of possible orbitals with the same value of l (a subshell) is 2*l* + 1. Thus, there is one *s*-orbital for *ml = 0*, there are three *p*-orbitals for *ml = 1*, five *d*-orbitals for *ml = 2*, seven *f*-orbitals for *ml = 3*, and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in Figure $5.7.3$.

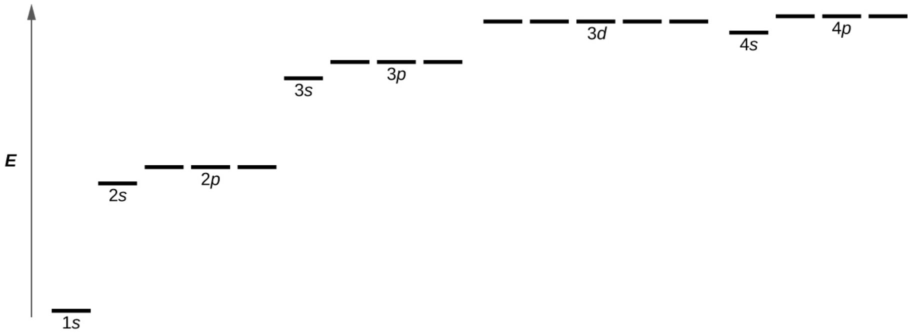


Figure $5.7.4$: *The chart shows the energies of electron orbitals in a multi-electron atom.*

Figure $5.7.4$ illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, *n*. The letter in the orbital name defines the subshell with a specific angular momentum quantum number *l* = 0 for *s* orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for *l* ≥ 1, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same *n* are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, *n*, are called degenerate energy levels. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies. Orbitals within the same subshell (for example *ns, np, nd, nf*, such as 2*p*, 3*s*) are still degenerate and have the same energy.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the spin quantum number, or m_s.

The other three quantum numbers, *n*, *l*, and m_l, are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian *x*, *y*, and *z*). Electron spin describes an intrinsic electron “rotation” or “spinning.” Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, even though this rotation cannot be observed in terms of the spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only “spin” in one of two quantized states. One is termed the α state, with the *z* component of the spin being in the positive direction of the *z* axis. This corresponds to the spin quantum number $m_s = \frac{1}{2}$. The other is called the β state, with the *z* component of the spin being negative and $m_s = -\frac{1}{2}$. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $m_s = -\frac{1}{2}$ and $m_s = \frac{1}{2}$ are different if an external magnetic field is applied.

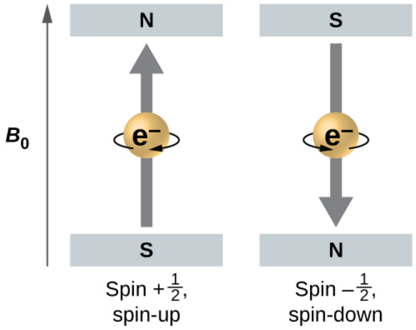


Figure 5.7.5: Electrons with spin values \(±\ce{1/2}\) *in an external magnetic field.*

Figure 5.7.5 illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the *z* axis) for the $\frac{1}{2}$ spin quantum number and down (in the negative *z* direction) for the spin quantum number of $-\frac{1}{2}$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $m_s = \frac{1}{2}$ has a slightly lower energy in an external field in the positive *z* direction, and an electron with $m_s = -\frac{1}{2}$ has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

Magnetic Quantum Number (ml) & Spin Quantum Number (ms): https://youtu.be/gbmGVUXBOBk

The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: *n*, *l*, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The Pauli exclusion principle can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that electrons can share the same orbital (the same set of the quantum numbers *n*, *l*, and m_l), but only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values $\left(\pm\frac{1}{2}\right)$, no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons. The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table 5.7.1.

Table 5.7.1: *Quantum Numbers, Their Properties, and Significance*

Name	Symbol	Allowed values	Physical meaning

Name	Symbol	Allowed values	Physical meaning
principal quantum number	n	1, 2, 3, 4, ….	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	l	$0 \leq l \leq n - 1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \leq m_l \leq l$	orientation of the orbital
spin quantum number	m_s	$\frac{1}{2}, -\frac{1}{2}$	direction of the intrinsic quantum "spinning" of the electron

✓ Example 5.7.1: Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the $n = 4$ shell of an atom.

Solution

For $n = 4$, l can have values of 0, 1, 2, and 3. Thus, *s*, *p*, *d*, and *f* subshells are found in the $n = 4$ shell of an atom. For $l = 0$ (the *s* subshell), m_l can only be 0. Thus, there is only one 4*s* orbital. For $l = 1$ (*p*-type orbitals), m can have values of –1, 0, +1, so we find three 4*p* orbitals. For $l = 2$ (*d*-type orbitals), m_l can have values of –2, –1, 0, +1, +2, so we have five 4*d* orbitals. When $l = 3$ (*f*-type orbitals), m_l can have values of –3, –2, –1, 0, +1, +2, +3, and we can have seven 4*f* orbitals. Thus, we find a total of 16 orbitals in the $n = 4$ shell of an atom.

? Exercise 5.7.1

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 3, l = 1$;
b. $n = 5, l = 3$;
c. $n = 2, l = 0$.

Answer a

3*p*

Answer b

5*f*

Answer c

2s

✓ Example 5.7.2: Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) $n = 2$, (b) $n = 5$, and (c) n as a variable. Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Solution

(a) When $n = 2$, there are four orbitals (a single 2*s* orbital, and three orbitals labeled 2*p*). These four orbitals can contain eight electrons.

(b) When $n = 5$, there are five subshells of orbitals that we need to sum:

$$\begin{array}{r} 1 \text{ orbital labeled } 5s \\ 3 \text{ orbitals labeled } 5p \\ 5 \text{ orbitals labeled } 5d \\ 7 \text{ orbitals labeled } 5f \\ \underline{+9 \text{ orbitals labeled } 5g} \\ 25 \text{ orbitals total} \end{array}$$

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.

(c) The number of orbitals in any shell *n* will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$

Exercise 5.7.2

If a shell contains a maximum of 32 electrons, what is the principal quantum number, *n*?

Answer

n = 4

Example 5.7.3: Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	*n*	*l*	m_l degeneracy	Radial nodes (no.)
4*f*				
	4	1		
	7		7	3
5*d*				

Solution

The table can be completed using the following rules:

- The orbital designation is *nl*, where *l* = 0, 1, 2, 3, 4, 5, … is mapped to the letter sequence s, *p*, *d*, *f*, *g*, *h*, …,
- The m_l degeneracy is the number of orbitals within an *l* subshell, and so is 2*l* + 1 (there is one *s* orbital, three *p* orbitals, five *d* orbitals, seven *f* orbitals, and so forth).
- The number of radial nodes is equal to *n* – *l* – 1.

Orbital	***n***	***l***	**m_l degeneracy**	**Radial nodes (no.)**
4*f*	4	3	7	0
4*p*	4	1	3	2
7*f*	7	3	7	3
5*d*	5	2	5	2

Summary of the Rules for Quantum Numbers: https://youtu.be/nRsRZUsOBzE

? Exercise 5.7.3

How many orbitals have *l* = 2 and *n* = 3?

Answer

The five degenerate 3*d* orbitals

Summary

The quantum mechanical model of atoms describes the three-dimensional position of the electron in a *probabilistic* manner according to a mathematical function called a wavefunction, often denoted as ψ. Atomic wavefunctions are also called orbitals. The squared magnitude of the wavefunction describes the distribution of the probability of finding the electron in a particular region in space. Therefore, atomic orbitals describe the areas in an atom where electrons are most likely to be found.

An atomic orbital is characterized by three quantum numbers. The principal quantum number, *n*, can be any positive integer. The general region for value of energy of the orbital and the average distance of an electron from the nucleus are related to *n*. Orbitals having the same value of *n* are said to be in the same shell. The angular momentum quantum number, *l*, can have any integer value from 0 to *n* – 1. This quantum number describes the shape or type of the orbital. Orbitals with the same principal quantum number and the same *l* value belong to the same subshell. The magnetic quantum number, m_l, with 2*l* + 1 values ranging from –*l* to +*l*, describes the orientation of the orbital in space. In addition, each electron has a spin quantum number, m_s, that can be equal to $\pm\frac{1}{2}$. No two electrons in the same atom can have the same set of values for all the four quantum numbers.

Glossary

angular momentum quantum number (*l*)

quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

atomic orbital

mathematical function that describes the behavior of an electron in an atom (also called the wavefunction), it can be used to find the probability of locating an electron in a specific region around the nucleus, as well as other dynamical variables

***d* orbital**

region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with *l* = 2. An electron in this orbital is called a *d* electron

electron density

a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

f orbital

multilobed region of space with high electron density, describes orbitals with $l = 3$. An electron in this orbital is called an f electron

magnetic quantum number (m_l)

quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of m_l but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field

p orbital

dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$. An electron in this orbital is called a p electron

Pauli exclusion principle

specifies that no two electrons in an atom can have the same value for all four quantum numbers

principal quantum number (n)

quantum number specifying the shell an electron occupies in an atom

quantum mechanics

field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

s orbital

spherical region of space with high electron density, describes orbitals with $l = 0$. An electron in this orbital is called an s electron

shell

set of orbitals with the same principal quantum number, n

spin quantum number (m_s)

number specifying the electron spin direction, either $+\frac{1}{2}$ or $-\frac{1}{2}$

subshell

set of orbitals in an atom with the same values of n and l

wavefunction (ψ)

mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

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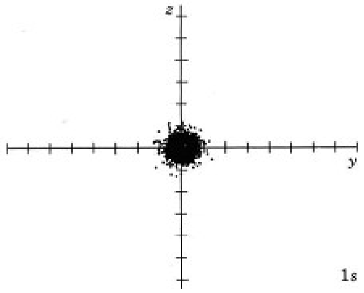
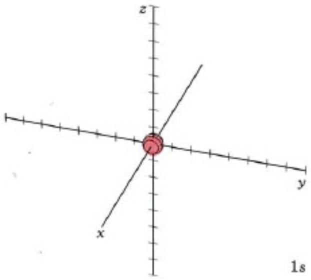
5.7.1: Visualizing Atomic Orbitals as Probability Densities

A characteristic of the diagram Figure 1 in Electron Waves in the Hydrogen Atom is that it has been assigned an identifying label, namely, 1*s*. This enables us to distinguish it from other wave patterns the electron could possibly adopt if it moved about the nucleus with a higher energy. Each of these three-dimensional wave patterns is different in shape, size, or orientation from all the others and is called an **orbital**. The word *orbital* is used in order to make a distinction between these wave patterns and the circular or elliptical *orbits* of the Bohr picture shown in The Wave Nature of the Electron.

At ordinary temperatures, the electron in a hydrogen atom is almost invariably found to have the lowest energy available to it. That is, the electron occupies the 1*s* orbital. The electron cloud looks like the dot-density diagram shown in Figure 1 from Electron Waves in the Hydrogen Atom. This orbital is shown below as both a boundary surface diagram[1] and a dot density diagram[1]

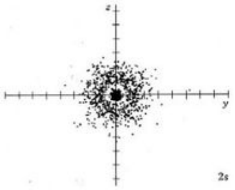
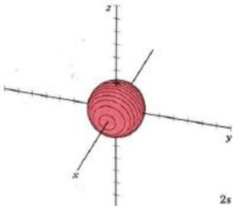
Table 5.7.1.1: 1s Orbital

Orbital	Dot Density Diagram(s)	Boundary Surface Diagram
1*s*	 A vertical and horizontal axes is labeled "z" and "y" respectively. Most of the black dots are concentrated in the center. Only a few black dots are located away from the central dense region of black dots.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Located in the axis origin is a small red sphere.

At a very high temperature, though, some collisions between the atoms are sufficiently hard to provide one of the electrons with enough energy so that it can occupy one of the other orbitals, say a 2*s* orbital, but this is unusual. Nevertheless, a knowledge of these higher energy orbitals is necessary since electron clouds having the same shapes as hydrogen are found to apply to all the other atoms in the periodic table as well. The 2*s* orbital is shown below, once again represented by a dot density diagram and a boundary surface diagram. Notice how the dot density diagram reveals a feature about the 2*s* orbital that boundary surface does not: A node divides the 2*s* orbital in two, a portion of the electron cloud is near the center, while another portion lies beyond the node (the circular region with no dots). At the node the wave has no amplitude, its square is also zero, and there is zero probability of finding the electron.

Table 5.7.1.2 2s Orbital

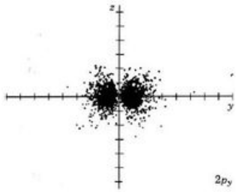
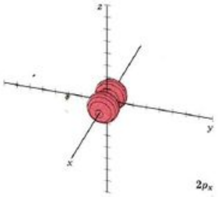
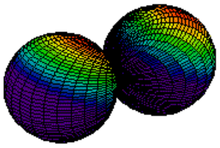
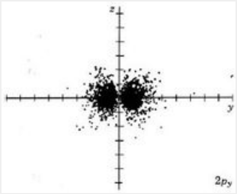
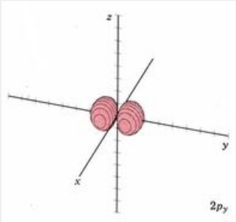
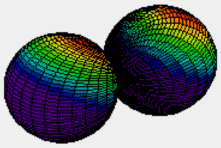
2s Orbital

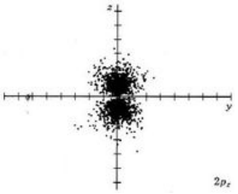
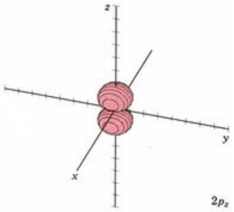
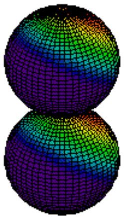
Orbital	Dot Density Diagram(s)	Boundary Surface Diagram
2*s*	 A vertical and horizontal axes is labeled "z" and "y" respectively. Right in the origin is a circular region where there is a large number of black dots. Beyond this center region is a ring shaped gap where there are very few to no dots. Beyond the gap is a ring shaped region concentrated with black dots.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Right in the origin is a red sphere.

In the case of a particle in a one-dimensional box, the energy was determined by a positive whole number *n*. Much the same situation prevails in the case of the hydrogen atom. An integer called the **principal quantum number**, also designated by the symbol *n*, is used to label each orbital. The larger the value of *n*, the greater the energy of the electron and the larger the average distance of the electron cloud from the nucleus. In the two orbitals already considered, $n = 1$ for the 1*s* orbital, $n= 2$ for the 2*s* orbital.

Because a greater number of different shapes is available in the case of three-dimensional, as opposed to one-dimensional, waves, two other labels are used in addition to *n*. The first consists of one of the lowercase letters *s*, *p*, *d*, or *f*. These tell us about the *overall shapes* of the orbitals.[2] Thus all *s* orbitals such as the 1*s*, 2*s* are *spherical*. An important point is that only a limited number of orbital shapes is possible for each value of *n*. If $n = 1$, then only the spherical 1*s* orbital is possible. When *n* is increased to *2*, though, two orbital types (2*s* and 2*p*) become possible. Thus along with the 2*s* orbital, 3 other orbitals exist when n=2; $2p_x$, $2p_y$, and $2p_z$. All *p* orbitals have a *dumbbell* shape. The third kind of label are subscripts which distinguish between orbitals which are basically the same shape but differ in their orientation in space. In the case of *p* orbitals there are always *three* orientations possible. A *p* orbital which extends along the *x* axis is labeled a p_x orbital. A *p* orbital along the *y* axis is labeled p_y and one along the *z* axis is a p_z orbital. Below are dot density diagrams, boundary surface diagrams, and a rotating image. Using the moving images, it is easy to see that the only difference between the 2*p* orbitals is their orientation in xyz 3-coordinate space.

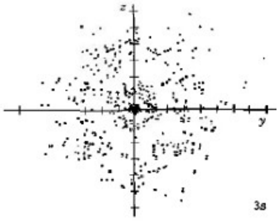
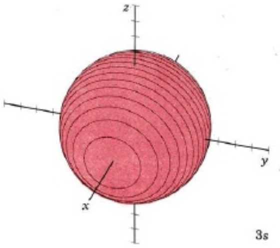
Table 5.7.1.3: 2p Orbitals

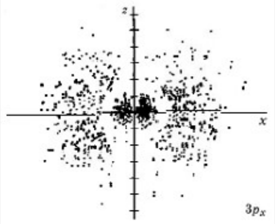
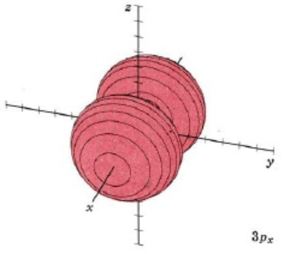
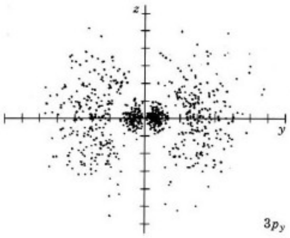
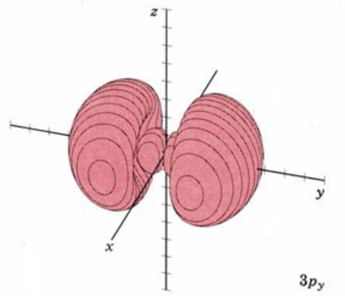
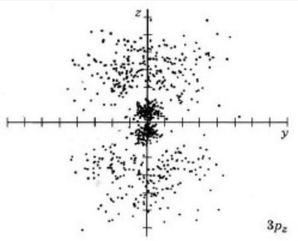
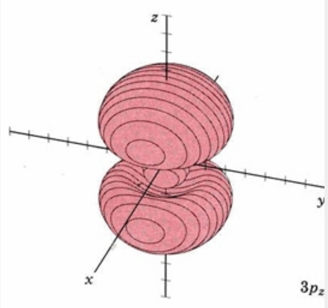
Orbital	Dot Density Diagram(s)	Boundary Surface Diagram	Rotating Image
$2p_x$	 A vertical and horizontal axes is labeled "z" and "y" respectively. The two lobe shaped region is concentrated with black dots and is located on opposite sides of the "y" axes. There are less and less black dots as we move further away from the center of the two axes.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Two red spheres located on opposite sides of the "x" axes meet at the origin.	 Gif of two horizontally rotating spheres, each with a continuous spectrum of colors from deep violet to red, corresponding to the different probability regions of finding electrons. Red regions are concentrated near the top end of both spheres. Concentric regions around from this end change colors from red to yellow, green, blue and finally purple. The bottom half of both spheres are occupied by purple regions.
$2p_y$	 A vertical and horizontal axes is labeled "z" and "y" respectively. The two lobe shaped region is concentrated with black dots and is located on opposite sides of the "y" axes. There are less and less black dots as we move further away from the center of the two axes.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Two red spheres located on opposite sides of the "y" axes meet at the origin.	 Gif of two horizontally rotating spheres, each with a continuous spectrum of colors from deep violet to red, corresponding to the different probability regions of finding electrons. Red regions are concentrated near the top end of both spheres. Concentric regions around from this end change colors from red to yellow, green, blue and finally purple. The bottom half of both spheres are occupied by purple regions.

Orbital	Dot Density Diagram(s)	Boundary Surface Diagram	Rotating Image
$2p_z$	 A vertical and horizontal axes is labeled "z" and "y" respectively. The two lobed shape region is concentrated with black dots and is located on opposite sides of the "z" axes. There are less and less black dots as we move further away from the center of the two axes.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Two red spheres located on opposite sides of the "z" axes meet at the origin.	 Gif of two spheres stacked vertically, rotating in unison. Each sphere has a continuous spectrum of colors from deep violet to red, corresponding to the different probability regions of finding electrons. Red regions are concentrated near the top end of both spheres. Concentric regions around from this end change colors from red to yellow, green, blue and finally purple. The bottom half of both spheres are occupied by purple regions.

When *n* equals *3*, *three* orbital types occur. The first two are familiar, the *s* orbital and *p* orbitals. The third, the *d* orbital, is discussed later. Below are representations of the 3*s* orbital, and the 3*p* orbitals. As the 2*s* orbital was slightly different in shape from the 1*s* orbital due to the introduction of a node, so the 3*s* and 3*p* orbitals differ slightly in shape from the 2*s* and 2*p* orbitals.

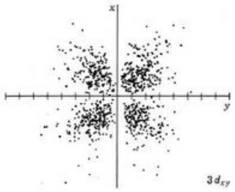
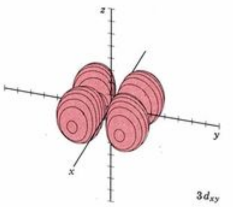
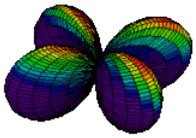
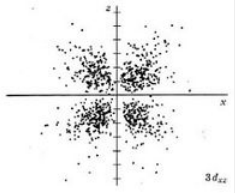
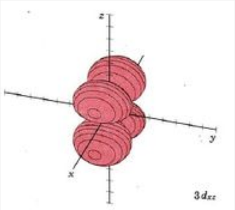
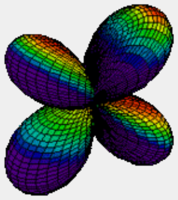
Table 5.7.1.4: 3s and 3p orbitals

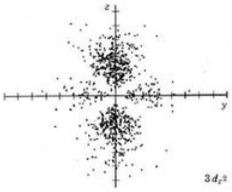
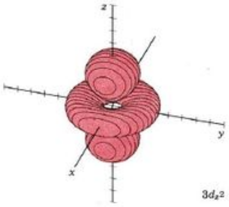
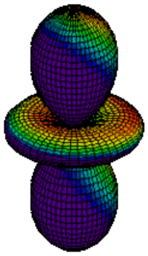
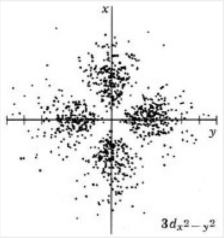
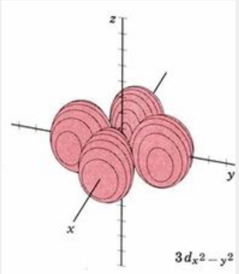
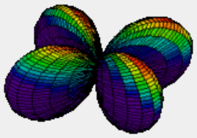
Orbital	Dot Density Diagram(s)	Boundary Surface Diagram
3*s*	 A vertical and horizontal axes is labeled "z" and "y" respectively. The circular area around the origin is concentrated with black dots. The two other regions with concentrated black dots form concentric circles with the origin. The spaces between each concentrated region has very few to no black dots in it. Fewer and fewer black dot are present as we move further away from the center.	 A three dimensional axis is shown that are perpendicular to each other. The "x" axis is pointing towards us, the "y" axis is pointing towards the right and the "z" axis is pointing straight upwards. A relatively large sphere occupies a large portion of the axes. The sphere has the center at the axis origin.

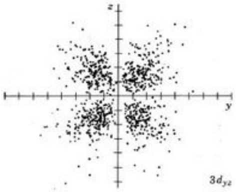
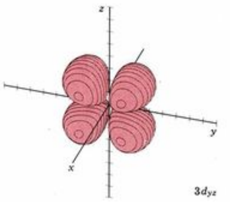
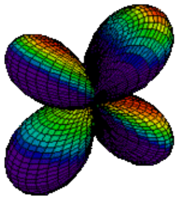
Orbital	Dot Density Diagram(s)	Boundary Surface Diagram
$3p_x$	 A vertical and horizontal axes is labeled "z" and "x" respectively. There is a relatively small circular region around the axis origin on opposites sides of the "x" axes. The other two regions are quarter annulus shaped and is symmetrical about both axes. There is a gap between the central regions and the outer region where very few to no black dots are present. The central region is more concentrated than the outer region.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. The view from this angle shows that there are two relatively large red spheres located on opposite sides of the "x" axes.
$3p_y$	 A vertical and horizontal axes is labeled "z" and "y" respectively. There is a relatively small circular concentrated region around the axis origin on opposites sides of the "y" axes. The other two regions are quarter annulus shaped and is symmetrical about both axes. There is a gap between the central regions and the outer region where very few to no black dots are present. The central region is far more concentrated than the outer region.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are two small spheres around the origin on opposite sides of the "y" axes. Following this region is a small gap followed by another sphere. The side of the sphere facing the central region is dented. The two spheres located on the "y" axes are symmetrical about all axes.
$3p_z$	 A vertical and horizontal axes is labeled "z" and "y" respectively. There is a relatively small circular concentrated region around the axis origin on opposites sides of the "z" axes. The other two regions are quarter annulus shaped and is symmetrical about both axes. There is a gap between the central regions and the outer region where very few to no black dots are present. The central region is far more concentrated than the outer region.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are two small spheres around the origin on opposite sides of the "z" axes. Following this region is a small gap followed by another sphere. The side of the sphere facing the central region is dented. The two spheres located on the "z" axes are symmetrical about all axes.

The d orbitals have more complex shapes than the *p* orbitals, In the case of the *d* orbitals the subscripts are more difficult to follow. You can puzzle them out from the rotating images, the dot density diagrams and the orbital surface diagrams if you like, but analysis of these orbitals is usually considered beyond the scope of general chemistry. You should, however, be aware that there are *five* possible orientations for *d* orbitals. Below are representations of the *d* orbitals.

Table 5.7.1.5: 3d Orbitals

Orbital	Dot Density Diagram(s)	Boundary Surface Diagram	Rotating Image
3d_{xy}	 A vertical and horizontal axes is labeled "x" and "y" respectively. There is a lobe shaped region of concentrated black dots in each quadrant of the axis which collectively makes an "X" shaped area centralized on the axis origin. There are fewer and fewer black dots as we move away from the axis origin.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on each quadrant of the "x" "y" plane. The structures are lobe shaped and form a "X" shape about the origin.	 Gif of a three dimensional structure rotating about the vertical "z" axes. The structure lies on the "x" and "y" plane and consist of four lobes forming a "X" shape centralized at the origin. The top half surface of the four lobes make up a continuous spectrum of colors from red to yellow to green to blue and to purple. The purple regions make up the bottom half of the lobes and makes a major portion of the structure.
3d_{xz}	 A vertical and horizontal axes is labeled "z" and "x" respectively. There is a lobe shaped region of concentrated black dots in each quadrant of the axis which collectively makes an "X" shaped area centralized on the axis origin. There are fewer and fewer black dots as we move away from the axis origin.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on each quadrant of the "x" "z" plane. The structures are lobe shaped and form a "X" shape about the origin.	 Gif of a three dimensional structure rotating about the vertical "z" axes. The structure lies on the "x" and "z" plane and consist of four lobes forming a "X" shape centralized at the origin. The surface of the lobes have a continuous spectrum of color from red to yellow to green, blue and purple. The spectrum of color moves around the surface of each lobe according to its rotating position. The red, yellow, green and blue region moves around the surface of the lobes to always accumulate on the right side of the structure. The purple region make up the rest of the structure as it rotates.

Orbital	Dot Density Diagram(s)	Boundary Surface Diagram	Rotating Image
$3d_{z^2}$	 A vertical and horizontal axes is labeled "z" and "y" respectively. There is a symmetrical pair of lobe shaped black dot concentrated reigons on opposite sides of the "z" axes. There is another symmetrical pair of lobe shaped black dot concentrated regions on opposite sides of the "y" axis. Note that the latter region is significantly smaller in size than the former one. Note that there is a gap around the origin where very few to no dots are present.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. The two lobe shaped three dimensional structures are symmetrical and are on opposite sides of the "z" axis. Between these two lobes, on the "x" "y" plane, is a three dimensional ring centralized on the axis origin.	 Gif of a three dimensional structure rotating about the vertical "z" axes. The structure consists of two identical three dimensional lobes located on opposite sides of the "z" axis. Between the two lobes is a three dimensional ring located on the "x" "y" plane. The entire structure is rotating about the "z" axis. The surface of the lobes and the ring have a continuous spectrum of color from red to yellow to green, blue and purple. The red regions are concentrated on the right sided face of the structure. Purple regions make up the left sided portion of the structure.
$3d_{x^2-y^2}$	 A vertical and horizontal axis is labeled "x" and "y" respectively. There are 4 symmetrical lobe shaped black dot concentrated reigons located on each side the axial line, centralized around the axis origin. There are fewer and fewer black dots as we move away from the origin. There is a gap between each lobe and a region around the origin where very few to no black dots are present.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on the "x" "y" plane. The structures are lobe shaped and are located on each side of the axial lines.	 Gif of three dimensional structure rotating about the vertical "z" axes. The structure lies on the "x" and "y" plane and consist of four lobes forming a "X" shape centralized at the origin. The top half surface of the four lobes make up a continuous spectrum of colors from red to yellow to green to blue and to purple. The purple regions make up the bottom half of the lobes and makes a major portion of the structure.

Orbital	Dot Density Diagram(s)	Boundary Surface Diagram	Rotating Image
3d_{yz}	 A vertical and horizontal axes is labeled "z" and "y" respectively. There is a lobe shaped region of concentrated black dots in each quadrant of the axis which collectively makes an "X" shaped area centralized on the axis origin. There are fewer and fewer black dots as we move away from the axis origin.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on each quadrant of the "z" "y" plane. The structures are lobe shaped and form a "X" shape about the origin.	 Gif of a three dimensional structure rotating about the vertical "z" axes. The structure lies on the "x" and "z" plane and consist of four lobes forming a "X" shape centralized at the origin. The surface of the lobes have a continuous spectrum of color from red to yellow to green, blue and purple. The spectrum of color moves around the surface of each lobe according to its rotating position. The red, yellow, green and blue region moves around the surface of the lobes to always accumulate on the right side of the structure. The purple region make up the rest of the structure as it rotates.

The same pattern extends to $n = 4$ where *four* orbital types, namely, 4*s*, 4*p*, 4*d* and 4*f*, are found. While none of these orbitals will be shown, the patterns seen in moving from 1*s* to 2*s* or from 2*p* to 3*p* continue with the *s*, *p*, and *d* orbitals. The new *f* orbitals are even more complicated than the *d* orbitals. For an understanding of general chemistry, it is important to know that there are *seven* different orientations for *f* orbitals, since the number of orbitals of each type (*s*, *p*, *d*, etc.) is important in determining the shell structure of the atom.

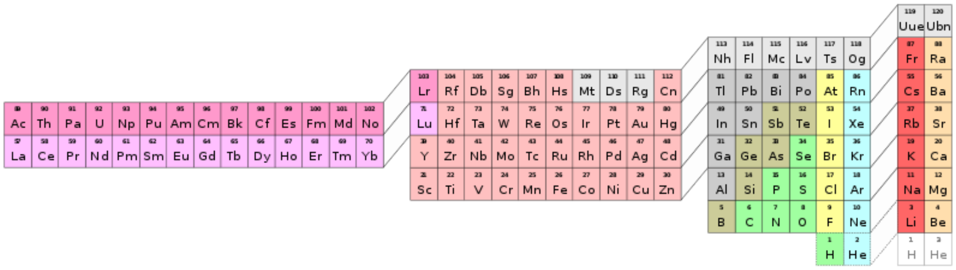
[1] All dot density diagrams and boundary-surface diagrams are Copyright © 1975 by W. G. Davies and J. W. Moore.

[2] The letters *s*, *p*, *d* and *f* originate from the words *sharp*, *principal*, *diffuse* and *fundamental* which were used to describe certain features of spectra before wave mechanics was developed. They later became identified with orbital shapes.

CHAPTER OVERVIEW

6: Periodic Law and Periodic Properties of the Elements

The periodic table is a tabular arrangement of the chemical elements, ordered by their atomic number (number of protons in the nucleus), electron configurations, and recurring chemical properties. The periodic table can be used to derive relationships between the properties of the elements, and predict the properties of new elements yet to be discovered or synthesized. The periodic table provides a useful framework for analyzing chemical behavior, and is widely used in chemistry and other sciences.



Chapter Sections

Image Attributions

1. https://chem.libretexts.org/@api/dek...r_6_Banner.png; made by Camille Kaslan under CC-BY-SA licensing
2. https://upload.wikimedia.org/wikiped...tal%29.svg.png

6.1: The Development of The Periodic Table

The Periodic Table is, for many, *the* symbol of Chemistry. It is a single image that contains all of the known elements in the universe combined into an easily readable format from which patterns can be discerned. How did this table come to be? How did humanity begin to identify the ~119 unique elements listed on The Periodic Table? In this section, an overview of the development of The Periodic Table will be provided. This history will provide a rich context for connecting the modern understanding of the atom to what is observed empirically about these substances.

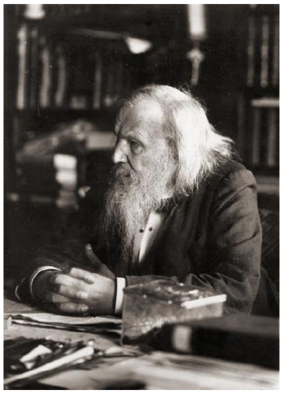


Figure 6.1.1: Dimitri Mendeleev, "The Father of The Periodic Table," c. ~1890

In 1649 the idea of elements departed from the Classical conception (Earth, Wind, Fire, and Water) when Hennig Brand discovered a new element: Phosphorous. Brand was an alchemist in search of the Philosopher's Stone, or an object that would turn any ordinary metal into gold. In his search he manipulated, combined, and observed reactions of a variety of materials, including distilling human urine. Upon distillation of human urine, Brand found a glowing white rock in his distillation flask. This was the new element he would call Phosphorous. The alchemists and scientists of the enlightenment era added incredible amounts of knowledge to the ideas about elements. By 1869 there were already 63 elements that had been discovered. With each new element that was found, scientists began to realize that there were patterns developing and some started to put the elements into a table. Scientists like John Newlands and Alexandre-Emile Béguyer de Chancourtois formed their own versions of periodic tables. These versions, however, were rudimentary, obscure and hard to read.

Figure 6.1.2: Depiction of Hennig Brand's discovery of elemental Phosohorous.

The scientist who brought it all together was Dmitri Mendeleev (1834 to 1907). Mendeleev was a Russian-born chemist and the first to publish a modern version of The Periodic Table. His table ordered the elements by atomic weights (molar masses). When the elements were ordered by their atomic weights, they exhibited similar chemical properties. The table that Mendeleev compiled was so good that he was able to predict elements that were not even known to him at the time. These elements included germanium, gallium, and scandium. There were some pitfalls to the table though. Since not all of the elements had been discovered at the time of Mendeleev's publishing, he left out important elements like the noble gases. After Mendeleev's publishing future scientists contributed to adding in the elements in their proper places. Sir William Ramsay added in the noble gases, and Henry

Mosley discovered a way to quantitatively find the atomic number of an element and changed the order around of Mendeleev's table to be organized by atomic number. Finally, in 1945 the Manhattan Project yielded the discovery of many new radioactive elements. Glenn T. Seaborg suggested a change to the table in the form of an addition of the actinide and lanthanide series at the bottom of the table. This idea came with the discovery of Americium and Curium and their unique properties. The change was not accepted at first, but is now included in all periodic tables.

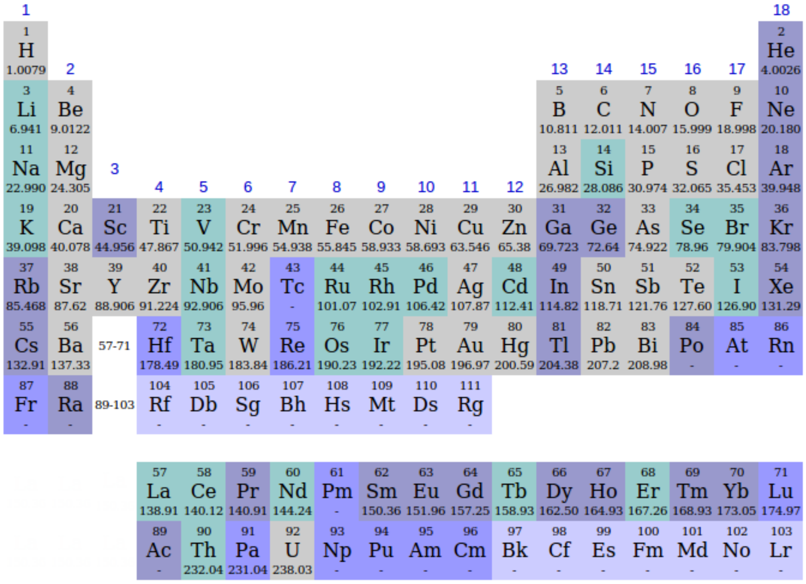


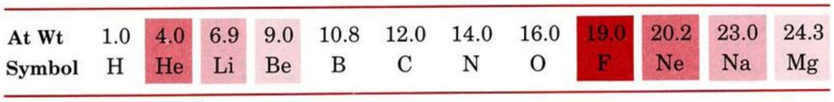
Figure 6.1.3: Periodic Table showing when each element was discovered

- Before 1800 (36 elements): discoveries during and before the Age of Enlightenment (gray).
- 1800-1849 (+22 elements): impulse from Scientific Revolution and Atomic theory and Industrial Revolution (green).
- 1850-1899 (+23 elements): the age of Classifying Elements received an impulse from the Spectrum analysis (dark purple-gray).
- 1900-1949 (+13 elements): impulse from the old quantum theory, the Refinements to the periodic table, and quantum mechanics (bright purple-blue).
- 1950-1999 (+15 elements): Manhattan Project and Particle physics issues, for atomic numbers 97 and above (lavender).

More on Mendeleev's Periodic Table

The similarities among macroscopic properties within each of the chemical families lead one to expect microscopic similarities as well. Atoms of sodium ought to be similar in some way to atoms of lithium, potassium, and the other alkali metals. This could account for the related chemical reactivities and analogous compounds of these elements.

According to Dalton’s atomic theory, different kinds of atoms may be distinguished by their relative masses (atomic weights). Therefore it seems reasonable to expect some correlation between this microscopic property and macroscopic chemical behavior. You can see that such a relationship exist by listing symbols for the first dozen elements in order of increasing relative mass. Obtaining atomic weights, we have

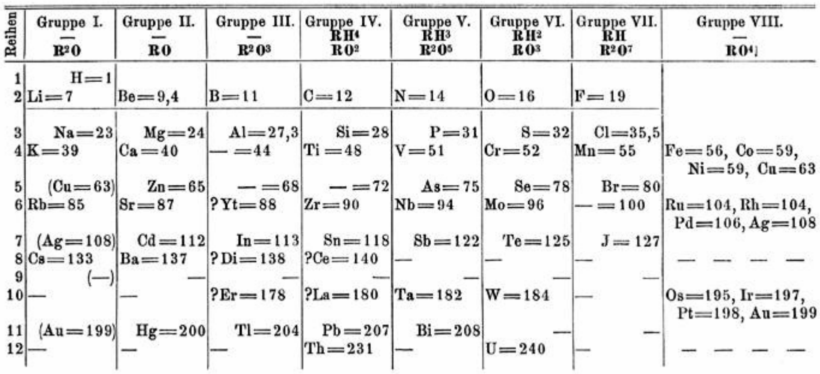


At Wt	1.0	4.0	6.9	9.0	10.8	12.0	14.0	16.0	19.0	20.2	23.0	24.3
Symbol	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg

Elements which belong to families we have already discussed are indicated by shading around their symbols. The second, third, and forth elements on the list (He, Li, and Be) are a noble gas, an alkali metal, and an alkaline-earth metal, respectively. Exactly the same sequence is repeated eight elements later (Ne, Na, and Mg), but this time a halogen (F) precedes the noble gas. If a list were made of all elements, we would find the sequence halogen, noble gas, alkali metal, and alkaline-earth metal several more times.

Dmitri Ivanovich Mendeleev proposed the **periodic law** behind his periodic table compiling. This law states that *when the elements are listed in order of increasing atomic weights, their properties vary periodically*. That is, similar elements do not have similar atomic weights. Rather, as we go down a list of elements in order of atomic weights, corresponding properties are observed at regular intervals. To emphasize this periodic repetition of similar properties, Mendeleev arranged the symbols and atomic weights of the elements in the table shown below. Each vertical column of this **periodic table** contains a **group** or **family** of related elements. The alkali metals are in group I (*Gruppe* I), alkaline earths in group II, chalcogens in group VI, and halogens in group VII. Mendeleev was not quite sure where to put the coinage metals, and so they appear twice. Each time, however, copper, silver, and gold are arranged in a vertical column.

The noble gases were discovered nearly a quarter century after Mendeleev's first periodic table was published, but they, too, fit the periodic arrangement. In constructing his table, Mendeleev found that sometimes there were not enough elements to fill all the available spaces in each horizontal row or **period**. When this was true, he assumed that eventually someone would discover the element or elements needed to complete a period. Mendeleev therefore left blank spaces for undiscovered elements and predicted their properties by averaging the characteristics of other elements in the same group.



Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
5	(Cu=63)	Zn=65	— =68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Figure 6.1.4: Mendeleev's periodic table, redrawn from Annalen der Chemie, supplemental volume 8, 1872. The German words Gruppe and Reihen indicate, respectively, the groups and rows (or periods) in the table. Mendeleev also used the European convention of a comma instead of a period for the decimal and J instead I for iodine. The noble gases had not yet been discovered when Mendeleev devised the periodic table, and are thus not displayed.

As an example of this predictive process, look at the fourth numbered row (*Reihen*). Scandium (Sc) was unknown in 1872; so titanium (Ti) followed calcium (Ca) in order of atomic weights. This would have placed titanium below boron (B) in group III, but Mendeleev knew that the most common oxide of titanium, TiO_2, had a formula similar to an oxide of carbon CO_2, rather than of boron, B_2O_3. Therefore he placed titanium below carbon in group IV. He proposed that an undiscovered element, ekaboron, would eventually be found to fit below boron. (The prefix *eka* means "below.") Properties predicted for ekaboron are shown in the following table. They agreed remarkably with those measured experimentally for scandium when it was discovered 7 years later. This agreement was convincing evidence that a periodic table is a good way to summarize a great many macroscopic, experimental facts.

Table 6.1.1: Comparison of Mendeleev's Predictions with the Observed Properties of the Element Scandium.

Property	Properties Predicted for Ekaboron (Eb)* by Mendeleev 1872	Properties Found for Scandium after its Discovery in 1879
Atomic weight	44	44†
Formula of oxide	Eb_2O_3	Sc_2O_3
Density of oxide	3.5	3.86
Acidity of oxide	Greater than MgO	Greater than MgO
Formula of chloride	$EbCl_3$	$ScCl_3$
Boiling point of chloride	Higher than for	Higher than for
Color of compounds	Colorless	Colorless

* Mendeleev used the name "eka"boron because the blank space into which the element should fit was "below" boron in his periodic table. † The modern value of the atomic weight of scandium is 44.96.

The modern periodic table differs in some ways from Mendeleev's original version. It contains more than 40 additional elements, and its rows are longer instead of being squeezed under one another in staggered columns. For example, Mendeleev's fourth and fifth rows are both contained in the fourth period of the modern table. This ends up placing gallium, not scandium underneath boron in the periodic table. This rearrangement is due to theory on the electronic structure of atoms, in particular ideas about orbitals and the relation of electronic configuration to the periodic table. The extremely important idea of vertical groups of related elements is still retained, as are Mendeleev's group numbers. The latter appear as roman numerals at the top of each column in the modern table.

Mendeleev was an extraordinary chemist that was able to compile the greatest chemical instrument of all time. He was not alone in compiling the elements, and many other great chemists contributed too. The idea of elements began over 5,000 years ago and started to finally take shape a mere 200 years ago with Mendeleev's periodic table. Yet, it was not the end of the formation of the periodic table. It has changed over time, and with continue to transform as more and more elements are discovered.

References

1. Scerri, E. R. (2006). The Periodic Table: Its Story and Its Significance; New York City, New York; Oxford University Press.

3. http://allperiodictables.com/ClientPages/AAEpages/aaeHistory.html

4. https://commons.wikimedia.org/wiki/F...Wright%29.jpeg

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6.2: Electron Configurations - The Quantum Model and Periodic Structure

Learning Objective

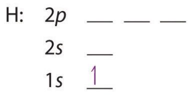
- To write the electron configuration of any element and relate its electron configuration to its position in the periodic table.

We know that each electron in an atom is described by a unique set of four quantum numbers: n, l ml, and ms. Beyond their Quantum Mechanical definitions, what do these numbers actually mean, and why are they important to know in a general chemistry course?

Quantum numbers and the quantum model that derived them depict our current best understanding of what an atom actually is and how it behaves based on the energetic structure of electrons within it. 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. From our theoretical understanding of the electronic structuring of electrons in each element, we will find that these electron configurations are innately related to the structure and organization of The Periodic Table.

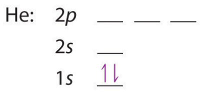
The Aufbau Principle

We construct The Periodic Table by following the *Aufbau Principle* (from German, meaning "building up"). This is the process used to build up the periodic table by adding protons one by one to the nucleus and adding the corresponding electrons to the lowest-energy orbital available without violating the Pauli exclusion principle. 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 Hydrogen, recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to m_s = +½, which is arbitrarily written first, and one with spin down ↓, corresponding to m_s = −½. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:



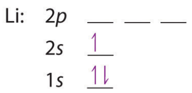
From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number *n* and their value of *l* (*s*, *p*, *d*, or *f orbital type*), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1*s* orbital, which is the orbital lowest in energy, 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 1*s* 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:



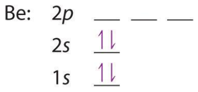
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle. Remember that because the helium nucleus has a positive charge of +2, the 1s level of helium lies considerably below the 1s level of hydrogen, although for the purposes of building up the periodic table we do not take that into consideration. The orbital diagrams are energy ordered, the levels are in the proper energy order from bottom (most bound) to least, but the energies are not scaled.

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

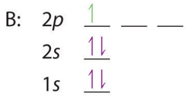


This electron configuration is written as $1s^2 2s^1$.

The next element is beryllium, with Z = 4 and four electrons. We fill both the 1s and 2s orbitals to achieve a $1s^22s^2$ electron configuration:

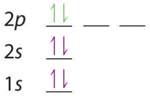


When we reach boron, with Z = 5 and five electrons, we must place the fifth electron in one of the 2p orbitals. Remember that the actual energy difference between the *2s* and *2p* levels is much smaller than that between the *1s* and *2s* levels. Because all three *2p* orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^22s^22p^1$:

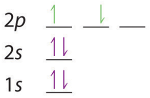


At carbon, with Z = 6 and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2p orbital that already has an electron, or should it go in one of the empty 2p orbitals? If it goes in an empty 2p orbital, will the sixth electron have its spin aligned with or be opposite 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?

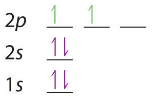
(a)



(b)



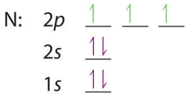
(c)



Because of electron-electron repulsions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice (a). Similarly, experiments have shown that choice (b) is slightly higher in energy (less stable) than choice (c) because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice (b).

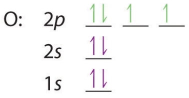
Choice (c) illustrates **Hund's rule** (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^22s^22p^2$, 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:

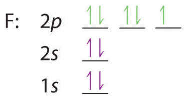


with three unpaired electrons. The electron configuration of nitrogen is thus $1s^22s^22p^3$.

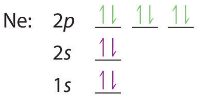
At oxygen, with Z = 8 and eight electrons, we have no choice. One electron must be paired with another in one of the 2p orbitals, which gives us two unpaired electrons and a $1s^22s^22p^4$ electron configuration. Because all the 2p orbitals are degenerate, it doesn't matter which one has the pair of electrons.



Similarly, fluorine has the electron configuration $1s^22s^22p^5$:



When we reach neon, with $Z = 10$, we have filled the 2p subshell, giving a $1s^22s^22p^6$ electron configuration:



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.

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 orbitals. 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]$3s^1$:

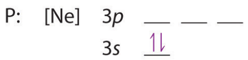
Neon	Z = 10	$1s^22s^22p^6$
Sodium	Z = 11	$1s^22s^22p^6\mathbf{3}s^1$ = [Ne]$\mathbf{3}s^1$

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

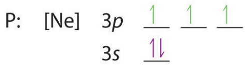
Sodium	$1s^22s^22p^63s^1$ = [Ne]$3s^1$
Lithium	$1s^22s^1$ = [He]$2s^1$

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

As we continue to build the eight elements of period 3, the 3s and 3p orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration [Ne]$3s^23p^6$, corresponding to a filled valence shell.



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 [Ne]$3s^23p^3$.

The general order in which orbitals are filled is depicted below. 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.

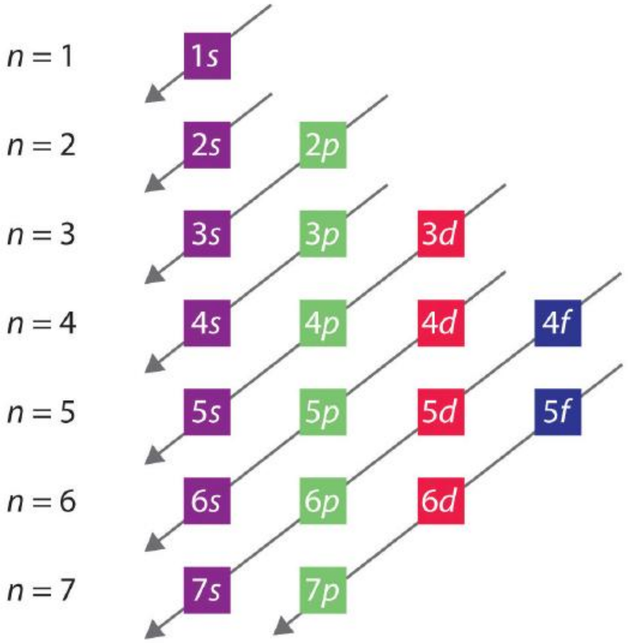


Figure 1: Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms *If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.*

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

Note that the Aufbau Principle has some exceptions. By definition, orbitals are most stable when they are either full or half-full. Thus, in some cases where valency is very near a stable configuration, the actual electron configuration of the element differs from what is predicted by Aufbau.

Blocks in the Periodic Table

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 2.3.3 . For example, the two columns on the left, known as the *s* blockThe elements in the left two columns of the periodic table in which the *ns* orbital is being filled., 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* blockThe elements in the six columns on the right of the periodic table in which the *np* orbitals are being filled.. In between are the 10 columns of the *d* blockThe elements in the periodic table in which the $(n − 1)d$ orbitals are being filled., elements in which the $(n − 1)d$ orbitals are filled. At the bottom lie the 14 columns of the *f* blockThe elements in the periodic table in which the $(n − 2)f$ orbitals are being filled., 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.

Note the Pattern

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.

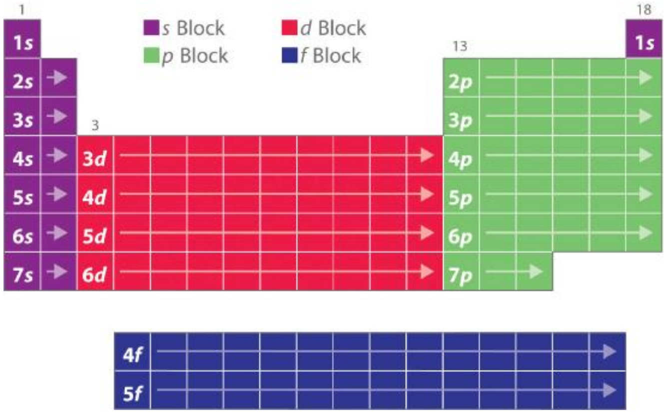


Figure 2: The Periodic Table, Showing How the Elements Are Grouped According to the Kind of Subshell (*s*, *p*, *d*, *f*) Being Filled with Electrons in the Valence Shell of Each Element

There is an alternate form, which integrates the f orbitals into the main table

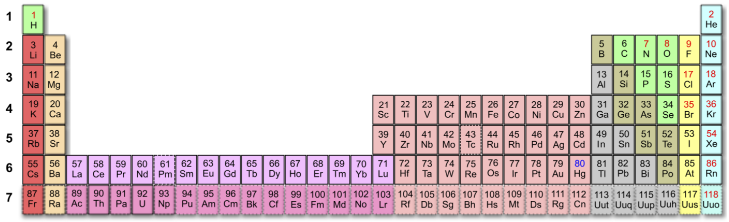
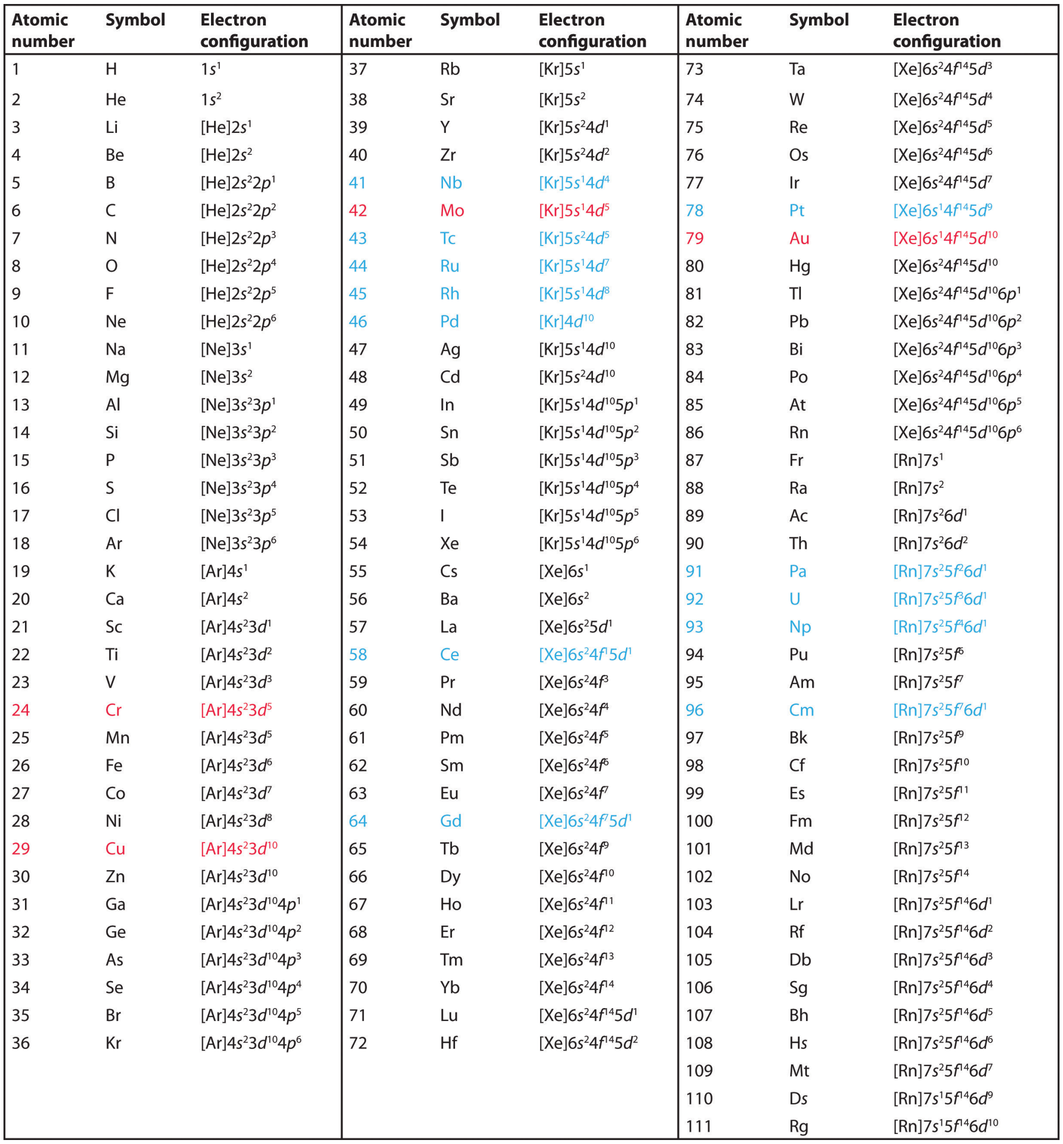


Figure 3: An Alternate Form of the Periodic Table *This wide form of the periodic table shows how the 4f/5f orbitals fit between the 6s/7s and 5d/6d orbitals*

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 making it unreactive like the other noble gases, justifying its placement above neon on the right. In Chapter 3, we will examine how electron configurations affect the properties and reactivity of the elements.



Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	$1s^{1}$	37	Rb	$\mathrm{[Kr]}5s^{1}$	73	Ta	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{3}$
2	He	$1s^{2}$	38	Sr	$\mathrm{[Kr]}5s^{2}$	74	W	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{4}$
3	Li	$\mathrm{[He]}2s^{1}$	39	Y	$\mathrm{[Kr]}5s^{2}4d^{1}$	75	Re	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{5}$
4	Be	$\mathrm{[He]}2s^{2}$	40	Zr	$\mathrm{[Kr]}5s^{2}4d^{2}$	76	Os	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{6}$
5	B	$\mathrm{[He]}2s^{2}2p^{1}$	41	Nb	$\mathrm{[Kr]}5s^{1}4d^{4}$	77	Ir	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{7}$
6	C	$\mathrm{[He]}2s^{2}2p^{2}$	42	Mo	$\mathrm{[Kr]}5s^{1}4d^{5}$	78	Pt	$\mathrm{[Xe]}6s^{1}4f^{14}5d^{9}$
7	N	$\mathrm{[He]}2s^{2}2p^{3}$	43	Tc	$\mathrm{[Kr]}5s^{2}4d^{5}$	79	Au	$\mathrm{[Xe]}6s^{1}4f^{14}5d^{10}$
8	O	$\mathrm{[He]}2s^{2}2p^{4}$	44	Ru	$\mathrm{[Kr]}5s^{1}4d^{7}$	80	Hg	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{10}$
9	F	$\mathrm{[He]}2s^{2}2p^{5}$	45	Rh	$\mathrm{[Kr]}5s^{1}4d^{8}$	81	Tl	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{10}6p^{1}$
10	Ne	$\mathrm{[He]}2s^{2}2p^{6}$	46	Pd	$\mathrm{[Kr]}4d^{10}$	82	Pb	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{10}6p^{2}$
11	Na	$\mathrm{[Ne]}3s^{1}$	47	Ag	$\mathrm{[Kr]}5s^{1}4d^{10}$	83	Bi	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{10}6p^{3}$
12	Mg	$\mathrm{[Ne]}3s^{2}$	48	Cd	$\mathrm{[Kr]}5s^{2}4d^{10}$	84	Po	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{10}6p^{4}$
13	Al	$\mathrm{[Ne]}3s^{2}3p^{1}$	49	In	$\mathrm{[Kr]}5s^{1}4d^{10}5p^{1}$	85	At	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{10}6p^{5}$
14	Si	$\mathrm{[Ne]}3s^{2}3p^{2}$	50	Sn	$\mathrm{[Kr]}5s^{1}4d^{10}5p^{2}$	86	Rn	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{10}6p^{6}$
15	P	$\mathrm{[Ne]}3s^{2}3p^{3}$	51	Sb	$\mathrm{[Kr]}5s^{1}4d^{10}5p^{3}$	87	Fr	$\mathrm{[Rn]}7s^{1}$
16	S	$\mathrm{[Ne]}3s^{2}3p^{4}$	52	Te	$\mathrm{[Kr]}5s^{1}4d^{10}5p^{4}$	88	Ra	$\mathrm{[Rn]}7s^{2}$
17	Cl	$\mathrm{[Ne]}3s^{2}3p^{5}$	53	I	$\mathrm{[Kr]}5s^{1}4d^{10}5p^{5}$	89	Ac	$\mathrm{[Rn]}7s^{2}6d^{1}$
18	Ar	$\mathrm{[Ne]}3s^{2}3p^{6}$	54	Xe	$\mathrm{[Kr]}5s^{1}4d^{10}5p^{6}$	90	Th	$\mathrm{[Rn]}7s^{2}6d^{2}$
19	K	$\mathrm{[Ar]}4s^{1}$	55	Cs	$\mathrm{[Xe]}6s^{1}$	91	Pa	$\mathrm{[Rn]}7s^{2}5f^{2}6d^{1}$
20	Ca	$\mathrm{[Ar]}4s^{2}$	56	Ba	$\mathrm{[Xe]}6s^{2}$	92	U	$\mathrm{[Rn]}7s^{2}5f^{3}6d^{1}$
21	Sc	$\mathrm{[Ar]}4s^{2}3d^{1}$	57	La	$\mathrm{[Xe]}6s^{2}5d^{1}$	93	Np	$\mathrm{[Rn]}7s^{2}5f^{4}6d^{1}$
22	Ti	$\mathrm{[Ar]}4s^{2}3d^{2}$	58	Ce	$\mathrm{[Xe]}6s^{2}4f^{1}5d^{1}$	94	Pu	$\mathrm{[Rn]}7s^{2}5f^{6}$
23	V	$\mathrm{[Ar]}4s^{2}3d^{3}$	59	Pr	$\mathrm{[Xe]}6s^{2}4f^{3}$	95	Am	$\mathrm{[Rn]}7s^{2}5f^{7}$
24	Cr	$\mathrm{[Ar]}4s^{2}3d^{5}$	60	Nd	$\mathrm{[Xe]}6s^{2}4f^{4}$	96	Cm	$\mathrm{[Rn]}7s^{2}5f^{7}6d^{1}$
25	Mn	$\mathrm{[Ar]}4s^{2}3d^{5}$	61	Pm	$\mathrm{[Xe]}6s^{2}4f^{5}$	97	Bk	$\mathrm{[Rn]}7s^{2}5f^{9}$
26	Fe	$\mathrm{[Ar]}4s^{2}3d^{6}$	62	Sm	$\mathrm{[Xe]}6s^{2}4f^{6}$	98	Cf	$\mathrm{[Rn]}7s^{2}5f^{10}$
27	Co	$\mathrm{[Ar]}4s^{2}3d^{7}$	63	Eu	$\mathrm{[Xe]}6s^{2}4f^{7}$	99	Es	$\mathrm{[Rn]}7s^{2}5f^{11}$
28	Ni	$\mathrm{[Ar]}4s^{2}3d^{8}$	64	Gd	$\mathrm{[Xe]}6s^{2}4f^{7}5d^{1}$	100	Fm	$\mathrm{[Rn]}7s^{2}5f^{12}$
29	Cu	$\mathrm{[Ar]}4s^{2}3d^{10}$	65	Tb	$\mathrm{[Xe]}6s^{2}4f^{9}$	101	Md	$\mathrm{[Rn]}7s^{2}5f^{13}$
30	Zn	$\mathrm{[Ar]}4s^{2}3d^{10}$	66	Dy	$\mathrm{[Xe]}6s^{2}4f^{10}$	102	No	$\mathrm{[Rn]}7s^{2}5f^{14}$
31	Ga	$\mathrm{[Ar]}4s^{2}3d^{10}4p^{1}$	67	Ho	$\mathrm{[Xe]}6s^{2}4f^{11}$	103	Lr	$\mathrm{[Rn]}7s^{2}5f^{14}6d^{1}$
32	Ge	$\mathrm{[Ar]}4s^{2}3d^{10}4p^{2}$	68	Er	$\mathrm{[Xe]}6s^{2}4f^{12}$	104	Rf	$\mathrm{[Rn]}7s^{2}5f^{14}6d^{2}$
33	As	$\mathrm{[Ar]}4s^{2}3d^{10}4p^{3}$	69	Tm	$\mathrm{[Xe]}6s^{2}4f^{13}$	105	Db	$\mathrm{[Rn]}7s^{2}5f^{14}6d^{3}$
34	Se	$\mathrm{[Ar]}4s^{2}3d^{10}4p^{4}$	70	Yb	$\mathrm{[Xe]}6s^{2}4f^{14}$	106	Sg	$\mathrm{[Rn]}7s^{2}5f^{14}6d^{4}$
35	Br	$\mathrm{[Ar]}4s^{2}3d^{10}4p^{5}$	71	Lu	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{1}$	107	Bh	$\mathrm{[Rn]}7s^{2}5f^{14}6d^{5}$
36	Kr	$\mathrm{[Ar]}4s^{2}3d^{10}4p^{6}$	72	Hf	$\mathrm{[Xe]}6s^{2}4f^{14}5d^{2}$	108	Hs	$\mathrm{[Rn]}7s^{2}5f^{14}6d^{6}$
						109	Mt	$\mathrm{[Rn]}7s^{2}5f^{14}6d^{7}$
						110	Ds	$\mathrm{[Rn]}7s^{1}5f^{14}6d^{9}$
						111	Rg	$\mathrm{[Rn]}7s^{1}5f^{14}6d^{10}$

Figure 4: 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.

Exercises

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:

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 $n = 2$.

Thus beryllium has an $[\mathrm{He}]s^2$ electron configuration. The next element down, magnesium, is expected to have exactly the same arrangement of electrons in the $n = 3$ principal shell: $[\mathrm{Ne}]s^2$. By extrapolation, we expect all the group 2 elements to have an ns^2 electron configuration.

2. 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.

3. A set of four quantum numbers specifies each wave function. What information is given by each quantum number? How does this information relate to the periodic table?

4. The periodic table is divided into blocks. Identify each block and explain the principle behind the divisions. Why does the p-block contain 6 total columns?

5. Propose an explanation as to why the noble gases are inert.

Key Takeaway

- The arrangement of atoms in the periodic table arises from the lowest energy arrangement of electrons in the valence shell.

This page was originally authored by Joshua Halpern, Scott Sinex and Scott Johnson with modifications/edits made by Camille Kaslan.

6.3: Periodicity

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 $6.3.1$. 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 $6.3.1$: General Properties of Group I Metals

Element	Electronic Configuration	Melting Point (°C)	Density (g/cm^3)	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 $6.3.1$):

- 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:

$$M \rightarrow M^+ + e-$$

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*

$$2M_{(s)} + H_{2(g)} \rightarrow 2MH(s)$$

(Note: hydrogen is present in the metal hydride as the ***hydride*** H$^-$ ion)

- React with sulfur to form solid *sulfides*

$$2M_{(s)} + S_{(s)} \rightarrow M_2S_{(s)}$$

React with chlorine to form solid *chlorides*

$$2M_{(s)} + Cl_{2(g)} \rightarrow 2MCl_{(s)}$$

Alkali metals react with water to produce hydrogen gas and alkali metal hydroxides; this is a very exothermic reaction (Figure 6.3.1).

$$2M_{(s)} + 2H_2O_{(l)} \rightarrow 2MOH_{(aq)} + H_{2(g)}$$

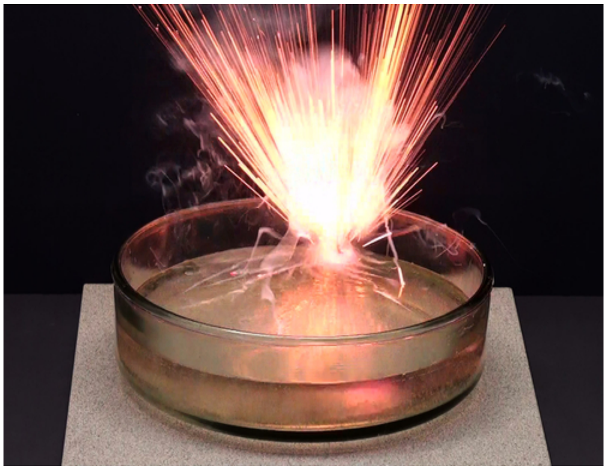


Figure 6.3.1: A small piece of potassium metal explodes as it reacts with water. (CC SA-BY 3.0; Tavoromann)

The reaction between alkali metals and oxygen is more complex:

- A common reaction is to form metal oxides which contain the ***O*$^{2-}$ *ion***

$$4Li_{(s)} + O_{2(g)} \rightarrow \underbrace{2Li_2O_{(s)}}_{\text{lithium oxide}}$$

Other alkali metals ***can*** form metal peroxides (contains O_2^{2-} ion)

$$2Na(s) + O_{2(g)} \rightarrow \underbrace{Na_2O_{2(s)}}_{\text{sodium peroxide}}$$

K, Rb and Cs ***can*** also form superoxides (O_2^- ion)

$$K(s) + O_{2(g)} \rightarrow \underbrace{KO_{2(s)}}_{\text{potassium superoxide}}$$

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 $6.3.2$.

Table $6.3.2$: General Properties of Group 2 Metals

Element	Electronic Configuration	Melting Point (°C)	Density (g/cm^3)	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:

$$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$

The tendency of the alkaline earths to lose their two valence electrons is demonstrated in the reactivity of Mg towards chlorine gas and oxygen:

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$

$$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$

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

- Mike Blaber (Florida State University)

Learning Objectives

- To understand the trends in properties and reactivity of the group 18 elements: the noble gases.

The noble gases were all isolated for the first time within a period of only five years at the end of the 19th century. Their very existence was not suspected until the 18th century, when early work on the composition of air suggested that it contained small amounts of gases in addition to oxygen, nitrogen, carbon dioxide, and water vapor. Helium was the first of the noble gases to be identified, when the existence of this previously unknown element on the sun was demonstrated by new spectral lines seen during a solar eclipse in 1868. Actual samples of helium were not obtained until almost 30 years later, however. In the 1890s, the English physicist J. W. Strutt (Lord Rayleigh) carefully measured the density of the gas that remained after he had removed all O_2, CO_2, and water vapor from air and showed that this residual gas was slightly denser than pure N_2 obtained by the thermal decomposition of ammonium nitrite. In 1894, he and the Scottish chemist William Ramsay announced the isolation of a new “substance” (not necessarily a new element) from the residual nitrogen gas. Because they could not force this substance to decompose or react with anything, they named it argon (Ar), from the Greek argos, meaning “lazy.” Because the measured molar mass of argon was 39.9 g/mol, Ramsay speculated that it was a member of a new group of elements located on the right side of the periodic table between the halogens and the alkali metals. He also suggested that these elements should have a preferred valence of 0, intermediate between the +1 of the alkali metals and the −1 of the halogens.

J. W. Strutt (Lord Rayleigh) (1842–1919)

Lord Rayleigh was one of the few members of British higher nobility to be recognized as an outstanding scientist. Throughout his youth, his education was repeatedly interrupted by his frail health, and he was not expected to reach maturity. In 1861 he entered Trinity College, Cambridge, where he excelled at mathematics. A severe attack of rheumatic fever took him abroad, but in 1873 he succeeded to the barony and was compelled to devote his time to the management of his estates. After leaving the entire management to his younger brother, Lord Rayleigh was able to devote his time to science. He was a recipient of honorary science and law degrees from Cambridge University.

Sir William Ramsay (1852–1916)

Born and educated in Glasgow, Scotland, Ramsay was expected to study for the Calvanist ministry. Instead, he became interested in chemistry while reading about the manufacture of gunpowder. Ramsay earned his PhD in organic chemistry at the University of Tübingen in Germany in 1872. When he returned to England, his interests turned first to physical chemistry and then to inorganic chemistry. He is best known for his work on the oxides of nitrogen and for the discovery of the noble gases with Lord Rayleigh.

In 1895, Ramsey was able to obtain a terrestrial sample of helium for the first time. Then, in a single year (1898), he discovered the next three noble gases: krypton (Kr), from the Greek kryptos, meaning “hidden,” was identified by its orange and green emission lines; neon (Ne), from the Greek neos, meaning “new,” had bright red emission lines; and xenon (Xe), from the Greek xenos, meaning “strange,” had deep blue emission lines. The last noble gas was discovered in 1900 by the German chemist Friedrich Dorn, who was investigating radioactivity in the air around the newly discovered radioactive elements radium and polonium. The element was named radon (Rn), and Ramsay succeeded in obtaining enough radon in 1908 to measure its density (and thus its atomic mass). For their discovery of the noble gases, Rayleigh was awarded the Nobel Prize in Physics and Ramsay the Nobel Prize in Chemistry in 1904. Because helium has the lowest boiling point of any substance known (4.2 K), it is used primarily as a cryogenic liquid. Helium and argon are both much less soluble in water (and therefore in blood) than N_2, so scuba divers often use gas mixtures that contain these gases, rather than N_2, to minimize the likelihood of the “bends,” the painful and potentially fatal formation of bubbles of $N_2(g)$ that can occur when a diver returns to the surface too rapidly.

Preparation and General Properties of the Group 18 Elements

Fractional distillation of liquid air is the only source of all the noble gases except helium. Although helium is the second most abundant element in the universe (after hydrogen), the helium originally present in Earth’s atmosphere was lost into space long ago because of its low molecular mass and resulting high mean velocity. Natural gas often contains relatively high concentrations of helium (up to 7%), however, and it is the only practical terrestrial source.

The elements of group 18 all have closed-shell valence electron configurations, either ns^2np^6 or $1s^2$ for He. Consistent with periodic trends in atomic properties, these elements have high ionization energies that decrease smoothly down the group. From their electron affinities, the data in Table $6.3.1$ indicate that the noble gases are unlikely to form compounds in negative oxidation states. A potent oxidant is needed to oxidize noble gases and form compounds in positive oxidation states. Like the heavier halogens, xenon and perhaps krypton should form covalent compounds with F, O, and possibly Cl, in which they have even formal oxidation states (+2, +4, +6, and possibly +8). These predictions actually summarize the chemistry observed for these elements.

Table $6.3.1$: Selected Properties of the Group 18 Elements

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
atomic symbol	He	Ne	Ar	Kr	Xe	Rn
atomic number	2	10	18	36	54	86
atomic mass (amu)	4.00	20.18	39.95	83.80	131.29	222
valence electron configuration*	$1s^2$	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$

*The configuration shown does not include filled d and f subshells. †This is the normal boiling point of He. Solid He does not exist at 1 atm pressure, so no melting point can be given.

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
triple point/boiling point (°C)	—/−269[†]	−249 (at 43 kPa)/−246	−189 (at 69 kPa)/−189	−157/−153	−112 (at 81.6 kPa)/−108	−71/−62
density (g/L) at 25°C	0.16	0.83	1.63	3.43	5.37	9.07
atomic radius (pm)	31	38	71	88	108	120
first ionization energy (kJ/mol)	2372	2081	1521	1351	1170	1037
normal oxidation state(s)	0	0	0	0 (+2)	0 (+2, +4, +6, +8)	0 (+2)
electron affinity (kJ/mol)	> 0	> 0	> 0	> 0	> 0	> 0
electronegativity	—	—	—	—	2.6	—
product of reaction with O_2	none	none	none	none	not directly with oxygen, but XeO_3 can be formed by Equation 6.3.5.	none
type of oxide	—	—	—	—	acidic	—
product of reaction with N_2	none	none	none	none	none	none
product of reaction with X_2	none	none	none	KrF_2	XeF_2, XeF_4, XeF_6	RnF_2
product of reaction with H_2	none	none	none	none	none	none

*The configuration shown does not include filled d and f subshells. [†]This is the normal boiling point of He. Solid He does not exist at 1 atm pressure, so no melting point can be given.

Reactions and Compounds of the Noble Gases

For many years, it was thought that the only compounds the noble gases could form were clathrates. Clathrates are solid compounds in which a gas, the guest, occupies holes in a lattice formed by a less volatile, chemically dissimilar substance, the host (Figure 6.3.1).

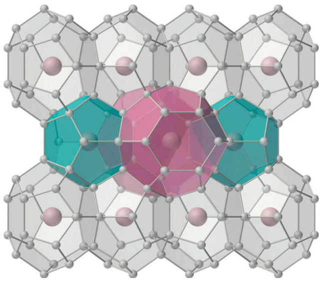


Figure 6.3.1: The Structure of Xenon Hydrate, a Clathrate. Small gaseous atoms or molecules such as Xe or CH_4 can occupy cavities in a lattice of hydrogen-bonded water molecules to produce a stable structure with a fixed stoichiometry (in this case, $Xe{\cdot}5.75H_2O$). (The hydrogen atoms of the water molecules have been omitted for clarity.) Warming the solid hydrate or decreasing the pressure of the gas causes it to collapse, with the evolution of gas and the formation of liquid water.

Because clathrate formation does not involve the formation of chemical bonds between the guest (Xe) and the host molecules (H_2O, in the case of xenon hydrate), the guest molecules are immediately released when the clathrate is melted or dissolved.

Methane Clathrates

In addition to the noble gases, many other species form stable clathrates. One of the most interesting is methane hydrate, large deposits of which occur naturally at the bottom of the oceans. It is estimated that the amount of methane in such deposits could have a major impact on the world's energy needs later in this century.

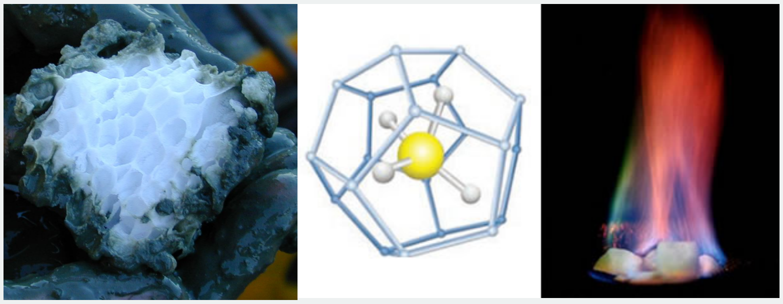


Figure 6.3.2: "Burning snowballs." Like xenon, methane (CH_4) forms a crystalline clathrate with water: methane hydrate. When the solid is warmed, methane is released and can be ignited to give what appears to be burning snow. (left) Structure of a gas hydrate (methane clathrate) block embedded in the sediment of hydrate ridge, off Oregon, USA (CC-SA-BY-3.0 Wusel007) (middle) A ball-and-stick model of methane hydrate showing the central methane molecule surrounded by a "cage" of water molecules. Other hydrocarbon molecules such as pentane and ethane can occupy the central position in this structure. (United States Department of Energy image). (Right): A burning specimen of methane hydrate ice (United States Geological Survey image).

The widely held belief in the intrinsic lack of reactivity of the noble gases was challenged when Neil Bartlett, a British professor of chemistry at the University of British Columbia, showed that PtF_6, a compound used in the Manhattan Project, could oxidize O_2. Because the ionization energy of xenon (1170 kJ/mol) is actually lower than that of O_2, Bartlett recognized that PtF_6 should also be able to oxidize xenon. When he mixed colorless xenon gas with deep red PtF_6 vapor, yellow-orange crystals immediately formed (Figure 6.3.3). Although Bartlett initially postulated that they were $\mathrm{Xe^+PtF_6^-}$, it is now generally agreed that the reaction also involves the transfer of a fluorine atom to xenon to give the $\mathrm{XeF^+}$ ion:

$$\mathrm{Xe(g) + PtF_6(g) \longrightarrow [XeF^+][PtF_5^-](s)} \tag{6.3.1}$$

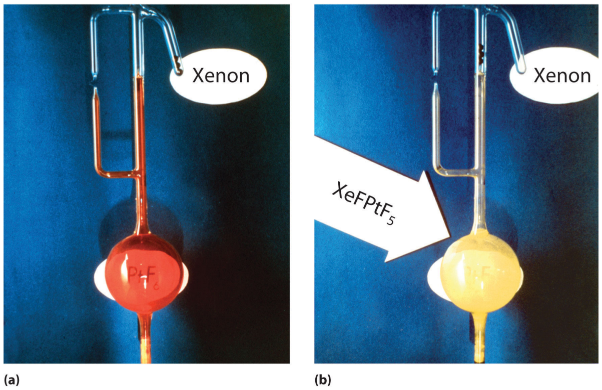


Figure 6.3.3: The Synthesis of the First Chemical Compound of Xenon. (a) An apparatus containing platinum hexafluoride, the red vapor at the bottom left, and xenon, the colorless gas in the small tube at the upper right. (b) When the glass seal separating the two gases is broken and the gases are allowed to mix, a bright yellow solid is formed, which is best described as $XeF^+PtF_5^-$.

Subsequent work showed that xenon reacts directly with fluorine under relatively mild conditions to give XeF_2, XeF_4, or XeF_6, depending on conditions; one such reaction is as follows:

$$\mathrm{Xe(g) + 2\,F_2(g) \longrightarrow XeF_4(s)} \tag{6.3.2}$$

The ionization energies of helium, neon, and argon are so high (Table 6.3.1) that no stable compounds of these elements are known. The ionization energies of krypton and xenon are lower but still very high; consequently only highly electronegative elements (F, O, and Cl) can form stable compounds with xenon and krypton without being oxidized themselves. Xenon reacts directly with only two elements: F_2 and Cl_2. Although $\mathrm{XeCl_2}$ and $\mathrm{KrF_2}$ can be prepared directly from the elements, they are substantially less stable than the xenon fluorides.

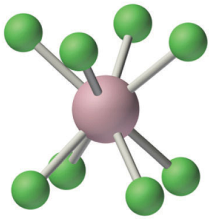
> *The ionization energies of helium, neon, and argon are so high that no stable compounds of these elements are known.*

Because halides of the noble gases are powerful oxidants and fluorinating agents, they decompose rapidly after contact with trace amounts of water, and they react violently with organic compounds or other reductants. The xenon fluorides are also Lewis acids; they react with the fluoride ion, the only Lewis base that is not oxidized immediately on contact, to form anionic complexes. For example, reacting cesium fluoride with XeF_6 produces $CsXeF_7$, which gives Cs_2XeF_8 when heated:

$$\mathrm{XeF_6(s) + CsF(s) \longrightarrow CsXeF_7(s)} \tag{6.3.3}$$

$$\mathrm{2\,CsXeF_7(s) \xrightarrow{\Delta} Cs_2XeF_8(s) + XeF_6(g)} \tag{6.3.4}$$

The XeF_8^{2-} ion contains eight-coordinate xenon and has the square antiprismatic structure, which is essentially identical to that of the IF_8^- ion. Cs_2XeF_8 is surprisingly stable for a polyatomic ion that contains xenon in the +6 oxidation state, decomposing only at temperatures greater than 300°C. Major factors in the stability of Cs_2XeF_8 are almost certainly the formation of a stable ionic lattice and the **high coordination number** of xenon, which protects the central atom from attack by other species. (Recall from that this latter effect is responsible for the extreme stability of SF_6.)



XeF_8^{2-}

For a previously “inert” gas, xenon has a surprisingly high affinity for oxygen, presumably because of π bonding between O and Xe. Consequently, xenon forms an extensive series of oxides and oxoanion salts. For example, hydrolysis of either XeF_4 or XeF_6 produces XeO_3, an explosive white solid:

$$\mathrm{XeF_6(aq) + 3\,H_2O(l) \longrightarrow XeO_3(aq) + 6\,HF(aq)} \tag{6.3.5}$$

Treating a solution of XeO_3 with ozone, a strong oxidant, results in further oxidation of xenon to give either XeO_4, a colorless, explosive gas, or the surprisingly stable perxenate ion (XeO_6^{4-}), both of which contain xenon in its highest possible oxidation state (+8). The chemistry of the xenon halides and oxides is best understood by analogy to the corresponding compounds of iodine. For example, XeO_3 is isoelectronic with the iodate ion (IO_3^-), and XeF_8^{2-} is isoelectronic with the IF_8^- ion.

> *Xenon has a high affinity for both fluorine and oxygen.*

Because the ionization energy of radon is less than that of xenon, in principle radon should be able to form an even greater variety of chemical compounds than xenon. Unfortunately, however, radon is so radioactive that its chemistry has not been extensively explored.

✓ Example 6.3.1

On a virtual planet similar to Earth, at least one isotope of radon is not radioactive. A scientist explored its chemistry and presented her major conclusions in a trailblazing paper on radon compounds, focusing on the kinds of compounds formed and their stoichiometries. Based on periodic trends, how did she summarize the chemistry of radon?

Given: nonradioactive isotope of radon

Asked for: summary of its chemistry

Strategy:

Based on the position of radon in the periodic table and periodic trends in atomic properties, thermodynamics, and kinetics, predict the most likely reactions and compounds of radon.

Solution

We expect radon to be significantly easier to oxidize than xenon. Based on its position in the periodic table, however, we also expect its bonds to other atoms to be weaker than those formed by xenon. Radon should be more difficult to oxidize to its highest possible oxidation state (+8) than xenon because of the inert-pair effect. Consequently, radon should form an extensive series of fluorides, including RnF_2, RnF_4, RnF_6, and possibly RnF_8 (due to its large radius). The ion RnF_8^{2-} should also exist. We expect radon to form a series of oxides similar to those of xenon, including RnO_3 and possibly RnO_4. The biggest surprise in radon chemistry is likely to be the existence of stable chlorides, such as $RnCl_2$ and possibly even $RnCl_4$.

? Exercise 6.3.1

Predict the stoichiometry of the product formed by reacting XeF_6 with a 1:1 stoichiometric amount of KF and propose a reasonable structure for the anion.

Answer

$KXeF_7$; the xenon atom in XeF_7^- has 16 valence electrons, which according to the valence-shell electron-pair repulsion model could give either a square antiprismatic structure with one fluorine atom missing or a pentagonal bipyramid if the $5s^2$ electrons behave like an inert pair that does not participate in bonding.

Summary

The noble gases are characterized by their high ionization energies and low electron affinities. Potent oxidants are needed to oxidize the noble gases to form compounds in positive oxidation states. The noble gases have a closed-shell valence electron configuration. The ionization energies of the noble gases decrease with increasing atomic number. Only highly electronegative elements can form stable compounds with the noble gases in positive oxidation states without being oxidized themselves. Xenon has a high affinity for both fluorine and oxygen, which form stable compounds that contain xenon in even oxidation states up to +8.

Contributors and Attributions

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    - Anonymous

6.4: Effective Nuclear Charge and Shielding

Estimate Time to Read: 8 min

Coulomb's Law

Coulomb's Law is from classical physics (Equation 1); it tells us that particles with opposite electrostatic charges (q_1, q_2) are attracted to each other, and the larger the charge on either particle or the closer the distance (r) between them, the stronger the force of attraction (F). Coulombs' law works well for predicting the energy of an electron in a hydrogen atom because H has only one electron. It also works for hydrogen-like atoms: any nucleus with exactly one electron (a He^+ ion, for example, has one electron). However, Coulomb's law is insufficient for predicting the energies of electrons in multi-electron atoms and ions.Coulomb's law explains why atomic size decreases as the charge on the nucleus increases, but it can't explain the nuances and variations in size as we go across the periodic table. Coulomb's Law also explains why electrons in different shells (n), at different distances from the nucleus, have different energies. But on its own, Coulomb's law doesn't quite explain why electron subshells within a shell (like 2s vs. 2p) would have different energies. To explain these things, we need to consider how both electron *shielding* and *penetration* result in variations in effective nuclear charge (Z*) that depend on shell and subshell.

Equation 6.4.1. Coulomb's Law

$$F = k\frac{q_1 q_2}{r^2}$$

Effective Nuclear Charge (Z*)

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. However, electrons within a multi-electron atom interact with the nucleus and with all other electrons. Each electron in a multi-electron atom experiences both attraction to the nucleus and repulsion from the other electrons. The presence of multiple electrons decreases the nuclear attraction to some extent. Each electron in a multi-electron atom experiences a different magnitude of (and attraction to) the nuclear charge depending on what specific shell and subshell the electron occupies. The amount of positive nuclear charge experienced by any individual electron is the **effective nuclear charge (Z*)**.

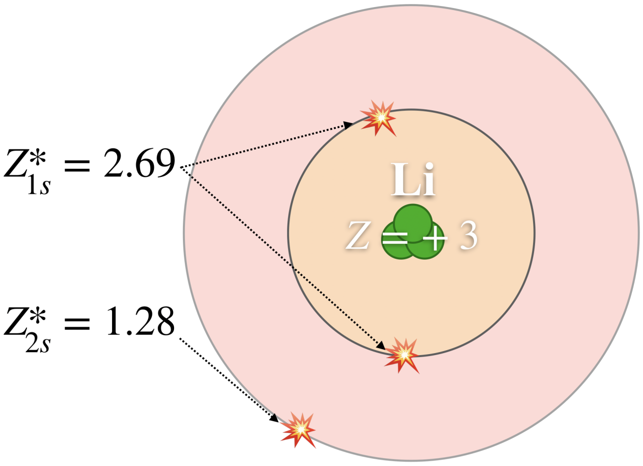

Figure 6.4.1: In a lithium atom, the nuclear charge (Z) is +3. 1s electrons experience an effective nuclear charge (Z*) of +2.69, and 2s electrons experience an Z* of +1.28. (CC-BY-NC-SA; Kathryn Haas)

For example, in lithium (Li), none of the three electrons "feel" the full +3 charge from the nucleus (Figure 6.4.1). Rather, each electron "feels" a Z* that is less than the actual Z and that depends on the electron's orbital. The actual nuclear charge in Li is $Z = +3$; the 1s electrons experience a $Z^* = +2.69$, and the 2s electron experiences a $Z^* = +1.28$. In general, core electrons (or the electrons closest to the nucleus), "feel" a Z* that is close to, but less than, Z. On the other hand, outer valence electrons experience a Z* that is much less than Z.

- Core electrons: $Z^* \lessapprox Z$
- Valence electrons: $Z^* \ll Z$

If an electron is far from the nucleus, then at any given moment most of the other electrons will be *between* that electron and the nucleus. Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. The farther an electron is from the nucleus, the more electrons between that electron and the nucleus, and the greater the actual nuclear charge Z is than the effective nuclear charge Z*. This effect is called *electron shielding*.

Shielding

Shielding *is the reduction of true nuclear charge (Z) to the effective nuclear charge (Z*) by other electrons in a multi-electron atom or ion*. Shielding occurs in all atoms and ions that have more than one electron. H is the only atom in which shielding does not occur.

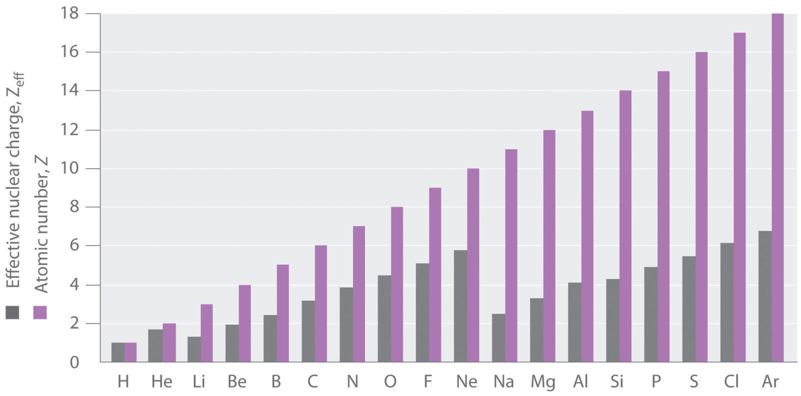

Figure 6.4.2: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, Z_{eff} is *always* less than Z, and Z_{eff} increases from left to right as you go across a row. (CC-BY-NC-SA, LibreText)

Electrons in a multi-electron atom interact with the nucleus and all other electrons in the atom. To describe shielding, we choose an electron-of-interest in a multi-electron atom and treat all the "other" electrons as a group. While the positive charge of the nucleus attracts our electron, the negative charges of the "other" electrons repel our electron-of-interest. The attractive and repulsive forces partially cancel each other; however, there are fewer "other" electrons than there are protons in our atom so the nuclear charge is never completely canceled. The "other" electrons partially block, or *shield*, part of the nuclear charge so that our electron-of-interest experiences a partially-reduced nuclear charge, the Z*.

In reality, there is not a one-for-one "canceling" of the nuclear charge by each electron. Partly due to *penetration*, no single electron can completely shield a full unit of positive charge. Core electrons shield valence electrons, but valence electrons have little effect on the Z* of core electrons. The ability to shield, and be shielded by, other electrons strongly depends the electron orbital's average distance from the nucleus and its penetration; thus shielding depends on both shell (n) and subshell (l).

Electron Penetration

Coulomb's law shows us that distance of an electron from its nucleus is important in determining the electron's energy (its attraction to the nucleus). The shell number (n) determines approximately how far an electron is from the nucleus *on average*. Thus, all orbitals in the same shell (s,p,d) have similar sizes and similar average distance of their electrons from the nucleus. But there is another distance-related factor that plays a critical role in determining orbital energy levels: penetration. **Penetration** *describes the ability of an electron in a given subshell to penetrate into other shells and subshells to get close to the nucleus*. **Penetration** ***is the extent to which an electron can approach the nucleus***. Penetration depends on both the shell (n) and subshell (l).

The penetration of individual orbitals can be visualized using the radial probability functions, which show the probability of locating an electron in an orbital as a function of distance from the nucleus. Figure $6.4.3$ shows the radial probability function of the 1s, 2s, and 2p orbitals. From these plots, we can see that the probability peak of the 1s orbital closest to the nucleus; thus it is the most penetrating. While the 2s and 2p have most of their probability at a farther distance from the nucleus (compared to 1s), the 2s orbital and the 2p orbital have different extents of penetration. Notice that the 2s orbital is able to penetrate the 1s orbital because of the central 2s lobe. The 2p orbital penetrates somewhat into the 1s, but it cannot approach the nucleus as closely as the

2s orbital can. While the 2s orbital penetrates more than 2p, the average probability of the 2p is slightly *closer* than that of the 2s. The order of Z* in 2s and 2p subshells depends on which factor (average distance or penetration) is more important. In the first two rows of the periodic table, penetration is the dominant factor that results in 2s having a lower energy than 2p.

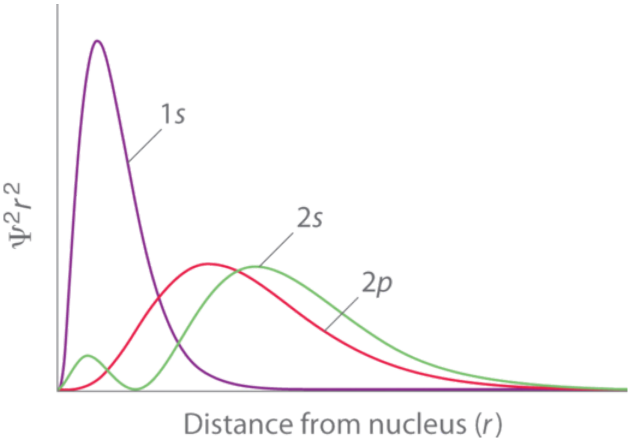

Figure 6.4.3: Orbital Penetration. A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z*, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital. (CC-BY-NC-SA, LibreText)

An electron orbital's penetration affects its ability to shield other electrons and affects the extent to which it is shielded by other electrons. In general, electron orbitals that have greater penetration experience stronger attraction to the nucleus and less shielding by other electrons; these electrons thus experience a larger Z*. Electrons in orbitals that have greater penetration also shield other electrons to a greater extent.

Within the same shell value (*n*), the penetrating power of an electron follows this trend in subshells (m_l):

$$s > p > d > f$$

Problems

Exercise 6.4.1

Compare the 2s and 2p orbitals:

1. Which is closer to the nucleus on average?
2. Which is more penetrating?
3. Which orbital experiences a stronger Z* and is thus lower in energy. Explain.

Answer

1. The 2s orbital is closer to the nucleus on average.
2. The 2s orbital is more penetrating than 2p.
3. You might "know" that the 2s orbital is lower in energy than 2p because 2s fills first. But a close inspection of Figures 1.1.2.3 and 1.1.2.4 indicates that while the 2s and 2p elements are degenerate in Ne (element 10), for elements with atomic number 11 and greater 2p has a higher Z* than 2s! This example illustrates that both average distance and penetration are factors in determining Z*, and the factor that is more important may change as we increase in atomic number.

Exercise 6.4.2

Peruse the Hyperphysics page that shows radial probability functions of several orbitals (click around on various orbitals). Compare the 2p and 3s orbitals:

1. Which is farther from the nucleus on average?
2. Which is more penetrating?
3. Which orbital is lower in energy?

Answer

1. The 3s orbital reaches farther away from the nucleus and is on average farther from the nucleus than 2p.
2. The 3s orbital is more penetrating than 2p, even though 3s is farther on average!
3. The 2p orbital is lower in energy than 3s; this is because 2p is still significantly closer to the nucleus on average and experiences a stronger Z*. (Penetration is not the only consideration!)

? Exercise 6.4.3

Which atom, Li, or N, has a stronger valence Z*? Explain why.

Answer

A nitrogen atom has a stronger effective nuclear charge (Z*) than lithium due to its greater number of protons; even though N also has more electrons that would shield the nuclear charge, each electron only partially shields each proton. This means that atoms with greater atomic number always have greater Z* for any given electron.

? Exercise 6.4.4

Explain why 2s and 2p subshells are completely degenerate in a hydrogen atom.

Answer

The hydrogen atom has only one electron; thus there is no shielding to consider. When there are not other electrons to shield the nucleus, penetration and shielding are irrelevant, and subshells within a shell are degenerate.

? Exercise 6.4.5

Which electrons shield others more effectively: 3p or 3d?

Answer

3p shields better than 3d because p orbitals penetrate more than d orbitals within the same shell.

? Exercise 6.4.6

Explain why the ground state (most energetically favorable) electron configuration of Be is $1s^22s^2$ rather than alternative configurations like $1s^22s^12p^1$ or $1s^22p^2$.

Answer

This question is asking why the 2s orbital fills in Be before 2p is occupied. This is a multi-electron atom, therefore core electrons shield the 2s and 2p orbitals to different extents. In Be we expect the 2s orbital to fill before 2p because 2s penetrates more and experiences a higher Z*.

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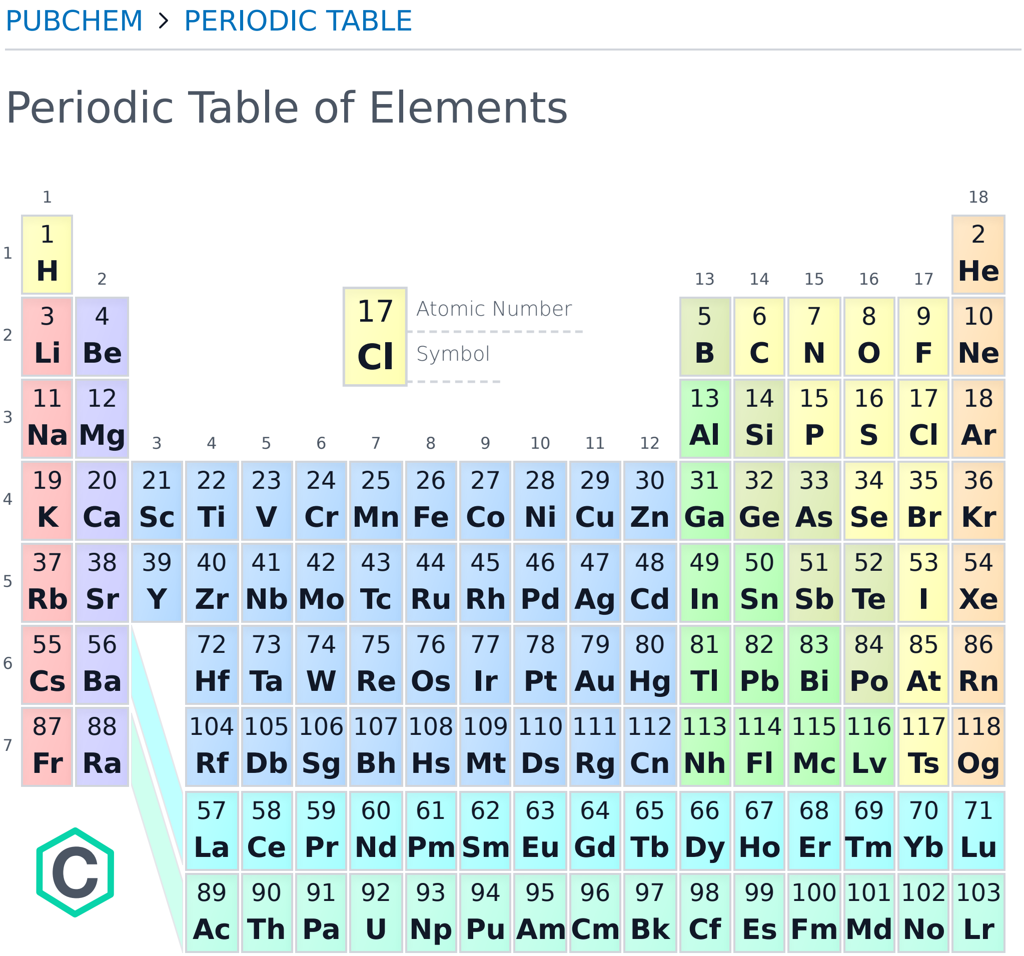
6.5: Periodic Trends

Periodic trends are specific patterns that are present in the periodic table that illustrate different aspects of a certain element, including its size and its electronic properties. Major periodic trends include: electronegativity, ionization energy, electron affinity, atomic radius, melting point, and metallic character. Periodic trends, arising from the arrangement of the periodic table, provide chemists with an invaluable tool to quickly predict an element's properties. These trends exist because of the similar atomic structure of the elements within their respective group families or periods, and because of the periodic nature of the elements.

Electronegativity Trends

Electronegativity can be understood as a chemical property describing an atom's ability to attract and bind with electrons. Because electronegativity is a qualitative property, there is no standardized method for calculating electronegativity. However, the most common scale for quantifying electronegativity is the Pauling scale (Table A2), named after the chemist Linus Pauling. The numbers assigned by the Pauling scale are dimensionless due to the qualitative nature of electronegativity. Electronegativity values for each element can be found on certain periodic tables. An example is provided below.



PUBCHEM › PERIODIC TABLE

Periodic Table of Elements

17 Atomic Number
Cl Symbol

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 6.5.1: Periodic Table of Electronegativity values

Electronegativity measures an atom's tendency to attract and form bonds with electrons. This property exists due to the electronic configuration of atoms. Most atoms follow the octet rule (having the valence, or outer, shell comprise of 8 electrons). Because elements on the left side of the periodic table have less than a half-full valence shell, the energy required to gain electrons is significantly higher compared with the energy required to lose electrons. As a result, the elements on the left side of the periodic table generally lose electrons when forming bonds. Conversely, elements on the right side of the periodic table are more energy-efficient in gaining electrons to create a complete valence shell of 8 electrons. The nature of electronegativity is effectively described thus: the more inclined an atom is to gain electrons, the more likely that atom will pull electrons toward itself.

- **From left to right across a period of elements, electronegativity increases.** If the valence shell of an atom is less than half full, it requires less energy to lose an electron than to gain one. Conversely, if the valence shell is more than half full, it is easier to pull an electron into the valence shell than to donate one.

- **From top to bottom down a group, electronegativity decreases.** This is because atomic number increases down a group, and thus there is an increased distance between the valence electrons and nucleus, or a greater atomic radius.
- **Important exceptions of the above rules include the noble gases, lanthanides, and actinides.** The noble gases possess a complete valence shell and do not usually attract electrons. The lanthanides and actinides possess more complicated chemistry that does not generally follow any trends. Therefore, noble gases, lanthanides, and actinides do not have electronegativity values.
- **As for the transition metals, although they have electronegativity values, there is little variance among them across the period and up and down a group.** This is because their metallic properties affect their ability to attract electrons as easily as the other elements.

According to these two general trends, the *most electronegative element is **fluorine***, with 3.98 Pauling units.

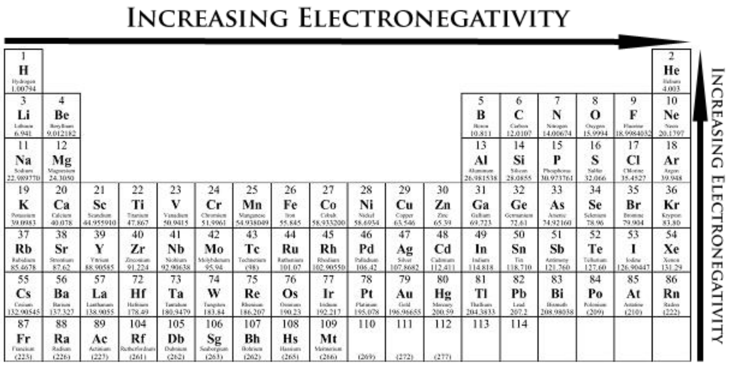


Figure 6.5.2: Periodic Table showing Electronegativity Trend

Ionization Energy Trends

Ionization energy is the energy required to remove an electron from a neutral atom in its gaseous phase. Conceptually, ionization energy is the opposite of electronegativity. The lower this energy is, the more readily the atom becomes a cation. Therefore, the higher this energy is, the more unlikely it is the atom becomes a cation. Generally, elements on the right side of the periodic table have a higher ionization energy because their valence shell is nearly filled. Elements on the left side of the periodic table have low ionization energies because of their willingness to lose electrons and become cations. Thus, ionization energy increases from left to right on the periodic table.

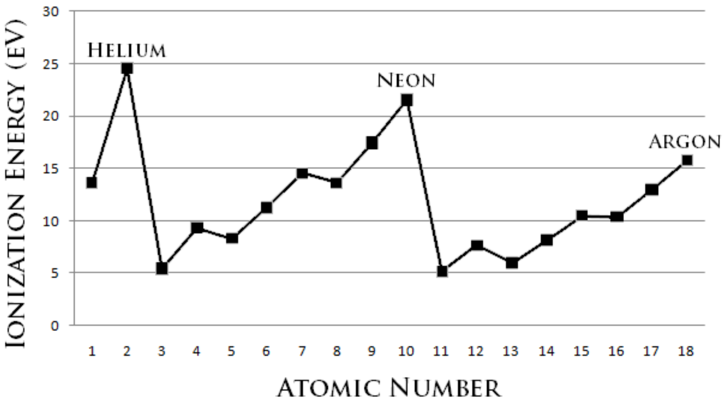


Figure 6.5.3: Graph showing the Ionization Energy of the Elements from Hydrogen to Argon

Another factor that affects ionization energy is *electron shielding*. Electron shielding describes the ability of an atom's inner electrons to shield its positively-charged nucleus from its valence electrons. When moving to the right of a period, the number of electrons increases and the strength of shielding increases. As a result, it is easier for valence shell electrons to ionize, and thus the ionization energy decreases down a group. Electron shielding is also known as *screening*.

Trends

- The ionization energy of the elements within a period generally increases from left to right. This is due to valence shell stability.
- The ionization energy of the elements within a group generally decreases from top to bottom. This is due to electron shielding.
- The noble gases possess very high ionization energies because of their full valence shells as indicated in the graph. Note that helium has the highest ionization energy of all the elements.

Some elements have several ionization energies; these varying energies are referred to as the first ionization energy, the second ionization energy, third ionization energy, etc. The first ionization energy is the energy requiredto remove the outermost, or highest, energy electron, the second ionization energy is the energy required to remove any subsequent high-energy electron from a gaseous cation, etc. Below are the chemical equations describing the first and second ionization energies:

First Ionization Energy:

$$X_{(g)} \rightarrow X^{+}_{(g)} + e^{-}$$

Second Ionization Energy:

$$X^{+}_{(g)} \rightarrow X^{2+}_{(g)} + e^{-}$$

Generally, any subsequent ionization energies (2nd, 3rd, etc.) follow the same periodic trend as the first ionization energy.

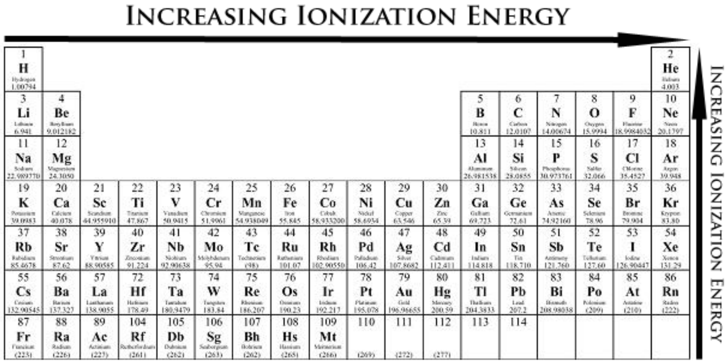


Figure 6.5.4: Periodic Table Showing Ionization Energy Trend

Ionization energies decrease as atomic radii increase. This observation is affected by n (the principal quantum number) and Z_{eff} (based on the atomic number and shows how many protons are seen in the atom) on the ionization energy (I). The relationship is given by the following equation:

$$I = \frac{R_H Z_{eff}^2}{n^2}$$

- Across a period, Z_{eff} *increases* and n (principal quantum number) *remains the same*, so the ionization energy *increases*.
- Down a group, n *increases* and Z_{eff} *increases slightly;* the ionization energy *decreases*.

Electron Affinity Trends

As the name suggests, electron affinity is the ability of an atom to accept an electron. Unlike electronegativity, electron affinity is a quantitative measurement of the energy change that occurs when an electron is added to a neutral gas atom. The more negative the electron affinity value, the higher an atom's affinity for electrons.

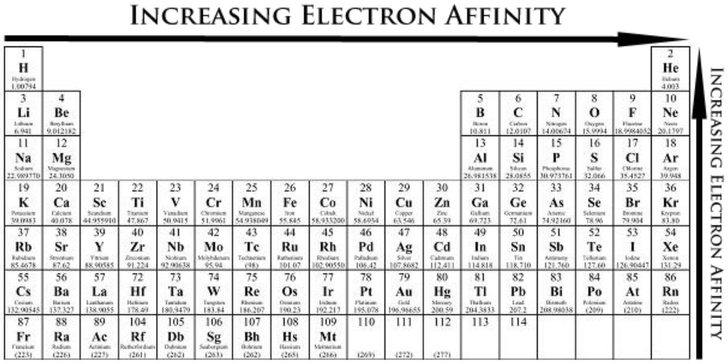


Figure 6.5.5: Periodic Table showing Electron Affinity Trend

Electron affinity generally decreases down a group of elements because each atom is larger than the atom above it (this is the atomic radius trend, discussed below). This means that an added electron is further away from the atom's nucleus compared with its position in the smaller atom. With a larger distance between the negatively-charged electron and the positively-charged nucleus, the force of attraction is relatively weaker. Therefore, electron affinity decreases. Moving from left to right across a period, atoms become smaller as the forces of attraction become stronger. This causes the electron to move closer to the nucleus, thus increasing the electron affinity from left to right across a period.

- Electron affinity increases from left to right within a period. This is caused by the decrease in atomic radius.
- Electron affinity decreases from top to bottom within a group. This is caused by the increase in atomic radius.

Atomic Radius Trends

The atomic radius is one-half the distance between the nuclei of two atoms (just like a radius is half the diameter of a circle). However, this idea is complicated by the fact that not all atoms are normally bound together in the same way. Some are bound by covalent bonds in molecules, some are attracted to each other in ionic crystals, and others are held in metallic crystals. Nevertheless, it is possible for a vast majority of elements to form covalent molecules in which two like atoms are held together by a single covalent bond. The covalent radii of these molecules are often referred to as atomic radii. This distance is measured in picometers. Atomic radius patterns are observed throughout the periodic table.

Atomic size gradually decreases from left to right across a period of elements. This is because, within a period or family of elements, all electrons are added to the same shell. However, at the same time, protons are being added to the nucleus, making it more positively charged. The effect of increasing proton number is greater than that of the increasing electron number; therefore, there is a greater nuclear attraction. This means that the nucleus attracts the electrons more strongly, pulling the atom's shell closer to the nucleus. The valence electrons are held closer towards the nucleus of the atom. As a result, the atomic radius decreases.

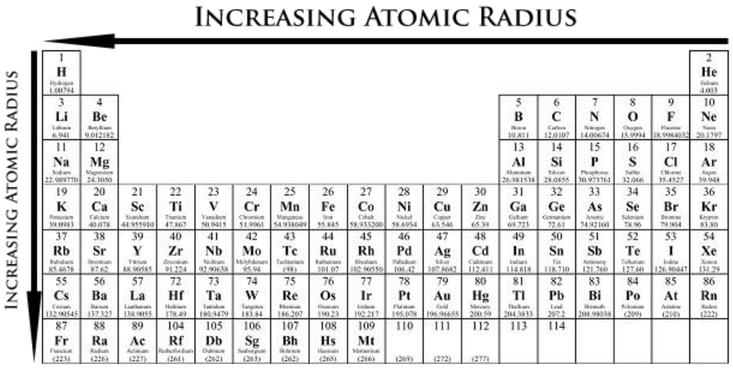


Figure 6.5.6: Periodic Table showing Atomic Radius Trend

Down a group, atomic radius increases. The valence electrons occupy higher levels due to the increasing quantum number (n). As a result, the valence electrons are further away from the nucleus as ‘n’ increases. Electron shielding prevents these outer electrons from being attracted to the nucleus; thus, they are loosely held, and the resulting atomic radius is large.

> - Atomic radius **decreases** from left to right within a period. This is caused by the **increase** in the number of protons and electrons across a period. One proton has a greater effect than one electron; thus, electrons are pulled towards the nucleus, resulting in a smaller radius.
> - Atomic radius **increases** from top to bottom within a group. This is caused by electron shielding.

Melting Point Trends

The melting points is the amount of energy required to break a bond(s) to change the solid phase of a substance to a liquid. Generally, the stronger the bond between the atoms of an element, the more energy required to break that bond. Because temperature is directly proportional to energy, a high bond dissociation energy correlates to a high temperature. Melting points are varied and do not generally form a distinguishable trend across the periodic table. However, certain conclusions can be drawn from Figure 6.5.7.

- Metals generally possess a *high melting point*.
- Most non-metals possess *low melting points*.
- The non-metal **carbon** possesses *the highest melting point of all the elements*. The semi-metal boron also possesses a high melting point.

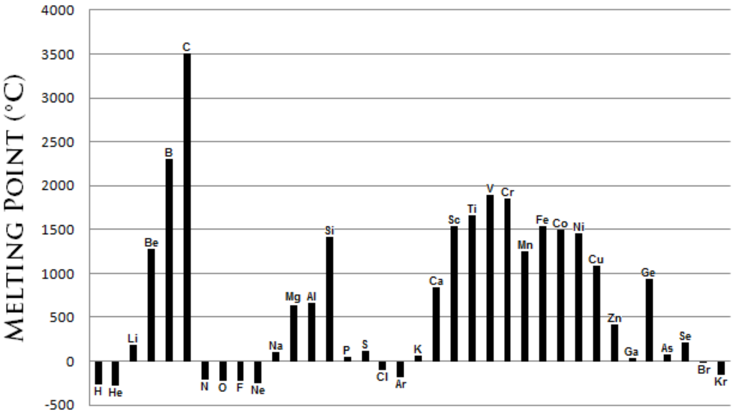


Figure 6.5.7: Chart of Melting Points of Various Elements

Metallic Character Trends

The metallic character of an element can be defined as how readily an atom can lose an electron. From right to left across a period, metallic character increases because the attraction between valence electron and the nucleus is weaker, enabling an easier loss of electrons. Metallic character increases as you move down a group because the atomic size is increasing. When the atomic size increases, the outer shells are farther away. The principal quantum number increases and average electron density moves farther from nucleus. The electrons of the valence shell have less attraction to the nucleus and, as a result, can lose electrons more readily. This causes an increase in metallic character.

> - Metallic characteristics decrease from left to right across a period. This is caused by the decrease in radius (caused by Z_{eff}, as stated above) of the atom that allows the outer electrons to ionize more readily.
> - Metallic characteristics increase down a group. Electron shielding causes the atomic radius to increase thus the outer electrons ionizes more readily than electrons in smaller atoms.
> - Metallic character relates to the ability to lose electrons, and nonmetallic character relates to the ability to gain electrons.

Another easier way to remember the trend of metallic character is that moving left and down toward the bottom-left corner of the periodic table, metallic character increases toward Groups 1 and 2, or the alkali and alkaline earth **metal groups**. Likewise, moving up and to the right to the upper-right corner of the periodic table, metallic character decreases because you are passing by to the right side of the staircase, which indicate the **nonmetals**. These include the Group 8, the **noble gases**, and other common gases such as oxygen and nitrogen.

- In other words:
- Move left across period and down the group: increase metallic character (heading towards alkali and alkaline metals)
- Move right across period and up the group: decrease metallic character (heading towards nonmetals like noble gases)

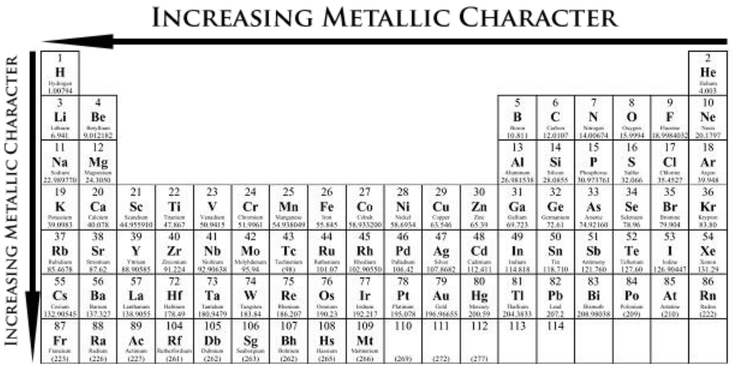


Figure 6.5.8: Periodic Table of Metallic Character Trend

Problems

The following series of problems reviews general understanding of the aforementioned material.

1. Based on the periodic trends for ionization energy, which element has the highest ionization energy?

a. Fluorine (F)
b. Nitrogen (N)
c. Helium (He)

2.) Nitrogen has a larger atomic radius than oxygen.

1. A.) True
2. B.) False

3.) Which has more metallic character, Lead (Pb) or Tin (Sn)?

4.) Which element has a higher melting point: chlorine (Cl) or bromine (Br)?

5.) Which element is more electronegative, sulfur (S) or selenium (Se)?

6) Why is the electronegativity value of most noble gases zero?

7) Arrange these atoms in order of decreasing effective nuclear charge by the valence electrons: Si, Al, Mg, S

8) Rewrite the following list in order of decreasing electron affinity: fluorine (F), phosphorous (P), sulfur (S), boron (B).

9) An atom with an atomic radius smaller than that of sulfur (S) is __________.

1. A.) Oxygen (O)
2. B.) Chlorine (Cl)
3. C.) Calcium (Ca)
4. D.) Lithium (Li)
5. E.) None of the above

10) A nonmetal has a smaller ionic radius compared with a metal of the same period.

1. A.) True B.) False

Solutions

1. Answer: C.) Helium (He)

Explanation: Helium (He) has the highest ionization energy because, like other noble gases, helium's valence shell is full. Therefore, helium is stable and does not readily lose or gain electrons.

2. Answer: A.) True

Explanation: Atomic radius increases from right to left on the periodic table. Therefore, nitrogen is larger than oxygen.

3. Answer: Lead (Pb)

Explanation: Lead and tin share the same column. Metallic character increases down a column. Lead is under tin, so lead has more metallic character.

4. Answer: Bromine (Br)

Explanation: In non-metals, melting point increases down a column. Because chlorine and bromine share the same column, bromine possesses the higher melting point.

5. Answer: Sulfur (S)

Explanation: Note that sulfur and selenium share the same column. Electronegativity increases up a column. This indicates that sulfur is more electronegative than selenium.

6. Answer: Most noble gases have full valence shells.

Explanation: Because of their full valence electron shell, the noble gases are extremely stable and do not readily lose or gain electrons.

7. Answer: S > Si > Al > Mg.

Explanation: The electrons above a closed shell are shielded by the closed shell. S has 6 electrons above a closed shell, so each one feels the pull of 6 protons in the nucleus.

8. Answer: Fluorine (F)>Sulfur (S)>Phosphorous (P)>Boron (B)

Explanation: Electron affinity generally increases from left to right and from bottom to top.

9. Answer: C.) Oxygen (O)

Explanation: Periodic trends indicate that atomic radius increases up a group and from left to right across a period. Therefore, oxygen has a smaller atomic radius sulfur.

10. Answer: B.) False

Explanation: The reasoning behind this lies in the fact that a metal usually loses an electron in becoming an ion while a non-metal gains an electron. This results in a smaller ionic radius for the metal ion and a larger ionic radius for the non-metal ion.

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6.5.1: Periodic Trends in Ions

Learning Objectives

- To correlate ionization energies with the chemistry of the elements

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

Ionization Energies

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

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad \text{energy required=I} \tag{6.5.1.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation $6.5.1.1$ Larger values of I mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol$$

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

$$\mathrm{E(g) \rightarrow E^+(g) + e^-} \qquad I_1 = \text{1st ionization energy} \tag{6.5.1.2}$$

$$\mathrm{E^+(g) \rightarrow E^{2+}(g) + e^-} \qquad I_2 = \text{2nd ionization energy} \tag{6.5.1.3}$$

$$\mathrm{E^{2+}(g) \rightarrow E^{3+}(g) + e^-} \qquad I_3 = \text{3rd ionization energy} \tag{6.5.1.4}$$

Values for the ionization energies of Li and Be listed in Table $6.5.1.1$ show that successive ionization energies for an element increase as they go; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

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

Table 6.5.1.1: Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Reaction	Electronic Transition	*I*	Reaction	Electronic Transition	*I*
$\mathrm{Li(g) \rightarrow Li^+(g) + e^-}$	$1s^22s^1 \rightarrow 1s^2$	I_1 = 520.2	$\mathrm{Be(g) \rightarrow Be^+(g) + e^-}$	$1s^22s^2 \rightarrow 1s^22s^1$	I_1 = 899.5
$\mathrm{Li^+(g) \rightarrow Li^{2+}(g) + e^-}$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$\mathrm{Be^+(g) \rightarrow Be^{2+}(g) + e^-}$	$1s^22s^1 \rightarrow 1s^2$	I_2 = 1757.1
$\mathrm{Li^{2+}(g) \rightarrow Li^{3+}(g) + e^-}$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$\mathrm{Be^{2+}(g) \rightarrow Be^{3+}(g) + e^-}$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$\mathrm{Be^{3+}(g) \rightarrow Be^{4+}(g) + e^-}$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The increase in successive ionization energies, however, is not linear, but increases drastically when removing electrons in lower n orbitals closer to the nucleus. The most important consequence of the values listed in Table $6.5.1.1$ is that the chemistry of Li is dominated by the $\mathrm{Li^+}$ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li:

$$\mathrm{Li^+(g) \rightarrow Li^{2+}(g) + e^-} \tag{6.5.1.5}$$

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

$$\mathrm{Be^{2+}(g) \rightarrow Be^{3+}(g) + e^-} \tag{6.5.1.6}$$

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

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

Ionization Energy: Ionization Energy, YouTube(opens in new window) [youtu.be] (opens in new window)

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

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of Li and Be (Table 6.5.1.2): successive ionization energies increase steadily as electrons are removed from the valence orbitals (3*s* or 3*p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table 6.5.1.2 Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from Al, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.

Table 6.5.1.2: Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table.Source: Data from CRC Handbook of Chemistry and Physics (2004).

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	577.4.4	1816.7	2744.8	**11,577.4.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1907.4.4	2914.1	4963.6	6274.0	**21,267.4.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,107.4.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2

*Inner-shell electron

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3
*Inner-shell electron							

✓ Example 6.5.1.1: Highest Fourth Ionization Energy

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

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

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

Solution:

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

- B: $[He]2s^22p^1$
- C: $[He]2s^22p^2$
- N: $[He]2s^22p^3$

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

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

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

? Exercise 6.5.1.1: Lowest Second Ionization Energy

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

Answer

Sr

The first column of data in Table 6.5.1.2 shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects represent two sides of the same coin: stronger electrostatic interactions between the electrons and the nucleus further increase the energy required to remove the electrons.

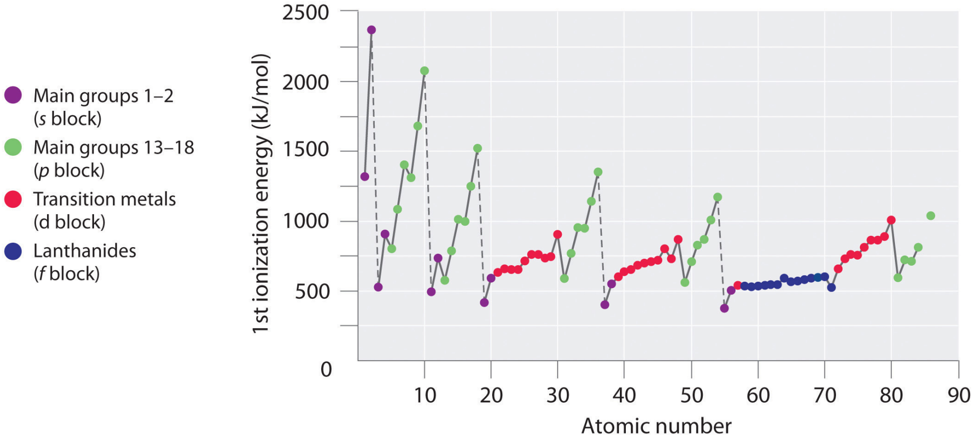


Figure 6.5.1.1: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

the main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

However, the first ionization energy decreases at Al ([Ne]$3s^23p^1$) and at S ([Ne]$3s^23p^4$). The electron configurations of these "exceptions" provide the answer why. The electrons in aluminum’s filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the *s* electrons penetrate closer to the nucleus than the *p* electron does and the *p* electron is more easily removed. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

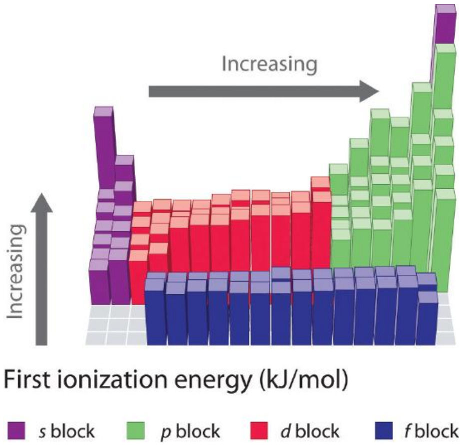


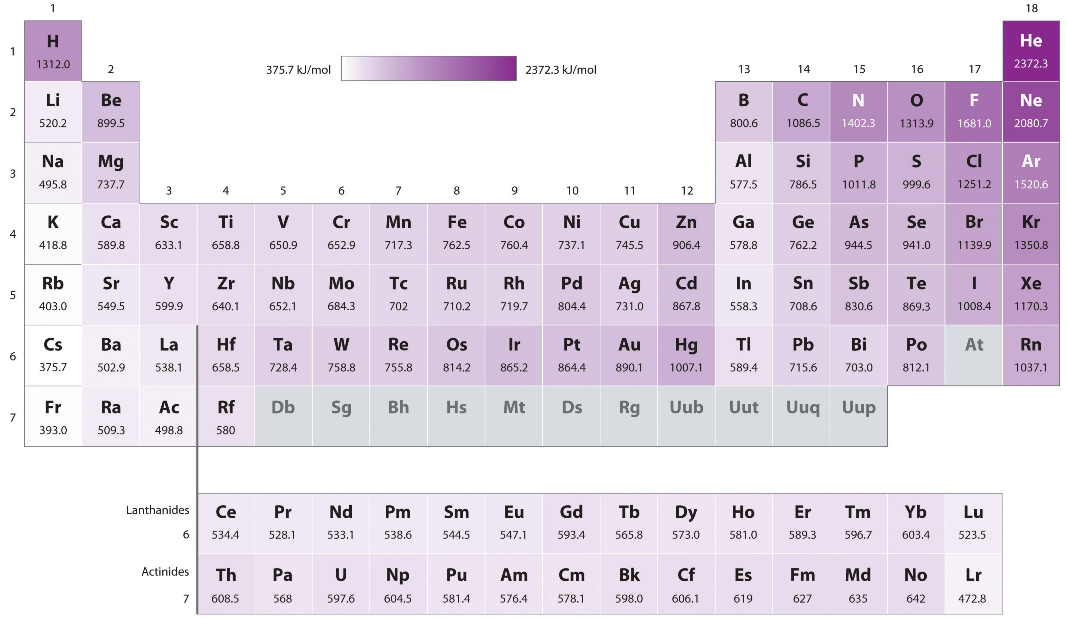
Figure 6.5.1.2: First Ionization Energies of the *s*-, *p*-, *d*-, and *f*-Block Elements

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. First ionization energy increase from left to right and from bottom to top.

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 6.5.1.1and are presented numerically and graphically in Figure 6.5.1.2 These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the *s* and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12).
2. First ionization energies generally decrease down a column. Although the principal quantum number *n* increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius typically corresponds to a lower ionization energy*.

3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1312.0																	He 2372.3
2	Li 520.2	Be 899.5											B 800.6	C 1086.5	N 1402.3	O 1313.9	F 1681.0	Ne 2080.7
3	Na 495.8	Mg 737.7											Al 577.5	Si 786.5	P 1011.8	S 999.6	Cl 1251.2	Ar 1520.6
4	K 418.8	Ca 589.8	Sc 633.1	Ti 658.8	V 650.9	Cr 652.9	Mn 717.3	Fe 762.5	Co 760.4	Ni 737.1	Cu 745.5	Zn 906.4	Ga 578.8	Ge 762.2	As 944.5	Se 941.0	Br 1139.9	Kr 1350.8
5	Rb 403.0	Sr 549.5	Y 599.9	Zr 640.1	Nb 652.1	Mo 684.3	Tc 702	Ru 710.2	Rh 719.7	Pd 804.4	Ag 731.0	Cd 867.8	In 558.3	Sn 708.6	Sb 830.6	Te 869.3	I 1008.4	Xe 1170.3
6	Cs 375.7	Ba 502.9	La 538.1	Hf 658.5	Ta 728.4	W 758.8	Re 755.8	Os 814.2	Ir 865.2	Pt 864.4	Au 890.1	Hg 1007.1	Tl 589.4	Pb 715.6	Bi 703.0	Po 812.1	At	Rn 1037.1
7	Fr 393.0	Ra 509.3	Ac 498.8	Rf 580	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			

Lanthanides 6	Ce 534.4	Pr 528.1	Nd 533.1	Pm 538.6	Sm 544.5	Eu 547.1	Gd 593.4	Tb 565.8	Dy 573.0	Ho 581.0	Er 589.3	Tm 596.7	Yb 603.4	Lu 523.5
Actinides 7	Th 608.5	Pa 568	U 597.6	Np 604.5	Pu 581.4	Am 576.4	Cm 578.1	Bk 598.0	Cf 606.1	Es 619	Fm 627	Md 635	No 642	Lr 472.8

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

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

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

Ionization Energies of Transition Metals & Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the *s*- and *p*-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the *ns* electrons before the $(n-1)d$ or $(n-2)f$ electrons, respectively. This means that transition metal cations have $(n-1)d^n$ valence electron configurations, and lanthanide cations have $(n-2)f^n$ valence electron configurations. Because the $(n-1)d$ and $(n-2)f$ shells are closer to the nucleus than the *ns* shell, the $(n-1)d$ and $(n-2)f$ electrons screen the *ns* electrons quite effectively, reducing the effective nuclear charge felt by the *ns* electrons. As *Z* increases, the increasing positive charge is largely canceled by the electrons added to the $(n-1)d$ or $(n-2)f$ orbitals.

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

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

✓ Example 6.5.1.2: Lowest First Ionization Energy

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

Given: six elements

Asked for: element with lowest first ionization energy

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

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

? Exercise 6.5.1.2: Highest First Ionization Energy

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

Answer

As

Summary

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

6.5.2: Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to cesium and francium which are the least electronegative at 0.7.

What if two atoms of equal electronegativity bond together?

Consider a bond between two atoms, A and B. If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found on average half way between the two atoms:

To get a bond like this, A and B would usually have to be the same atom. You will find this sort of bond in, for example, H_2 or Cl_2 molecules. **Note:** It's important to realize that this is an average picture. The electrons are actually in a molecular orbital, and are moving around all the time within that orbital. This sort of bond could be thought of as being a "pure" covalent bond - where the electrons are shared evenly between the two atoms.

What if B is slightly more electronegative than A?

B will attract the electron pair rather more than A does.

That means that the B end of the bond has more than its fair share of electron density and so becomes slightly negative. At the same time, the A end (rather short of electrons) becomes slightly positive. In the diagram, "δ" (read as "delta") means "slightly" - so $\delta+$ means "slightly positive".

A polar bond is a covalent bond in which there is a separation of charge between one end and the other - in other words in which one end is slightly positive and the other slightly negative. Examples include most covalent bonds. The hydrogen-chlorine bond in HCl or the hydrogen-oxygen bonds in water are typical.

If B is a lot more electronegative than A, then the electron pair is dragged right over to B's end of the bond. To all intents and purposes, A has lost control of its electron, and B has complete control over both electrons. Ions have been formed. The bond is then an ionic bond rather than a covalent bond.

A "spectrum" of bonds

The implication of all this is that there is no clear-cut division between covalent and ionic bonds. In a pure covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end. How far does this dragging have to go before the bond counts as ionic? There is no real answer to that. Sodium chloride is typically considered an ionic solid, but even here the sodium has not completely lost control of its electron. Because of the properties of sodium chloride, however, we tend to count it as if it were purely ionic. Lithium iodide, on the other hand, would be described as being "ionic with some covalent character". In this case, the pair of electrons has not moved entirely over to the iodine end of the bond. Lithium iodide, for example, dissolves in organic solvents like ethanol - not something which ionic substances normally do.

Summary

- No electronegativity difference between two atoms leads to a pure non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond.
- A large electronegativity difference leads to an ionic bond.

Example 1: Polar Bonds vs. Polar Molecules

In a simple diatomic molecule like HCl, if the bond is polar, then the whole molecule is polar. What about more complicated molecules?

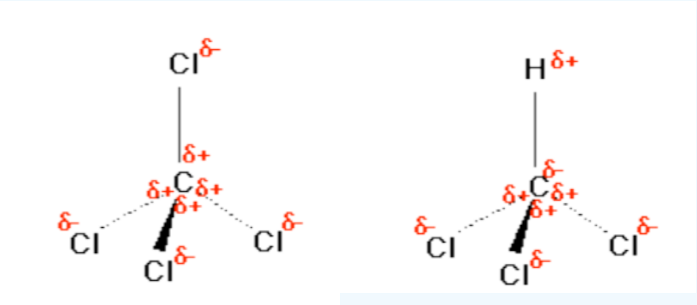


Figure 6.5.2.1: (left) CCl_4 (right) $CHCl_3$

Consider CCl_4, (left panel in figure above), which as a molecule is not polar - in the sense that it doesn't have an end (or a side) which is slightly negative and one which is slightly positive. The whole of the outside of the molecule is somewhat negative, but there is no overall separation of charge from top to bottom, or from left to right.

In contrast, $CHCl_3$ is a polar molecule (right panel in figure above). The hydrogen at the top of the molecule is less electronegative than carbon and so is slightly positive. This means that the molecule now has a slightly positive "top" and a slightly negative "bottom", and so is overall a polar molecule.

A polar molecule will need to be "lop-sided" in some way.

Patterns of electronegativity in the Periodic Table

The distance of the electrons from the nucleus remains relatively constant in a periodic table row, but not in a periodic table column. The force between two charges is given by Coulomb’s law.

$$F = k\frac{Q_1Q_2}{r^2} \tag{6.5.2.1}$$

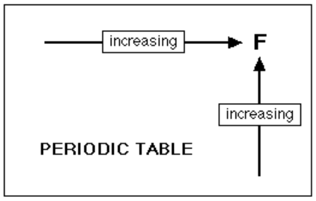
In this expression, Q represents a charge, k represents a constant and r is the distance between the charges. When r = 2, then $r^2 = 4$. When r = 3, then $r^2 = 9$. When r = 4, then $r^2 = 16$. It is readily seen from these numbers that, as the distance between the charges increases, the force decreases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

The result of this change is that electronegativity increases from bottom to top in a column in the periodic table even though there are more protons in the elements at the bottom of the column. Elements at the top of a column have greater electronegativities than elements at the bottom of a given column.

The overall trend for electronegativity in the periodic table is diagonal from the lower left corner to the upper right corner. Since the electronegativity of some of the important elements cannot be determined by these trends (they lie in the wrong diagonal), we have to memorize the following order of electronegativity for some of these common elements.

F > O > Cl > N > Br > I > S > C > H > metals

The most electronegative element is fluorine. If you remember that fact, everything becomes easy, because electronegativity must always increase towards fluorine in the Periodic Table.

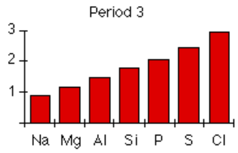


Note

This simplification ignores the noble gases. Historically this is because they were believed not to form bonds - and if they do not form bonds, they cannot have an electronegativity value. Even now that we know that some of them do form bonds, data sources still do not quote electronegativity values for them.

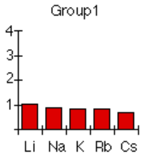
Trends in electronegativity across a period

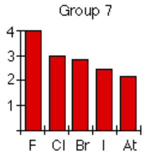
The positively charged protons in the nucleus attract the negatively charged electrons. As the number of protons in the nucleus increases, the electronegativity or attraction will increase. Therefore electronegativity **increases** from **left to right** in a row in the periodic table. This effect only holds true for a row in the periodic table because the attraction between charges falls off rapidly with distance. The chart shows electronegativities from sodium to chlorine (ignoring argon since it does not does not form bonds).



Trends in electronegativity down a group

As you go down a group, electronegativity decreases. (If it increases up to fluorine, it must decrease as you go down.) The chart shows the patterns of electronegativity in Groups 1 and 7.





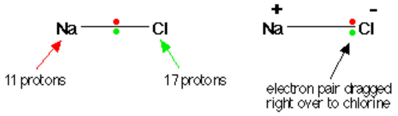
Explaining the patterns in electronegativity

The attraction that a bonding pair of electrons feels for a particular nucleus depends on:

- the number of protons in the nucleus;
- the distance from the nucleus;
- the amount of screening by inner electrons.

Why does electronegativity increase across a period?

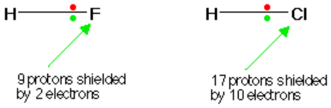
Consider sodium at the beginning of period 3 and chlorine at the end (ignoring the noble gas, argon). Think of sodium chloride as if it were covalently bonded.



Both sodium and chlorine have their bonding electrons in the 3-level. The electron pair is screened from both nuclei by the 1s, 2s and 2p electrons, but the chlorine nucleus has 6 more protons in it. It is no wonder the electron pair gets dragged so far towards the chlorine that ions are formed. Electronegativity increases across a period because the number of charges on the nucleus increases. That attracts the bonding pair of electrons more strongly.

Why does electronegativity fall as you go down a group?

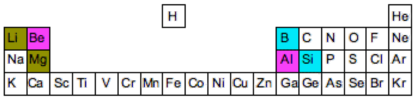
As you go **down** a group, electronegativity **decreases** because the bonding pair of electrons is increasingly distant from the attraction of the nucleus. Consider the hydrogen fluoride and hydrogen chloride molecules:



The bonding pair is shielded from the fluorine's nucleus only by the $1s^2$ electrons. In the chlorine case it is shielded by all the $1s^22s^22p^6$ electrons. In each case there is a net pull from the center of the fluorine or chlorine of +7. But fluorine has the bonding pair in the 2-level rather than the 3-level as it is in chlorine. If it is closer to the nucleus, the attraction is greater.

Diagonal relationships in the Periodic Table

At the beginning of periods 2 and 3 of the Periodic Table, there are several cases where an element at the top of one group has some similarities with an element in the next group. Three examples are shown in the diagram below. Notice that the similarities occur in elements which are diagonal to each other - not side-by-side.



For example, boron is a non-metal with some properties rather like silicon. Unlike the rest of Group 2, beryllium has some properties resembling aluminum. And lithium has some properties which differ from the other elements in Group 1, and in some ways resembles magnesium. There is said to be a diagonal relationship between these elements. There are several reasons for this, but each depends on the way atomic properties like electronegativity vary around the Periodic Table. So we will have a quick look at this with regard to electronegativity - which is probably the simplest to explain.

Explaining the diagonal relationship with regard to electronegativity

Electronegativity increases across the Periodic Table. So, for example, the electronegativities of beryllium and boron are:

Be	1.5
B	2.0

Electronegativity falls as you go down the Periodic Table. So, for example, the electronegativities of boron and aluminum are:

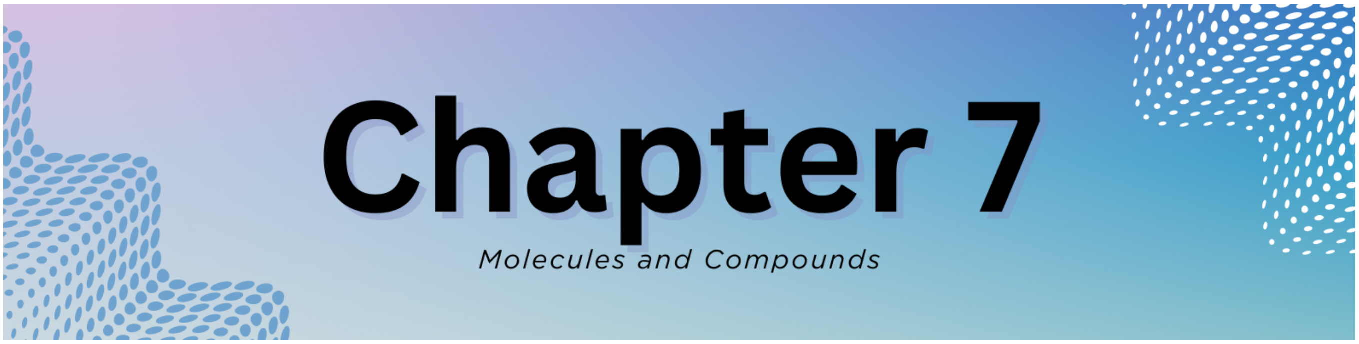
B	2.0
Al	1.5

So, comparing Be and Al, you find the values are (by chance) exactly the same. The increase from Group 2 to Group 3 is offset by the fall as you go down Group 3 from boron to aluminum. Something similar happens from lithium (1.0) to magnesium (1.2), and from boron (2.0) to silicon (1.8). In these cases, the electronegativities are not exactly the same, but are very close.

Similar electronegativities between the members of these diagonal pairs means that they are likely to form similar types of bonds, and that will affect their chemistry. You may well come across examples of this later on in your course.

CHAPTER OVERVIEW

7: Molecules and Compounds



Swimming pools have long been a popular means of recreation, exercise, and physical therapy. Since it is impractical to refill large pools with fresh water frequently, pool water is regularly treated with chemicals to prevent the growth of harmful bacteria and algae. Proper pool maintenance requires regular additions of various chemical compounds in carefully measured amounts. For example, the relative amount of calcium ion, Ca^{2+}, in the water should be maintained within certain limits to prevent eye irritation and avoid damage to the pool bed and plumbing. To maintain proper calcium levels, calcium cations are added to the water in the form of an ionic compound that also contains anions; thus, it is necessary to know both the relative amount of Ca^{2+} in the compound and the volume of water in the pool in order to achieve the proper calcium level.

Qualitative descriptions of substances (such as water), the types of bonds present in the substances, and quantitative aspects of the *composition* of matter are the subject of this chapter.

Figure 1. The water in a swimming pool is a complex mixture of substances whose relative amounts must be carefully maintained to ensure the health and comfort of people using the pool. (credit: modification of work by Vic Brincat)

Chapter Sections

7.1: Chemical Formulas - Atomic Ratios

Chemistry is the experimental and theoretical study of materials on their properties at the macroscopic and microscopic levels.

A chemical formula is a format used to express the structure of atoms. The formula tells which elements and how many of each element are present in a compound. Formulas are written using the elemental symbol of each atom and a subscript to denote the number of elements.

Molecular Formula

The molecular formula is based on the actual makeup of the compound. Although the molecular formula can sometimes be the same as the empirical formula, molecular compounds tend to be more helpful. However, they do not describe how the atoms are put together.

Ex. Molecular Formula for Ethanol: C_2H_6O.

It is important to note that a subscript following a symbol and a number in front of a symbol does not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure 7.1.1).

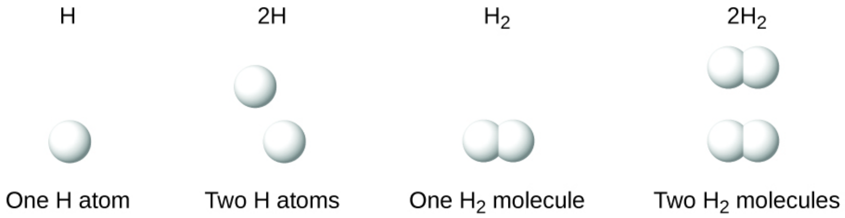


Figure 7.1.1: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

Empirical Formula

An empirical formula shows the most basic form of a compound. Empirical formulas show the number of atoms of each element in a compound in the most simplified state using whole numbers. While empirical formulas cannot determine the structure, shape, or properties of the compound, it usually is one of the first experiments to know what atoms and in which relationship are present in an unknown sample.

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

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

Binary compounds

Binary compounds are formed between two elements, either a metal paired with a nonmetal or two nonmetals paired together.

When two nonmetals are paired together, the compound is a molecular compound always represented using the Molecular Formula. When writing out the formula, the element with a more metallic character (with a positive oxidation state) is placed first.

Ex. Molecular Compound: N_2O_4 (Dinitrogen Tetroxide)

When a metal is paired with a nonmetal, they form an ionic compound, representing it using Empirical Formulas. In ionic compounds, each atom is in the form of an ion; one atom is a negatively charged ion (anion), and the other is a positively charged ion (cation). The net charge of the compound must be neutral using the minimal amount of each atom.

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

✓ Example 7.1.1: Empirical and Molecular Formulas

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

Solution

The molecular formula is $C_6H_{12}O_6$ because one molecule contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH_2O.

? Exercise 7.1.1

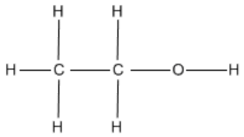
A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

Answer

Molecular formula, $C_8H_{16}O_4$; empirical formula, C_2H_4O

Structural Formula

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

Ex. Structural Formula for Ethanol: 

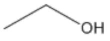
Condensed Structural Formula

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

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

Line-Angle Formula

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

Ex. Line-Angle Formula for Ethanol: 

Ball-and-stick model

A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.

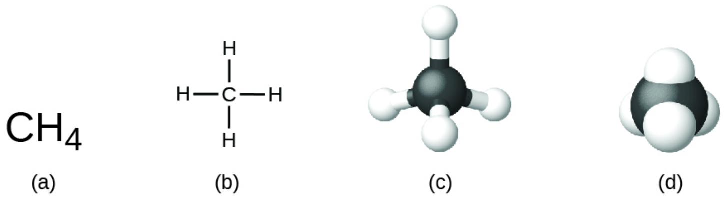
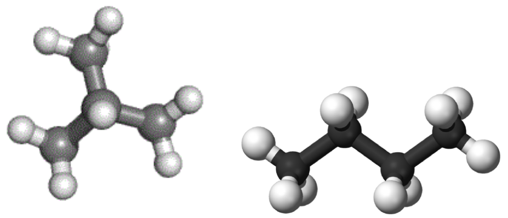


Figure 7.1.2: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Molecular Geometry and Structural Formula

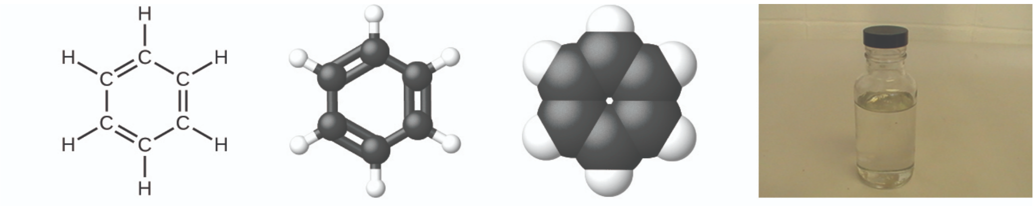
Understanding how atoms in a molecule are arranged and how they are bonded together is very important in giving the molecule its identity. Isomers are compounds in which two molecules can have the same number of atoms, and thus the same molecular formula, but can have completely different physical and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



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

Summary

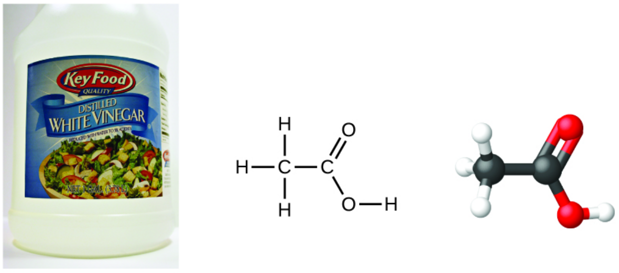
As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from the experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6 (Figure 7.1.3).



(a) (b) (c) (d)

Figure 7.1.3: Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

If we know a compound's molecular formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is $C_2H_4O_2$. This formula indicates that a molecule of acetic acid (Figure 7.1.4) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O. Note that a molecular formula is always a whole-number multiple of an empirical formula.



(a) (b) (c)

Figure 7.1.4: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

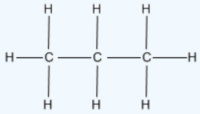
Exercise 7.1.1

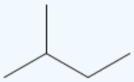
1. Which of the following formulas can not be considered an Empirical Formula?
   a. HClO
   b. C_5H_{10}
   c. CO_2
2. Write the empirical formula for the following compounds
   a. $C_{12}H_{10}O_6$
   b. $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
   c. H_3O^+

Answer

1. b. C_5H_{10}
2. a. $C_6H_5O_3$, b. C_7H_{16}, c. H_3O^+

Exercise 7.1.1

1. What is the Classification of the following formula? 

2. What is the name of the representation and the chemical formula of the following molecule? 

Answer

1. Structural Formula
2. Line-Angle, C_5H_{12}

Contributors and Attributions

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7.2: Types of Compounds - Differences in Atomic Connections

Learning Objectives

- To quantitatively describe the energetic factors involved in the formation of an ionic bond.

Chemical bonds form when electrons can be simultaneously close to two or more nuclei, but beyond this, there is no simple, easily understood theory that would not only explain why atoms bind together to form molecules, but would also predict the three-dimensional structures of the resulting compounds as well as the energies and other properties of the bonds themselves. Unfortunately, no one theory exists that accomplishes these goals in a satisfactory way for all of the many categories of compounds that are known. Moreover, it seems likely that if such a theory does ever come into being, it will be far from simple.

When we are faced with a scientific problem of this complexity, experience has shown that it is often more useful to concentrate instead on developing **models**. A scientific model is something like a theory in that it should be able to explain observed phenomena and to make useful predictions. But whereas a theory can be discredited by a single contradictory case, a model can be useful even if it does not encompass all instances of the phenomena it attempts to explain. We do not even require that a model be a credible representation of reality; all we ask is that be able to explain the behavior of those cases to which it is applicable in terms that are consistent with the model itself. An example of a model that you may already know about is the kinetic molecular theory of gases. Despite its name, this is really a model (at least at the level that beginning students use it) because it does not even try to explain the observed behavior of real gases. Nevertheless, it serves as a tool for developing our understanding of gases, and as a starting point for more elaborate treatments.Given the extraordinary variety of ways in which atoms combine into aggregates, it should come as no surprise that a number of useful bonding models have been developed. Most of them apply only to certain classes of compounds, or attempt to explain only a restricted range of phenomena. In this section we will provide brief descriptions of some of the bonding models; the more important of these will be treated in much more detail in later parts of this chapter.

Ionic Bonding

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge. Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged. Ionic bonding is the attraction between positively- and negatively-charged **ions**. These oppositely charged ions attract each other to form ionic networks (or lattices). Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

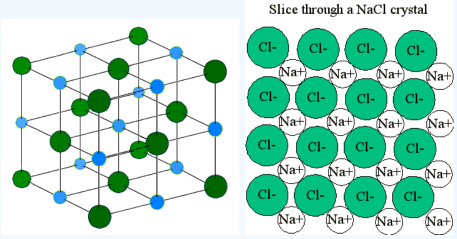
Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding.

Example 7.2.1: Sodium Chloride

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is **NaCl**.

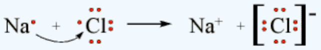
$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)} \tag{7.2.1}$$

These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):



NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattes. Images used with permission from Wikipedia and Mike Blaber.

The chlorine has a high affinity for electrons, and the sodium has a low ionization potential. Thus the chlorine gains an electron from the sodium atom. This can be represented using ***electron-dot symbols*** (here we will consider one chlorine atom, rather than Cl_2):



The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^{+} metal ion and the Cl^{-} chloride ion. Each ion now has an **octet** of electrons in its valence shell:

- $Na^{+:}$ $2s^{2}2p^{6}$
- Cl^{-}: $3s^{2}3p^{6}$

Covalent Bonding

Formation of an ionic bond by complete transfer of an electron from one atom to another is possible only for a fairly restricted set of elements. Covalent bonding, in which neither atom loses complete control over its valence electrons, is much more common. In a **covalent bond** the electrons occupy a region of space *between* the two nuclei and are said to be *shared* by them. This model originated with the theory developed by G.N. Lewis in 1916, and it remains the most widely-used model of chemical bonding. The essential element s of this model can best be understood by examining the simplest possible molecule. This is the **hydrogen molecule ion** H_2^{+}, which consists of two nuclei and one electron. First, however, think what would happen if we tried to make the even simpler molecule H_2^{2+}. Since this would consist only of two protons whose electrostatic charges would repel each other at all distances, it is clear that such a molecule cannot exist; something more than two nuclei are required for bonding to occur.

In the hydrogen molecule ion H_2^{+} we have a third particle, an electron. The effect of this electron will depend on its location with respect to the two nuclei. If the electron is in the space between the two nuclei, it will attract both protons toward itself, and thus toward each other. If the total attraction energy exceeds the internuclear repulsion, there will be a net bonding effect and the molecule will be stable. If, on the other hand, the electron is off to one side, it will attract both nuclei, but it will attract the closer one much more strongly, owing to the inverse-square nature of Coulomb's law. As a consequence, the electron will now help the electrostatic repulsion to push the two nuclei apart.

We see, then, that the electron is an essential component of a chemical bond, but that it must be in the right place: between the two nuclei. Coulomb's law can be used to calculate the forces experienced by the two nuclei for various positions of the electron. This allows us to define two regions of space about the nuclei, as shown in the figure. One region, the binding region, depicts locations at which the electron exerts a net binding effect on the new nuclei. Outside of this, in the antibinding region, the electron will actually work against binding.Summary

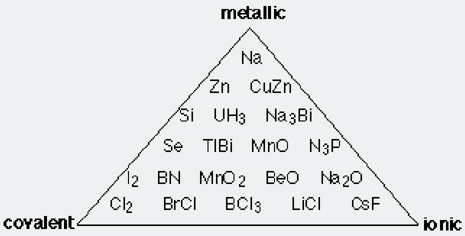
The amount of energy needed to separate a gaseous ion pair is its bond energy. The formation of ionic compounds are usually ***extremely exothermic***. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

Metallic Bonding

Metals have several qualities that are unique, such as the ability to conduct electricity, a low ionization energy, and a low electronegativity (so they will give up electrons easily, i.e., they are cations). **Metallic bonding** is sort of like covalent bonding, because it involves sharing electrons. The simplest model of metallic bonding is the "sea of electrons" model, which imagines that the atoms sit in a sea of valence electrons that are delocalized over all the atoms. Because there are not specific bonds between individual atoms, metals are more flexible. The atoms can move around and the electron sea will keep holding them together. Some metals are very hard and have very high melting points, while others are soft and have low melting points. This depends roughly on the number of valence electrons that form the sea.

A False Dichotomy: The Ionic vs. Colvalent

The covalent-ionic continuum described above is certainly an improvement over the old covalent -*versus* - ionic dichotomy that existed only in the textbook and classroom, but it is still only a one-dimensional view of a multidimensional world, and thus a view that hides more than it reveals. The main thing missing is any allowance for the type of bonding that occurs between more pairs of elements than any other: metallic bonding. Intermetallic compounds are rarely even mentioned in introductory courses, but since most of the elements are metals, there are a lot of them, and many play an important role in metallurgy. In metallic bonding, the valence electrons lose their association with individual atoms; they form what amounts to a mobile "electron fluid" that fills the space between the crystal lattice positions occupied by the atoms, (now essentially positive ions.) The more readily this electron delocalization occurs, the more "metallic" the element.



A triangular diagram whose corners are labeled metallic, covalent, and ionic. The chemical formula of some elements and compounds are listed inside the triangle.

Thus instead of the one-dimension chart shown above, we can construct a triangular diagram whose corners represent the three extremes of "pure" covalent, ionic, and metallic bonding.

Contributors

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7.3: Ionic Compounds - Names and Formulas

Chemistry is the experimental and theoretical study of materials on their properties at the macroscopic and microscopic levels.

A chemical formula is a format used to express the structure of atoms. The formula tells which elements and how many of each element are present in a compound. Formulas are written using the elemental symbol of each atom and a subscript to denote the number of elements.

Molecular Formula

The molecular formula is based on the actual makeup of the compound. Although the molecular formula can sometimes be the same as the empirical formula, molecular compounds tend to be more helpful. However, they do not describe how the atoms are put together.

Ex. Molecular Formula for Ethanol: C_2H_6O.

It is important to note that a subscript following a symbol and a number in front of a symbol does not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure $7.3.1$).

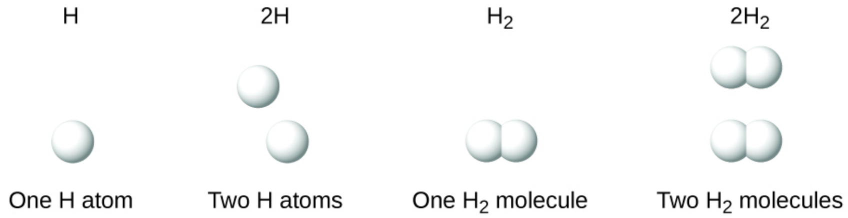


Figure $7.3.1$: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

Empirical Formula

An empirical formula shows the most basic form of a compound. Empirical formulas show the number of atoms of each element in a compound in the most simplified state using whole numbers. While empirical formulas cannot determine the structure, shape, or properties of the compound, it usually is one of the first experiments to know what atoms and in which relationship are present in an unknown sample.

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

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

Binary compounds

Binary compounds are formed between two elements, either a metal paired with a nonmetal or two nonmetals paired together.

When two nonmetals are paired together, the compound is a molecular compound always represented using the Molecular Formula. When writing out the formula, the element with a more metallic character (with a positive oxidation state) is placed first.

Ex. Molecular Compound: N_2O_4 (Dinitrogen Tetroxide)

When a metal is paired with a nonmetal, they form an ionic compound, representing it using Empirical Formulas. In ionic compounds, each atom is in the form of an ion; one atom is a negatively charged ion (anion), and the other is a positively charged ion (cation). The net charge of the compound must be neutral using the minimal amount of each atom.

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

✓ Example $7.3.1$: Empirical and Molecular Formulas

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

Solution

The molecular formula is $C_6H_{12}O_6$ because one molecule contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH_2O.

? Exercise 7.3.1

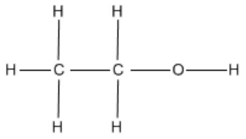
A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

Answer

Molecular formula, $C_8H_{16}O_4$; empirical formula, C_2H_4O

Structural Formula

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

Ex. Structural Formula for Ethanol: 

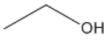
Condensed Structural Formula

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

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

Line-Angle Formula

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

Ex. Line-Angle Formula for Ethanol: 

Ball-and-stick model

A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.

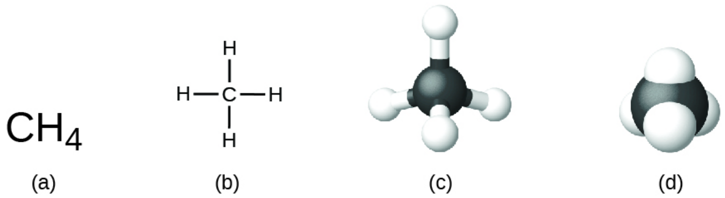
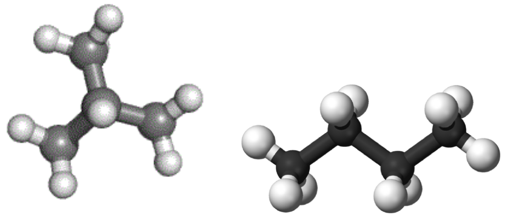


Figure 7.3.2: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Molecular Geometry and Structural Formula

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



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

Summary

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from the experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6 (Figure $7.3.3$).

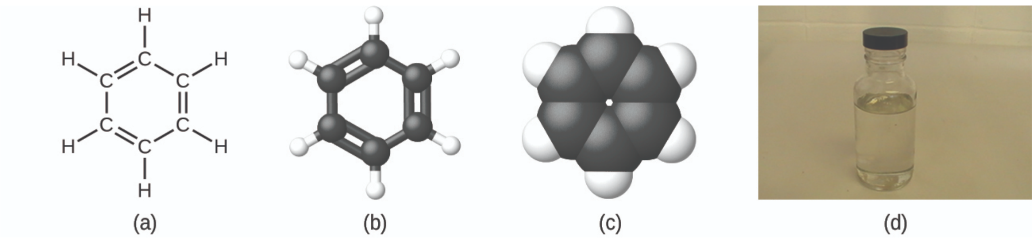


Figure $7.3.3$: Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

If we know a compound's molecular formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is $C_2H_4O_2$. This formula indicates that a molecule of acetic acid (Figure $7.3.4$) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O. Note that a molecular formula is always a whole-number multiple of an empirical formula.

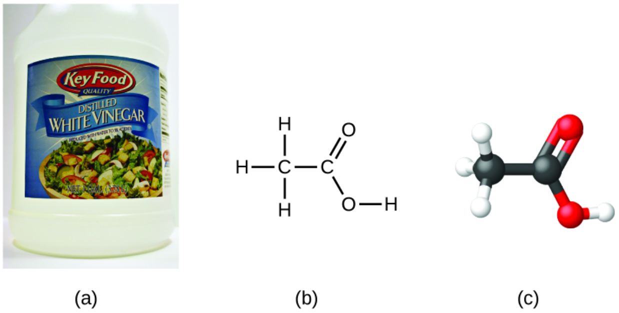


Figure $7.3.4$: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

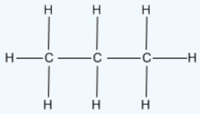
Exercise 7.3.1

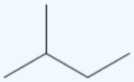
1. Which of the following formulas can not be considered an Empirical Formula?
    a. HClO
    b. C_5H_{10}
    c. CO_2
2. Write the empirical formula for the following compounds
    a. $C_{12}H_{10}O_6$
    b. $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
    c. H_3O^+

Answer

1. b. C_5H_{10}
2. a. $C_6H_5O_3$, b. C_7H_{16}, c. H_3O^+

Exercise 7.3.1

1. What is the Classification of the following formula? 

2. What is the name of the representation and the chemical formula of the following molecule? 

Answer

1. Structural Formula
2. Line-Angle, C_5H_{12}

Contributors and Attributions

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7.4: Covalent Compounds - Names and Formulas

Learning Objectives

- Derive names for common types of inorganic compounds using a systematic approach

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

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table $7.4.3$.

Table $7.4.3$: Nomenclature Prefixes

Number	**Prefix**	**Number**	**Prefix**
1 (sometimes omitted)	mono-	6	hexa-
2	di-	7	hepta-

Number	Prefix		Number	Prefix
3	tri-		8	octa-
4	tetra-		9	nona-
5	penta-		10	deca-

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table $7.4.4$.

Table $7.4.4$: Names of Some Molecular Compounds Composed of Two Elements

Compound	Name		Compound	Name
SO_2	sulfur dioxide		BCl_3	boron trichloride

Compound	Name	Compound	Name
SO_3	sulfur trioxide	SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide	PF_5	phosphorus pentafluoride

Compound	Name	Compound	Name
N_2O_4	dinitrogen tetroxide	P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide	IF_7	iodine heptafluoride

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

Naming Covalent Compounds

Name the following covalent compounds:

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

Solution

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

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

Exercise 7.4.2

Write the formulas for the following compounds:

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

Answer:

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

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 7.4.5.

Table 7.4.5: Names of Some Simple Acids

Name of Gas	Name of Acid
$HF(g)$, hydrogen fluoride	$HF(aq)$, hydrofluoric acid
$HCl(g)$, hydrogen chloride	$HCl(aq)$, hydrochloric acid
$HBr(g)$, hydrogen bromide	$HBr(aq)$, hydrobromic acid
$HI(g)$, hydrogen iodide	$HI(aq)$, hydroiodic acid
$H_2S(g)$, hydrogen sulfide	$H_2S(aq)$, 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 replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table $7.4.6$. 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 $7.4.6$: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	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

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding “acid;” HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion to *–ic*, and adding “acid;” H_2CO_3 is carbonic acid.

Contributors and Attributions

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7.5: Chemical Composition

Learning Objectives

- To understand the definition and difference between empirical formulas and chemical formulas
- To understand how combustion analysis can be used to identify chemical formulas

Chemical formulas tell you how many atoms of each element are in a compound, and empirical formulas tell you the simplest or most reduced ratio of elements in a compound. If a compound's chemical formula cannot be reduced any more, then the empirical formula is the same as the chemical formula. Combustion analysis can determine the empirical formula of a compound, but cannot determine the chemical formula (other techniques can though). Once known, the chemical formula can be calculated from the empirical formula.

Empirical Formulas

An empirical formula tells us the relative ratios of different atoms in a compound. The ratios hold true on the *molar* level as well. Thus, H_2O is composed of two atoms of hydrogen and 1 atom of oxygen. Likewise, **1.0 mole of H_2O** is composed **of 2.0 moles of hydrogen** and **1.0 mole of oxygen**. We can also work backwards from molar ratios since *if we know the molar amounts of each element in a compound we can determine the empirical formula*.

Example 7.5.1: Mercury Chloride

Mercury forms a compound with chlorine that is 73.9% mercury and 26.1% chlorine by mass. What is the empirical formula?

Solution

Let's say we had a 100 gram sample of this compound. The sample would therefore contain 73.9 grams of mercury and 26.1 grams of chlorine. How many moles of each atom do the individual masses represent?

For Mercury:

$$(73.9\ g) \times \left(\frac{1\ mol}{200.59\ g}\right) = 0.368\ moles$$

For Chlorine:

$$(26.1\ g) \times \left(\frac{1\ mol}{35.45\ g}\right) = 0.736\ mol$$

What is the molar ratio between the two elements?

$$\frac{0.736\ mol\ Cl}{0.368\ mol\ Hg} = 2.0$$

Thus, we have twice as many moles (i.e. atoms) of Cl as Hg. The empirical formula would thus be (remember to list cation first, anion last):

$$\mathrm{HgCl_2}$$

Chemical Formula from Empirical Formula

The chemical formula for a compound obtained by composition analysis is always the empirical formula. We can obtain the chemical formula from the empirical formula if we know the molecular weight of the compound. The chemical formula will always be some *integer multiple* of the empirical formula (i.e. integer multiples of the subscripts of the empirical formula). The general flow for this approach is shown in Figure $7.5.1$ and demonstrated in Example $7.5.2$.

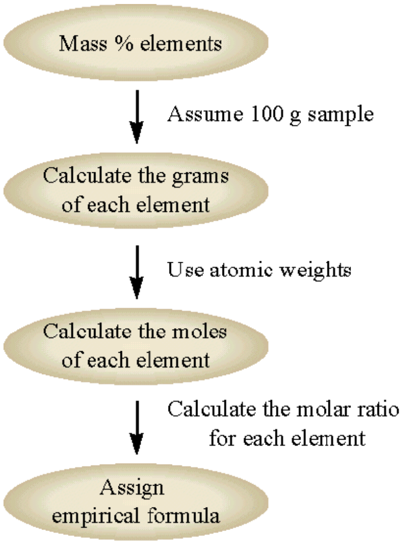


Figure 7.5.1: The general flow chart for solving empirical formulas from known mass percentages.

Flowchart. From mass % elements, calculate the grams of each element. Then, use atomic weights to calculate the moles of each element. Then, assign empirical formula by calculating the molar ratio for each element.

✓ Example 7.5.2: Ascorbic Acid

Vitamin C (ascorbic acid) contains 40.92 % C, 4.58 % H, and 54.50 % O, by mass. The experimentally determined molecular mass is 176 amu. What is the empirical and chemical formula for ascorbic acid?

Solution

Consider an arbitrary amount of 100 grams of ascorbic acid, so we would have:

- 40.92 grams C
- 4.58 grams H
- 54.50 grams O

This would give us how many moles of each element?

- Carbon

$$(40.92\ \ g\,\cancel{C}) \times \left(\frac{1\ mol\ C}{12.011\ \ g\,\cancel{C}}\right) = 3.407\ mol\ C$$

- Hydrogen

$$(4.58\ \ g\,\cancel{H}) \times \left(\frac{1\ mol\ H}{1.008\ \ g\,\cancel{H}}\right) = 4.544\ mol\ H$$

- Oxygen

$$(54.50\ \ g\,\cancel{O}) \times \left(\frac{1\ mol\ O}{15.999\ \ g\,\cancel{O}}\right) = 3.406\ mol\ O$$

Determine the simplest whole number ratio by dividing by the smallest molar amount (3.406 moles in this case - see oxygen):

- Carbon

$$C = \frac{3.407\ mol}{3.406\ mol} \approx 1.0$$

- Hydrogen

$$C = \frac{4.544\ mol}{3.406\ mol} = 1.333$$

- Oxygen

$$C = \frac{3.406\ mol}{3.406\ mol} = 1.0$$

The relative molar amounts of carbon and oxygen appear to be equal, but the relative molar amount of hydrogen is higher. Since we cannot have "fractional" atoms in a compound, we need to normalize the relative amount of hydrogen to be equal to an integer. 1.333 would appear to be 1 and 1/3, so if we multiply the relative amounts of each atom by '3', we should be able to get integer values for each atom.

C = (1.0)*3 = 3

H = (1.333)*3 = 4

O = (1.0)*3 = 3

or

$$C_3H_4O_3$$

This is our ***empirical formula*** for ascorbic acid.

What about the chemical formula? We are told that the experimentally determined molecular mass is **176 *amu***. What is the molecular mass of our empirical formula?

(3*12.011) + (4*1.008) + (3*15.999) = 88.062 *amu*

The molecular mass from our empirical formula is significantly lower than the experimentally determined value. What is the ratio between the two values?

(176 *amu*/88.062 *amu*) = 2.0

Thus, it would appear that our empirical formula is essentially one half the mass of the actual molecular mass. If we multiplied our empirical formula by '2', then the molecular mass would be correct. Thus, the actual chemical formula is:

2* $C_3H_4O_3$ = $\mathbf{C_6H_8O_6}$

Empirical Formulas: Empirical Formulas, YouTube(opens in new window) [youtu.be]

Combustion Analysis

When a compound containing carbon and hydrogen is subject to combustion with oxygen in a special combustion apparatus all the carbon is converted to CO_2 and the hydrogen to H_2O (Figure $7.5.2$). The amount of carbon produced can be determined by measuring the amount of CO_2 produced. This is trapped by the sodium hydroxide, and thus we can monitor the mass of CO_2 produced by determining the increase in mass of the CO_2 trap. Likewise, we can determine the amount of H produced by the amount of H_2O trapped by the magnesium perchlorate.

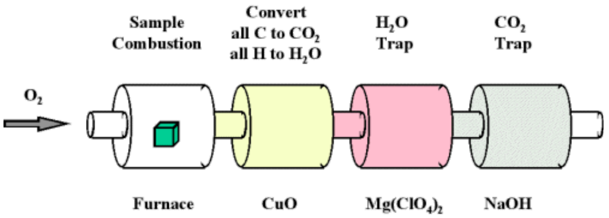
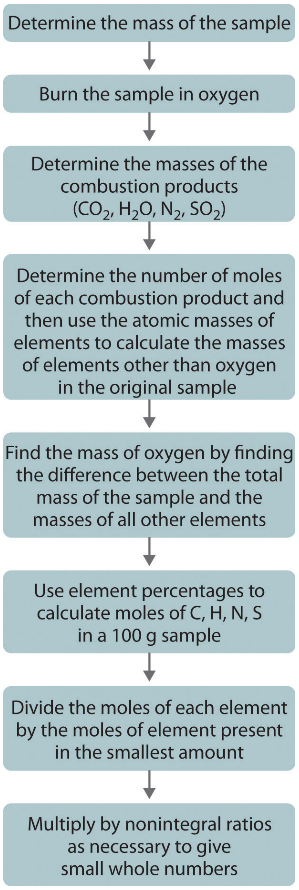


Figure 7.5.2: Combustion analysis apparatus

Diagram of a combustion chamber. O 2 enters the furnace and combusts the sample. All carbon is converted to C O 2 and all hydrogen is converted to H 2 O in the presence of C u O in the next chamber. The next chamber is an H 2 O trap with M g (C l O 4) 2 inside. The next chamber is a C O 2 trap with N a O H inside.

One of the most common ways to determine the elemental composition of an unknown hydrocarbon is an analytical procedure called combustion analysis. A small, carefully weighed sample of an unknown compound that may contain carbon, hydrogen, nitrogen, and/or sulfur is burned in an oxygen atmosphere,Other elements, such as metals, can be determined by other methods. and the quantities of the resulting gaseous products (CO_2, H_2O, N_2, and SO_2, respectively) are determined by one of several possible methods. One procedure used in combustion analysis is outlined schematically in Figure 7.5.3 and a typical combustion analysis is illustrated in Examples 7.5.3 and 7.5.4.



Determine the mass of the sample

Burn the sample in oxygen

Determine the masses of the combustion products (CO_2, H_2O, N_2, SO_2)

Determine the number of moles of each combustion product and then use the atomic masses of elements to calculate the masses of elements other than oxygen in the original sample

Find the mass of oxygen by finding the difference between the total mass of the sample and the masses of all other elements

Use element percentages to calculate moles of C, H, N, S in a 100 g sample

Divide the moles of each element by the moles of element present in the smallest amount

Multiply by nonintegral ratios as necessary to give small whole numbers

Figure 7.5.3: Steps for Obtaining an Empirical Formula from Combustion Analysis. (CC BY-NC-SA; anonymous)

✓ Example 7.5.3: Combustion of Isopropyl Alcohol

What is the empirical formulate for isopropyl alcohol (which contains only C, H and O) if the combustion of a 0.255 grams isopropyl alcohol sample produces 0.561 grams of CO_2 and 0.306 grams of H_2O?

Solution

From this information quantitate the amount of C and H in the sample.

$$(0.561 \quad g\, \cancel{CO_2}) \left(\frac{1\ mol\ CO_2}{44.0 \quad g\, \cancel{CO_2}} \right) = 0.0128\ mol\ CO_2$$

Since one mole of CO_2 is made up of one mole of C and two moles of O, if we have 0.0128 moles of CO_2 in our sample, then we know we have 0.0128 moles of C in the sample. How many grams of C is this?

$$(0.0128 \quad \cancel{mol\, C}) \left(\frac{12.011\ g\ C}{1 \quad \cancel{mol\, C}} \right) = 0.154\ g\ C$$

How about the hydrogen?

$$(0.306 \quad g\, \cancel{H_2O}) \left(\frac{1\ mol\ H_2O}{18.0 \quad g\, \cancel{H_2O}} \right) = 0.017\ mol\ H_2O$$

Since one mole of H_2O is made up of one mole of oxygen and ***two*** moles of hydrogen, if we have 0.017 moles of H_2O, then we have 2*(0.017) = 0.034 moles of hydrogen. Since hydrogen is about 1 gram/mole, we must have **0.034 grams of hydrogen** in our original sample.

When we add our carbon and hydrogen together we get:

0.154 grams (C) + 0.034 grams (H) = **0.188 grams**

But we know we combusted *0.255 grams* of isopropyl alcohol. The 'missing' mass must be from the oxygen atoms in the isopropyl alcohol:

0.255 grams - 0.188 grams = 0.067 grams oxygen

This much oxygen is how many moles?

$$(0.067 \quad g\, \cancel{O}) \left(\frac{1\ mol\ O}{15.994 \quad g\, \cancel{O}} \right) = 0.0042\ mol\ O$$

Overall therefore, we have:

- 0.0128 moles Carbon
- 0.0340 moles Hydrogen
- 0.0042 moles Oxygen

Divide by the smallest molar amount to normalize:

- C = 3.05 atoms
- H = 8.1 atoms
- O = 1 atom

Within experimental error, the most likely empirical formula for propanol would be C_3H_8O

✓ Example 7.5.4: Combustion of Naphalene

Naphthalene, the active ingredient in one variety of mothballs, is an organic compound that contains carbon and hydrogen only. Complete combustion of a 20.10 mg sample of naphthalene in oxygen yielded 69.00 mg of CO_2 and 11.30 mg of H_2O. Determine the empirical formula of naphthalene.

Given: mass of sample and mass of combustion products

Asked for: empirical formula

Strategy:

A. Use the masses and molar masses of the combustion products, CO_2 and H_2O, to calculate the masses of carbon and hydrogen present in the original sample of naphthalene.
B. Use those masses and the molar masses of the elements to calculate the empirical formula of naphthalene.

Solution:

A Upon combustion, 1 mol of CO_2 is produced for each mole of carbon atoms in the original sample. Similarly, 1 mol of H_2O is produced for every 2 mol of hydrogen atoms present in the sample. The masses of carbon and hydrogen in the original sample can be calculated from these ratios, the masses of CO_2 and H_2O, and their molar masses. Because the units of molar mass are grams per mole, we must first convert the masses from milligrams to grams:

$$mass\,of\,C = 69.00\,mg\,CO_2 \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,CO_2}{44.010\,g\,CO_2} \times \frac{1\,molC}{1\,mol\,CO_2} \times \frac{12.011\,g}{1\,mol\,C}$$
$$= 1.883 \times 10^{-2}\,g\,C$$
$$mass\,of\,H = 11.30\,mg\,H_2O \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,H_2O}{18.015\,g\,H_2O} \times \frac{2\,molH}{1\,mol\,H_2O} \times \frac{1.0079\,g}{1\,mol\,H}$$
$$= 1.264 \times 10^{-3}\,g\,H$$

B To obtain the relative numbers of atoms of both elements present, we need to calculate the number of moles of each and divide by the number of moles of the element present in the smallest amount:

$$moles\,C = 1.883 \times 10^{-2}\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 1.568 \times 10^{-3}\,molC$$
$$moles\,H = 1.264 \times 10^{-3}\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 1.254 \times 10^{-3}\,molH$$

Dividing each number by the number of moles of the element present in the smaller amount gives

$$H : \frac{1.254 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.000 \quad C : \frac{1.568 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.250$$

Thus naphthalene contains a 1.25:1 ratio of moles of carbon to moles of hydrogen: $C_{1.25}H_{1.0}$. Because the ratios of the elements in the empirical formula must be expressed as small whole numbers, multiply both subscripts by 4, which gives C_5H_4 as the empirical formula of naphthalene. In fact, the chemical formula of naphthalene is $C_{10}H_8$, which is consistent with our results.

? Exercise 7.5.4

a. Xylene, an organic compound that is a major component of many gasoline blends, contains carbon and hydrogen only. Complete combustion of a 17.12 mg sample of xylene in oxygen yielded 56.77 mg of CO_2 and 14.53 mg of H_2O. Determine the empirical formula of xylene.
b. The empirical formula of benzene is CH (its chemical formula is C_6H_6). If 10.00 mg of benzene is subjected to combustion analysis, what mass of CO_2 and H_2O will be produced?

Answer a

The empirical formula is C_4H_5. (The chemical formula of xylene is actually C_8H_{10}.)

Answer b

33.81 mg of CO_2; 6.92 mg of H_2O

Combustion Analysis: Combustion Analysis, YouTube(opens in new window) [youtu.be]

7.5.1: Empirical Formulas

In the previous section, we discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, we were able to determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, we will explore how to apply these very same principles in order to derive the chemical formulas of unknown substances from experimental mass measurements.

Derivation of Molecular Formulas

Recall that empirical formulas are symbols representing the *relative* numbers of a compound's elements. Determining the *absolute* numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molecular mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in the previous chapter on atoms and molecules). Molar mass can be measured by a number of experimental methods, many of which will be introduced in later chapters of this text.

Molecular formulas are derived by comparing the compound's molecular or molar mass to its empirical formula mass. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If we know the molecular (or molar) mass of the substance, we can divide this by the empirical formula mass in order to identify the number of empirical formula units per molecule, which we designate as *n*:

$$\frac{\text{molecular or molar mass}\left(\text{amu or }\dfrac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{amu or }\dfrac{\text{g}}{\text{mol}}\right)}=n\,\text{formula units/molecule} \tag{7.5.1.1}$$

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

$$(\mathrm{A_xB_y})_\mathrm{n}=\mathrm{A_{nx}B_{nx}} \tag{7.5.1.2}$$

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

$$\frac{180\text{ amu/molecule}}{30\,\dfrac{\text{amu}}{\text{formula unit}}}=6\text{ formula units/molecule} \tag{7.5.1.3}$$

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

$$(\mathrm{CH_2O})_6=\mathrm{C_6H_{12}O_6} \tag{7.5.1.4}$$

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

Determination of the Molecular Formula for Nicotine

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

Solution

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

$$(74.02 \text{ g C})\left(\frac{1 \text{ mol C}}{12.01 \text{ g C}}\right) = 6.163 \text{ mol C} \tag{7.5.1.5}$$

$$(8.710 \text{ g H})\left(\frac{1 \text{ mol H}}{1.01 \text{ g H}}\right) = 8.624 \text{ mol H} \tag{7.5.1.6}$$

$$(17.27 \text{ g N})\left(\frac{1 \text{ mol N}}{14.01 \text{ g N}}\right) = 1.233 \text{ mol N} \tag{7.5.1.7}$$

Next, we calculate the molar ratios of these elements.

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

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

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

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

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

Thus, we can derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(C_5H_7N)_6 = C_{10}H_{14}N_2$$

Exercise 7.5.1.5

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

Answer

$C_8H_{10}N_4O_2$

Summary

The chemical identity of a substance is defined by the types and relative numbers of atoms composing its fundamental entities (molecules in the case of covalent compounds, ions in the case of ionic compounds). A compound’s percent composition provides the mass percentage of each element in the compound, and it is often experimentally determined and used to derive the compound’s empirical formula. The empirical formula mass of a covalent compound may be compared to the compound’s molecular or molar mass to derive a molecular formula.

Combustion Analysis

When a compound containing carbon and hydrogen is subject to combustion with oxygen in a special combustion apparatus all the carbon is converted to CO_2 and the hydrogen to H_2O (Figure 7.5.1.2). The amount of carbon produced can be determined by measuring the amount of CO_2 produced. This is trapped by the sodium hydroxide, and thus we can monitor the mass of CO_2 produced by determining the increase in mass of the CO_2 trap. Likewise, we can determine the amount of H produced by the amount of H_2O trapped by the magnesium perchlorate.

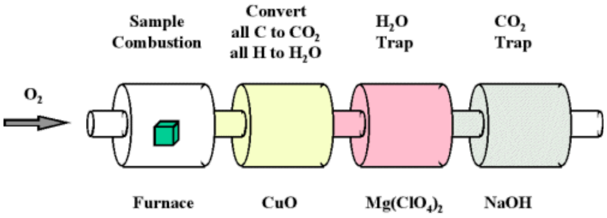


Figure $7.5.1.2$: Combustion analysis apparatus

One of the most common ways to determine the elemental composition of an unknown hydrocarbon is an analytical procedure called combustion analysis. A small, carefully weighed sample of an unknown compound that may contain carbon, hydrogen, nitrogen, and/or sulfur is burned in an oxygen atmosphere,Other elements, such as metals, can be determined by other methods. and the quantities of the resulting gaseous products (CO_2, H_2O, N_2, and SO_2, respectively) are determined by one of several possible methods. One procedure used in combustion analysis is outlined schematically in Figure $7.5.1.3$and a typical combustion analysis is illustrated in Examples $7.5.1.3$and $7.5.1.4$

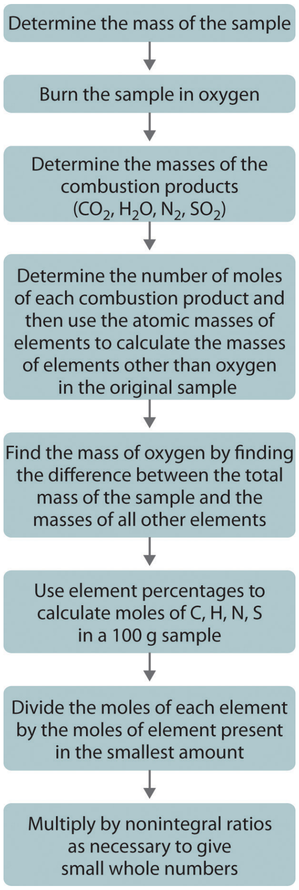


Figure $7.5.1.3$: Steps for Obtaining an Empirical Formula from Combustion Analysis

Example $7.5.1.3$: Combustion of Isopropyl Alcohol

What is the empirical formulate for isopropyl alcohol (which contains only C, H and O) if the combustion of a 0.255 grams isopropyl alcohol sample produces 0.561 grams of CO_2 and 0.306 grams of H_2O?

Solution

From this information quantitate the amount of C and H in the sample.

$$(0.561 \;\; g\, \cancel{CO_2}) \left(\frac{1 \; mol \; CO_2}{44.0 \;\; g \, \cancel{CO_2}} \right) = 0.0128 \; mol \; CO_2 \tag{7.5.1.8}$$

Since one mole of CO_2 is made up of one mole of C and two moles of O, if we have 0.0128 moles of CO_2 in our sample, then we know we have 0.0128 moles of C in the sample. How many grams of C is this?

$$(0.0128 \;\; \cancel{mol \, C}) \left(\frac{12.011 \; g \, C}{1 \;\; \cancel{mol \, C}} \right) = 0.154 \; g \, C \tag{7.5.1.9}$$

How about the hydrogen?

$$(0.306 \;\; g\; \cancel{H_2O}) \left(\frac{1 \; mol \; H_2O}{18.0 \;\; g\; \cancel{H_2O}} \right) = 0.017 \; mol \; H_2O \tag{7.5.1.10}$$

Since one mole of H_2O is made up of one mole of oxygen and ***two*** moles of hydrogen, if we have 0.017 moles of H_2O, then we have 2*(0.017) = 0.034 moles of hydrogen. Since hydrogen is about 1 gram/mole, we must have **0.034 grams of hydrogen** in our original sample.

When we add our carbon and hydrogen together we get:

0.154 grams (C) + 0.034 grams (H) = **0.188 grams**

But we know we combusted *0.255 grams* of isopropyl alcohol. The 'missing' mass must be from the oxygen atoms in the isopropyl alcohol:

0.255 grams - 0.188 grams = 0.067 grams oxygen

This much oxygen is how many moles?

$$(0.067 \;\; g\; \cancel{O}) \left(\frac{1 \; mol \; O}{15.994 \;\; g\; \cancel{O}} \right) = 0.0042 \; mol \; O \tag{7.5.1.11}$$

Overall therefore, we have:

- 0.0128 moles Carbon
- 0.0340 moles Hydrogen
- 0.0042 moles Oxygen

Divide by the smallest molar amount to normalize:

- C = 3.05 atoms
- H = 8.1 atoms
- O = 1 atom

Within experimental error, the most likely empirical formula for propanol would be C_3H_8O

Example 7.5.1.4: Combustion of Naphalene

Naphthalene, the active ingredient in one variety of mothballs, is an organic compound that contains carbon and hydrogen only. Complete combustion of a 20.10 mg sample of naphthalene in oxygen yielded 69.00 mg of CO_2 and 11.30 mg of H_2O. Determine the empirical formula of naphthalene.

Given: mass of sample and mass of combustion products

Asked for: empirical formula

Strategy:

A. Use the masses and molar masses of the combustion products, CO_2 and H_2O, to calculate the masses of carbon and hydrogen present in the original sample of naphthalene.
B. Use those masses and the molar masses of the elements to calculate the empirical formula of naphthalene.

Solution:

A Upon combustion, 1 mol of CO**2** is produced for each mole of carbon atoms in the original sample. Similarly, 1 mol of H_2O is produced for every 2 mol of hydrogen atoms present in the sample. The masses of carbon and hydrogen in the original sample can be calculated from these ratios, the masses of CO_2 and H_2O, and their molar masses. Because the units of molar mass are grams per mole, we must first convert the masses from milligrams to grams:

$$mass\, of\; C = 69.00\, mg\, CO_2 \times \frac{1\, g}{1000\, mg} \times \frac{1\, mol\, CO_2}{44.010\, g\, CO_2} \times \frac{1\, molC}{1\, mol\, CO_2} \times \frac{12.011\, g}{1\, mol\, C} \tag{7.5.1.12}$$

$$= 1.883 \times 10^{-2}\, g\, C \tag{7.5.1.13}$$

$$mass\,of\;H = 11.30\,mg\,H_2O \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\;H_2O}{18.015\,g\,H_2O} \times \frac{2\,molH}{1\,mol\;H_2O} \times \frac{1.0079\,g}{1\,mol\;H} \tag{7.5.1.14}$$

$$= 1.264 \times 10^{-3}\,g\,H \tag{7.5.1.15}$$

B To obtain the relative numbers of atoms of both elements present, we need to calculate the number of moles of each and divide by the number of moles of the element present in the smallest amount:

$$moles\,C = 1.883 \times 10^{-2}\,g\,C \times \frac{1\,mol\;C}{12.011\,g\,C} = 1.568 \times 10^{-3}\;molC \tag{7.5.1.16}$$

$$moles\,H = 1.264 \times 10^{-3}\,g\,H \times \frac{1\,mol\;H}{1.0079\,g\,H} = 1.254 \times 10^{-3}\;molH \tag{7.5.1.17}$$

Dividing each number by the number of moles of the element present in the smaller amount gives

$$H: \frac{1.254 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.000 \quad C: \frac{1.568 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.250 \tag{7.5.1.18}$$

Thus naphthalene contains a 1.25:1 ratio of moles of carbon to moles of hydrogen: $C_{1.25}H_{1.0}$. Because the ratios of the elements in the empirical formula must be expressed as small whole numbers, multiply both subscripts by 4, which gives C_5H_4 as the empirical formula of naphthalene. In fact, the molecular formula of naphthalene is $C_{10}H_8$, which is consistent with our results.

Exercise 7.5.1.4

a. Xylene, an organic compound that is a major component of many gasoline blends, contains carbon and hydrogen only. Complete combustion of a 17.12 mg sample of xylene in oxygen yielded 56.77 mg of CO_2 and 14.53 mg of H_2O. Determine the empirical formula of xylene.
b. The empirical formula of benzene is CH (its molecular formula is C_6H_6). If 10.00 mg of benzene is subjected to combustion analysis, what mass of CO_2 and H_2O will be produced?

Answer a

The empirical formula is C_4H_5. (The molecular formula of xylene is actually C_8H_{10}.)

Answer b

33.81 mg of CO_2; 6.92 mg of H_2O

Contributors and Attributions

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CHAPTER OVERVIEW

8: Chemical Bonding I - The Lewis Model

The Lewis Theory used observations from chemists and physicists to form a theory about chemical bonding. This work was essentially a compilation of the knowledge at the time. It revolved around the importance of valence electrons in chemical bonding. These are the electrons that are in the outermost shell. For example Na may have 11 electrons, but only one is a valence electron, the one in $3s^1$. Meanwhile P has 15 electrons, but has five valence electrons, $3s^2$ and $3p^2$. The bonding of an element is based on how they fill their octets i.e. achieve a noble gas electron configurations. Lewis went on to explain how certain elements such as Boron did not necessarily follow these same rules. By drawing schematics of molecules called Lewis Dot Structures, important characteristics of molecules can be described.

Chapter Sections

References:

1. Lewis, Gilbert Newton. *Valence and the Structure of Atoms and Molecules,*. New York: Chemical Catalog, 1923. Print.
2. Pauling, Linus. *The Nature of the Chemical Bond: and the Structure of Molecules and Crystals : Introduction to Modern Structural Chemistry*. Ithaca, NY: Cornell UP, 1960. Print.
3. Petrucci, Ralph H. *General Chemistry: Principles and Modern Applications*. Toronto, Ont.: Pearson Canada, 2011. Print.

Outside Links:

- http://en.Wikipedia.org/wiki/Lewis_structure
- http://osulibrary.oregonstate.edu/sp...-19160400.html

Contributors

- Nilpa Shah (UCD)

8.1: Lewis Symbols

Learning Objectives

- To use Lewis electron dot symbols to predict the number of bonds an element will form.

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond wil be discussed and the general properties found in typical substances in which the bond type occurs

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involves a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involves one nonmetallic element with another
3. Metallic bonds These bonds are found in solid metals (copper, iron, aluminum) with each metal bonded to several neighboring groups and bonding electrons free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

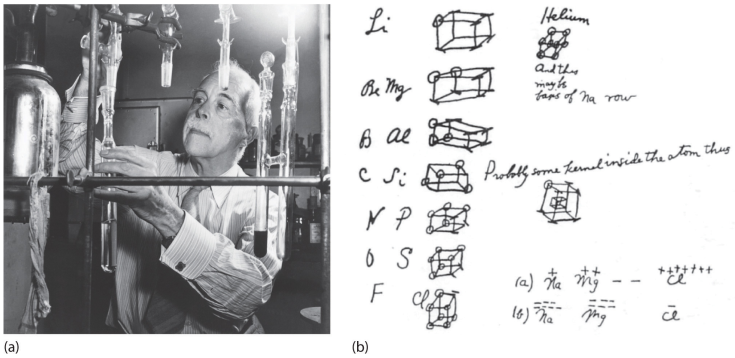


Figure 8.1.1: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

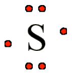
Lewis Symbols

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

Lewis Dot symbols:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

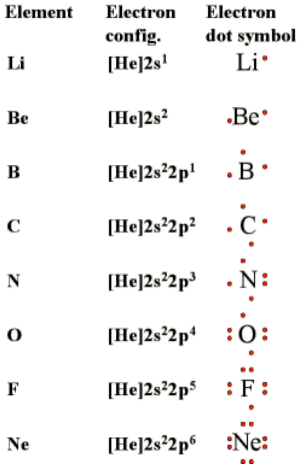
To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is [Ne]$3s^2 3p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration [He]$2s^2 2p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:

Figure 8.1.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 8.1.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.



Element	Electron config.	Electron dot symbol
Li	[He]$2s^1$	Li
Be	[He]$2s^2$	Be
B	[He]$2s^2 2p^1$	B
C	[He]$2s^2 2p^2$	C
N	[He]$2s^2 2p^3$	N
O	[He]$2s^2 2p^4$	O
F	[He]$2s^2 2p^5$	F
Ne	[He]$2s^2 2p^6$	Ne

Figure 8.1.2: Lewis Dot Symbols for the Elements in Period 2

L i has one dot on the right, B e has one dot on the left and right, B has one dot on the left, right, and above. C has one dot above, below, on the left and on the right. N has one dot above, below, on the left and two dots on the right. O has two dots on the left and right and one dot above and below. F has two dots above, on the left, on the right and on dot below. N e has two dots above, below, on the right, and on the left.

The Octet Rule

In 1904, Richard Abegg formulated what is now known as *Abegg's rule*, which states that the difference between the maximum positive and negative valences of an element is frequently eight. This rule was used later in 1916 when Gilbert N. Lewis formulated the "octet rule" in his cubical atom theory. The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. Atoms will react to get in the most stable state possible. A complete octet is very stable because all orbitals will be full. Atoms with greater stability have less energy, so a reaction that increases the stability of the atoms will release energy in the form of heat or light ;reactions that decrease stability must absorb energy, getting colder.

When discussing the octet rule, we do not consider *d* or *f* electrons. Only the s and p electrons are involved in the octet rule, making it a useful rule for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6.

Definition: Octet Rule

A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

1. Normally two electrons pairs up and forms a bond, e.g., H_2
2. For most atoms there will be a maximum of eight electrons in the valence shell (octet structure), e.g., CH_4

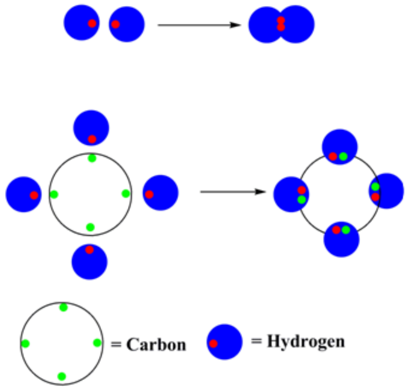


Figure 1: Bonding in H_2 and methane (CH_4)

A hydrogen bonds with each of the four valence electrons of a carbon meaning that four hydrogens can bond with one carbon.

The other tendency of atoms is to maintain a neutral charge. Only the noble gases (the elements on the right-most column of the periodic table) have zero charge with filled valence octets. All of the other elements have a charge when they have eight electrons all to themselves. The result of these two guiding principles is the explanation for much of the reactivity and bonding that is observed within atoms: atoms seek to share electrons in a way that minimizes charge while fulfilling an octet in the valence shell.

> The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

Example 8.1.1: Salt

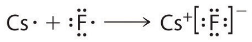
The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why?

Solution

Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium has one valence electron, so giving it up would result in the same electron configuration as neon. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon when it gains an electron.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gasses, with a full valence shell. However, their charges would be much higher. It would be Na^{7-} and Cl^{7+}, which is much less stable than Na^+ and Cl^-. Atoms are more stable when they have no charge, or a small charge.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



$$\mathrm{Cs}\cdot + :\ddot{\underset{..}{\mathrm{F}}}\cdot \longrightarrow \mathrm{Cs}^{+}[:\ddot{\underset{..}{\mathrm{F}}}:]^{-}$$

No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

> *Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.*

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe elsewhere. These include molecules in which one or more atoms contain fewer or more than eight electrons.

Summary

Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds. One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

Contributors and Attributions

- Mike Blaber (Florida State University)
- Wikipedia
- National Programme on Technology Enhanced Learning (India)

8.2: Covalent Bonding and Lewis Dot Structures

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure 8.2.1):

- The electrons in the two atoms repel each other because they have the same charge (
- *The electrons in the two atoms repel each other because they have the same charge (E > 0).*
- *Similarly, the protons in adjacent atoms repel each other (E > 0).*
- *The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa (E < 0). Recall that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.*

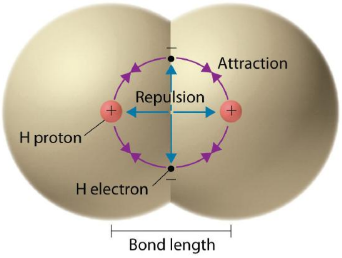


Figure 8.2.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 8.2.2) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figures 8.2.1 and 8.2.2, which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

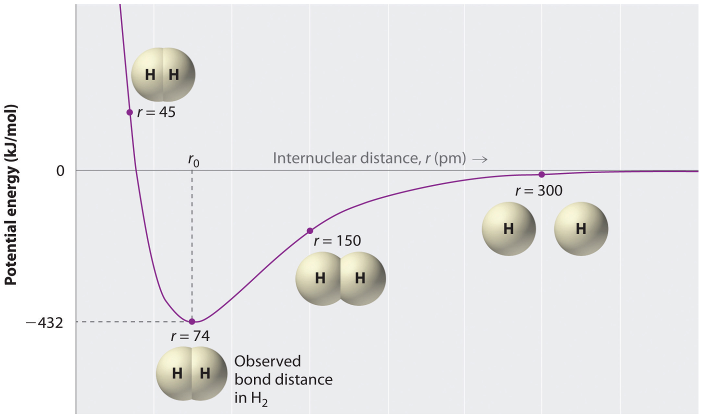


Figure 8.2.2: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

Using Lewis Dot Symbols to Describe Covalent Bonding

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:

Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond. Examples of this type of bonding are presented in Section 8.6 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:

The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:

The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.

5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:

This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^- Ion

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:

Both the oxygen and chlorine have 3 electron pairs drawn around them with a bond drawn between them. The molecule has square brackets placed around it and has a negative charge.

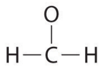
Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

The CH_2O Molecule

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:

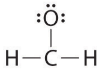
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

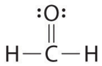
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



The bond between the oxygen and carbon is replaced with a double bond. The oxygen also has two lone pairs drawn.

Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 8.2.1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

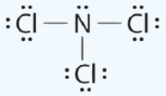
Asked for: Lewis electron structures

Strategy:

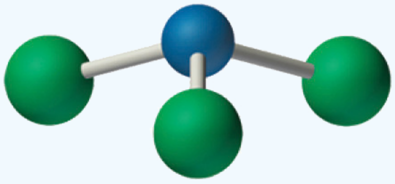
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

a. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

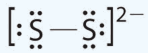


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



Nitrogen trichloride

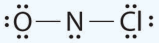
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



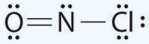
c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:

O—N—Cl

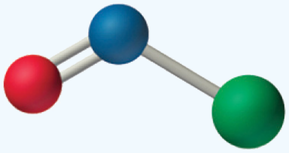
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



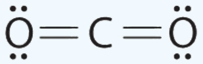
Nitrosyl chloride

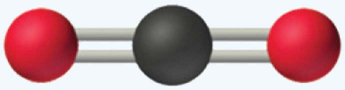
Exercise 8.2.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer

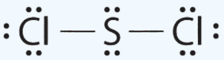
1.



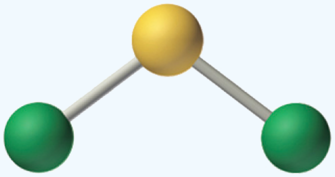


Carbon dioxide

2.



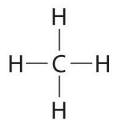
Two chlorines are bonded to a sulfur. The sulfur has 2 lone pairs while the chlorines have 3 lone pairs each.



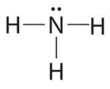
Sulfur dichloride

Using Lewis Electron Structures to Explain Stoichiometry

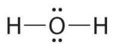
Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of Group 17 (the halogens), this number is one; for the elements of Group 16 (the chalcogens), it is two; for Group 15 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



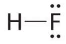
Group 14



Group 15

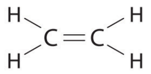


Group 16



Group 17

Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Ethylene

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

> Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 8.2.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

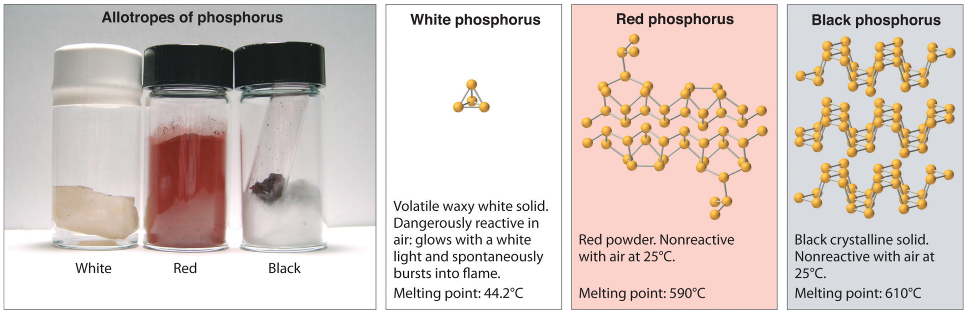


Figure 8.2.3: The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

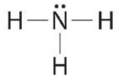
- Nonbonding electrons are assigned to the atom on which they are located.

- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$formal\ charge = \underset{(free\ atom)}{valence\ e^-} - \underset{(atom\ in\ Lewis\ structure)}{\left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right)}$$ (atom in Lewis structure)

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding e^-/2)]. Substituting into Equation 8.2.1, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \tag{8.2.1}$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^-/2)]. Using Equation 8.2.1 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \tag{8.2.2}$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

> An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.

Example 8.2.2: The Ammonium Ion

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

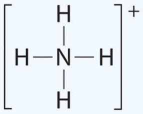
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 8.2.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



The central nitrogen is bonded to four hydrogens. The molecule is surrounded by square brackets. Outside the bracket is where the positive charge is placed.

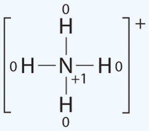
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation ???, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus



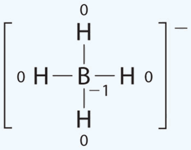
In the Lewis structure, each hydrogen has a zero placed nearby while the nitrogen has a +1 placed nearby.

Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 8.2.2

Write the formal charges on all atoms in BH_4^-.

Answer



Four hydrogens are bonded to a central boron. Each hydrogen has a zero placed nearby while the boron has a -1. The molecule is surrounded by square brackets. Outside of the brackets is a negative charge.

If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable Lewis Structures

8.2.1: Exceptions to Octet

Learning Objectives

- To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Three cases can be constructed that do not follow the octet rule, and as such, they are known as the exceptions to the octet rule. Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. However, it is hard to imagine that one rule could be followed by all molecules. There is always an exception, and in this case, three exceptions:

1. When there are an odd number of valence electrons
2. When there are too few valence electrons
3. When there are too many valence electrons

Exception 1: Species with Odd Numbers of Electrons

The first exception to the Octet Rule is when there are an odd number of valence electrons. An example of this would be Nitrogen (II) Oxide also called nitric oxide (NO. Nitrogen has 5 valence electrons while Oxygen has 6. The total would be 11 valence electrons to be used. The Octet Rule for this molecule is fulfilled in the above example, however that is with 10 valence electrons. The last one does not know where to go. The lone electron is called an unpaired electron. But where should the unpaired electron go? The unpaired electron is usually placed in the Lewis Dot Structure so that each element in the structure will have the *lowest* formal charge possible. The formal charge is *the perceived charge on an individual atom in a molecule when atoms do not contribute equal numbers of electrons to the bonds they participate in.*

No formal charge at all is the most ideal situation. An example of a stable molecule with an odd number of valence electrons would be nitric oxide. nitric oxide has 11 valence electrons. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitric oxide had ten valence electrons we would come up with the Lewis Structure (Figure $8.2.1.1$):

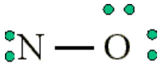


Figure $8.2.1.1$: This is if nitric oxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure $8.2.1.2$ based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure $8.2.1.1$, it has two lone pair electrons and it participates in two bonds (a double bond) with oxygen. This results in nitrogen having a formal charge of +1. Oxygen normally has six valence electrons. In Figure $8.2.1.1$, oxygen has four lone pair electrons and it participates in two bonds with nitrogen. Oxygen therefore has a formal charge of 0. The overall molecule here has a formal charge of +1 (+1 for nitrogen, 0 for oxygen. +1 + 0 = +1). However, if we add the eleventh electron to nitrogen (because we want the molecule to have the *lowest* total formal charge), it will bring both the nitrogen and the molecule's overall charges to zero, the most ideal formal charge situation. That is exactly what is done to get the correct Lewis structure for nitric oxide (Figure $8.2.1.2$):

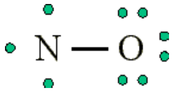


Figure $8.2.1.2$: The proper Lewis structure for NO molecule

Free Radicals

There are actually very few stable molecules with odd numbers of electrons that exist, since that unpaired electron is willing to react with other unpaired electrons. Most odd electron species are highly reactive, which we call Free Radicals. Because of their instability, free radicals bond to atoms in which they can take an electron from in order to become stable, making them very chemically reactive. Radicals are found as both reactants and products, but generally react to form more stable molecules as soon as they can. In order to emphasize the existence of the unpaired electron, radicals are denoted with a dot in front of their chemical symbol as with $\cdot OH$, the hydroxyl radical. An example of a radical you may by familiar with already is the gaseous chlorine atom, denoted $\cdot Cl$. Interestingly, an odd Number of Valence Electrons will result in the molecule being paramagnetic.

Exception 2: Incomplete Octets

The second exception to the Octet Rule is when there are too few valence electrons that results in an incomplete Octet. There are even more occasions where the octet rule does not give the most correct depiction of a molecule or ion. This is also the case with incomplete octets. Species with incomplete octets are pretty rare and generally are only found in some beryllium, aluminum, and boron compounds including the boron hydrides. Let's take a look at one such hydride, BH_3 (Borane).

If one were to make a Lewis structure for BH_3 following the basic strategies for drawing Lewis structures, one would probably come up with this structure (Figure $8.2.1.2$):

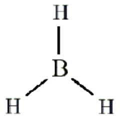


Figure $8.2.1.3$: The structure of BH_3 is square planer.

The problem with this structure is that boron has an incomplete octet; it only has six electrons around it. Hydrogen atoms can naturally only have only 2 electrons in their outermost shell (their version of an octet), and as such there are no spare electrons to form a double bond with boron. One might surmise that the failure of this structure to form complete octets must mean that this bond should be ionic instead of covalent. However, boron has an electronegativity that is very similar to hydrogen, meaning there is likely very little ionic character in the hydrogen to boron bonds, and as such this Lewis structure, though it does not fulfill the octet rule, is likely the best structure possible for depicting BH_3 with Lewis theory. One of the things that may account for BH_3's incomplete octet is that it is commonly a transitory species, formed temporarily in reactions that involve multiple steps.

Let's take a look at another incomplete octet situation dealing with boron, BF_3 (Boron trifluorine). Like with BH_3, the initial drawing of a Lewis structure of BF_3 will form a structure where boron has only six electrons around it (Figure $8.2.1.4$).

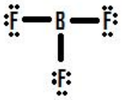


Figure 8.2.1.4

If you look Figure $8.2.1.4$, you can see that the fluorine atoms possess extra lone pairs that they can use to make additional bonds with boron, and you might think that all you have to do is make one lone pair into a bond and the structure will be correct. If we add one double bond between boron and one of the fluorines we get the following Lewis Structure (Figure $8.2.1.5$):

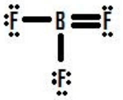


Figure 8.2.1.5

Each fluorine has eight electrons, and the boron atom has eight as well! Each atom has a perfect octet, right? Not so fast. We must examine the formal charges of this structure. The fluorine that shares a double bond with boron has six electrons around it (four from its two lone pairs of electrons and one each from its two bonds with boron). This is one less electron than the number of valence electrons it would have naturally (Group Seven elements have seven valence electrons), so it has a formal charge of +1. The two flourines that share single bonds with boron have seven electrons around them (six from their three lone pairs and one from their single bonds with boron). This is the same amount as the number of valence electrons they would have on their own, so they both have a formal charge of zero. Finally, boron has four electrons around it (one from each of its four bonds shared with fluorine). This is one more electron than the number of valence electrons that boron would have on its own, and as such boron has a formal charge of -1.

This structure is supported by the fact that the experimentally determined bond length of the boron to fluorine bonds in BF_3 is less than what would be typical for a single bond (see Bond Order and Lengths). However, this structure contradicts one of the major rules of formal charges: Negative formal charges are supposed to be found on the more electronegative atom(s) in a bond, but in the structure depicted in Figure $8.2.1.5$, a *positive* formal charge is found on fluorine, which not only is the most electronegative element in the structure, but the most electronegative element in the entire periodic table ($\chi = 4.0$). Boron on the other hand, with the much lower electronegativity of 2.0, has the negative formal charge in this structure. This formal charge-electronegativity disagreement makes this double-bonded structure impossible.

However the large electronegativity difference here, as opposed to in BH_3, signifies significant polar bonds between boron and fluorine, which means there is a high ionic character to this molecule. This suggests the possibility of a semi-ionic structure such as seen in Figure 8.2.1.6:

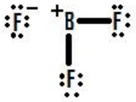


Figure 8.2.1.6

A bond is broken between one of the fluorine's and the boron making the free fluorine negatively charged and the boron positively charged.

None of these three structures is the "correct" structure in this instance. The most "correct" structure is most likely a resonance of all three structures: the one with the incomplete octet (Figure 8.2.1.4), the one with the double bond (Figure 8.2.1.5), and the one with the ionic bond (Figure 8.2.1.6). The most contributing structure is probably the incomplete octet structure (due to Figure 8.2.1.5 being basically impossible and Figure 8.2.1.6 not matching up with the behavior and properties of BF_3). As you can see even when other possibilities exist, incomplete octets may best portray a molecular structure.

As a side note, it is important to note that BF_3 frequently bonds with a F^- ion in order to form BF_4^- rather than staying as BF_3. This structure completes boron's octet and it is more common in nature. This exemplifies the fact that incomplete octets are rare, and other configurations are typically more favorable, including bonding with additional ions as in the case of BF_3 .

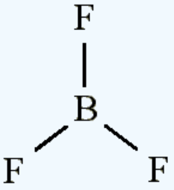
8.2.1.1 NF_3 Example :

Draw the Lewis structure for boron trifluoride (BF_3).

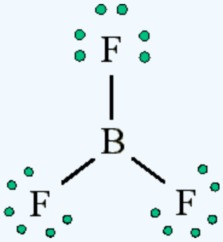
Solution

1. Add electrons (3*7) + 3 = **24**

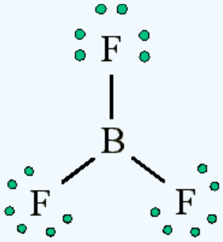
2. Draw connectivities:



3. Add octets to outer atoms:



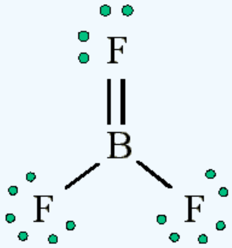
4. Add extra electrons (24-24=0) to central atom:



5. Does central electron have octet?

- NO. It has 6 electrons

- Add a multiple bond (double bond) to see if central atom can achieve an octet:

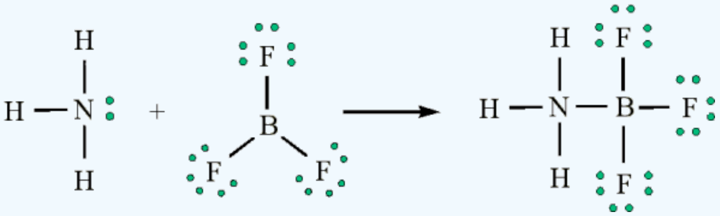


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

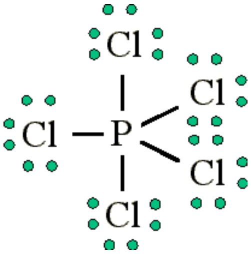
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single bonds, and 6 valence electrons around the central boron is the most likely structure***

BF_3 reacts strongly with compounds which have an unshared pair of electrons which can be used to form a bond with the boron:



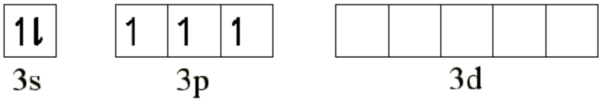
Exception 3: Expanded Valence Shells

More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, and a nonmetal central atom found in the third period or below*, which those terminal atoms bond to. For example, PCl_5 is a legitimate compound (whereas NCl_5) is not:



> Expanded valence shells are observed **only** for elements in period 3 (i.e. n=3) and beyond

The 'octet' rule is based upon available n*s* and n*p* orbitals for valence electrons (2 electrons in the *s* orbitals, and 6 in the *p* orbitals). Beginning with the n=3 principle quantum number, the d orbitals become available (*l*=2). The orbital diagram for the valence shell of phosphorous is:



Hence, the third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons. Size is also an important consideration:

- The larger the central atom, the larger the number of electrons which can surround it
- Expanded valence shells occur most often when the central atom is bonded to small electronegative atoms, such as F, Cl and O.

There is currently much scientific exploration and inquiry into the reason why expanded valence shells are found. The top area of interest is figuring out where the extra pair(s) of electrons are found. Many chemists think that there is not a very large energy difference between the 3p and 3d orbitals, and as such it is plausible for extra electrons to easily fill the 3d orbital when an expanded octet is more favorable than having a complete octet. This matter is still under hot debate, however and there is even debate as to what makes an expanded octet more favorable than a configuration that follows the octet rule.

One of the situations where expanded octet structures are treated as more favorable than Lewis structures that follow the octet rule is when the formal charges in the expanded octet structure are smaller than in a structure that adheres to the octet rule, or when there are less formal charges in the expanded octet than in the structure a structure that adheres to the octet rule.

8.2.1.2 SO_4^{-2} Example : The ion

Such is the case for the sulfate ion, SO_4^{-2}. A strict adherence to the octet rule forms the following Lewis structure:

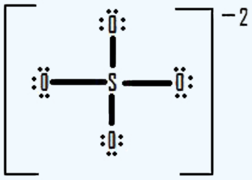


Figure 8.2.1.12

Four oxygens are bonded to a central sulfur. Each oxygen has 3 lone pairs. The molecule has a minus 2 charge.

If we look at the formal charges on this molecule, we can see that all of the oxygen atoms have seven electrons around them (six from the three lone pairs and one from the bond with sulfur). This is one more electron than the number of valence electrons then they would have normally, and as such each of the oxygens in this structure has a formal charge of -1. Sulfur has four electrons around it in this structure (one from each of its four bonds) which is two electrons more than the number of valence electrons it would have normally, and as such it carries a formal charge of +2.

If instead we made a structure for the sulfate ion with an expanded octet, it would look like this:

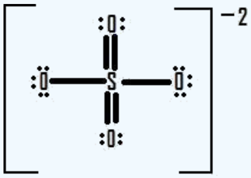


Figure 8.2.1.13

Looking at the formal charges for this structure, the sulfur ion has six electrons around it (one from each of its bonds). This is the same amount as the number of valence electrons it would have naturally. This leaves sulfur with a formal charge of zero.

The two oxygens that have double bonds to sulfur have six electrons each around them (four from the two lone pairs and one each from the two bonds with sulfur). This is the same amount of electrons as the number of valence electrons that oxygen atoms have on their own, and as such both of these oxygen atoms have a formal charge of zero. The two oxygens with the single bonds to sulfur have seven electrons around them in this structure (six from the three lone pairs and one from the bond to sulfur). That is one electron more than the number of valence electrons that oxygen would have on its own, and as such those two oxygens carry a formal charge of -1. Remember that with formal charges, the goal is to keep the formal charges (or the difference between the formal charges of each atom) as small as possible. The number of and values of the formal charges on this structure (-1 and 0 (difference of 1) in Figure $8.2.1.12$, as opposed to +2 and -1 (difference of 3) in Figure $8.2.1.12$) is significantly lower than on the structure that follows the octet rule, and as such an expanded octet is plausible, and even preferred to a normal octet, in this case.

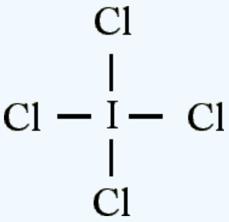
8.2.1.3 ICl_4^- Example : The Ion

Draw the Lewis structure for ICl_4^- ion.

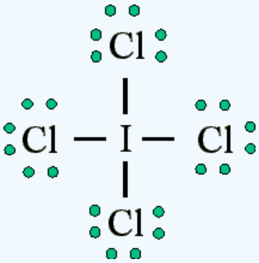
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

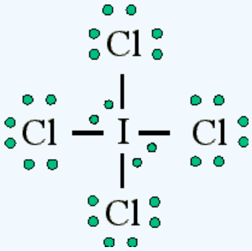
2. Draw the connectivities:



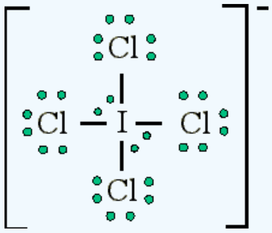
3. Add octet of electrons to outer atoms:



4. Add extra electrons (36-32=**4**) to central atom:



5. The ICl_4^- ion thus has 12 valence electrons around the central Iodine (in the 5*d* orbitals)



> Expanded Lewis structures are also plausible depictions of molecules when experimentally determined bond lengths suggest partial double bond characters even when single bonds would already fully fill the octet of the central atom. Despite the cases for expanded octets, as mentioned for incomplete octets, it is important to keep in mind that, in general, the octet rule applies.

Summary

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an odd number of valence electrons, (2) When there are too few valence electrons, and (3) when there are too many valence electrons

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Contributors and Attributions

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8.3: Resonance Structures and Formal Charge

Learning Objectives

- To understand the concept of resonance.

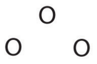
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integral number of covalent bonds.

Sometimes one Lewis Structure is not Enough

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

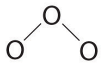
Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



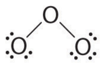
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



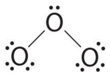
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain



and have 2 electrons left over.

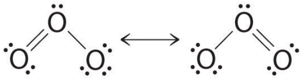
5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either

Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



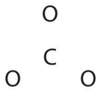
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> *When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.*

The Carbonate (CO_3^{2-}) Ion

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

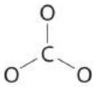
1. Because carbon is the least electronegative element, we place it in the central position:



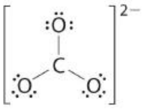
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:



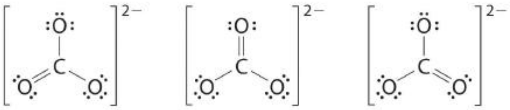
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:



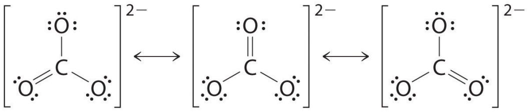
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



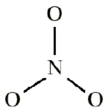
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

The actual structure is an average of these three resonance structures.

The Nitrate (NO_3^-) ion

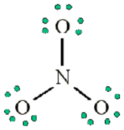
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

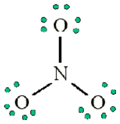


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

3. Add octet electrons to the atoms bonded to the center atom:

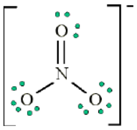


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

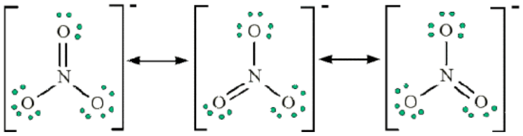
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



A double bond is added between one oxygen and the central nitrogen. The molecule has a negative charge.

6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the NO_3^- ion to be somewhat shorter than a single bond.

Example 8.3.1: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

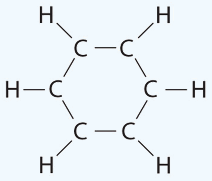
Asked for: resonance structures

Strategy:

A. Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.
B. Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.
C. Draw the resonance structures for benzene.

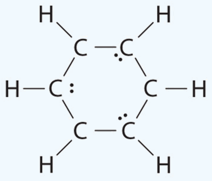
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



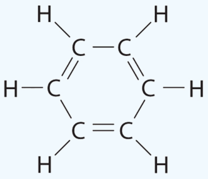
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

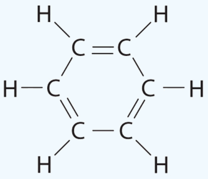


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

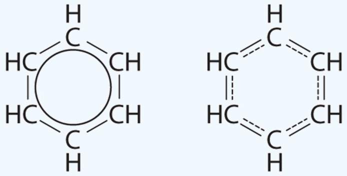
C There are, however, two ways to do this:



and



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:

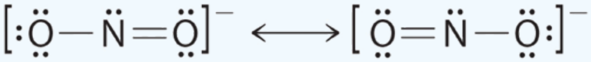


Benzene

Exercise 8.3.1: Nitrite Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



There is a double bond between one oxygen and the nitrogen, It can be found on the left oxygen or the right oxygen.

Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

Warning

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example 8.3.1. One would expect the double bonds to be shorter than the single bonds, but if one overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

Resonance structures is a mechanism that allows us to use all of the possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms can be in between - a carbon-carbon bond could be mostly single bond with a little bit of double bond character and a partial negative charge, for example.

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

8.4: Polar Covalent Bonds

Learning Objectives

- To define electronegativity and bond polarity
- To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, while the bonding electron pair is shared equally in the covalent bond in Cl_2, in $NaCl$ the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. As demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity** (represented by the Greek letter *chi*, χ, pronounced "ky" as in "sky"), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom's electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

> *Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.*

Electronegativity is a function of:

1. the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and
2. the atom's ***electron affinity*** (how strongly the atom attracts other electrons).

Both of these are properties of the *isolated* atom. An element will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always endothermic, or positive for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

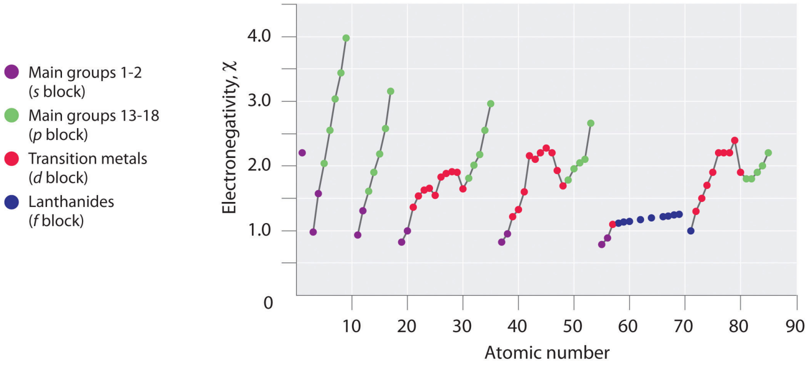
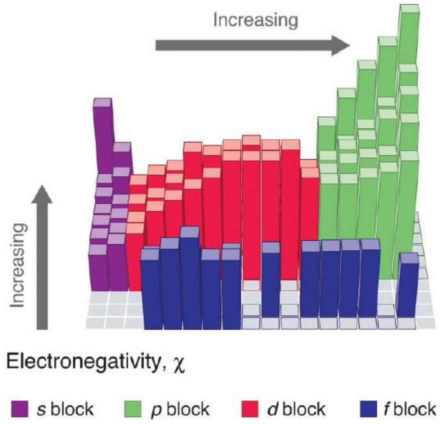


Figure 8.4.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

The main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

Periodic variations in Pauling's electronegativity values are illustrated in Figures 8.4.1 and 8.4.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

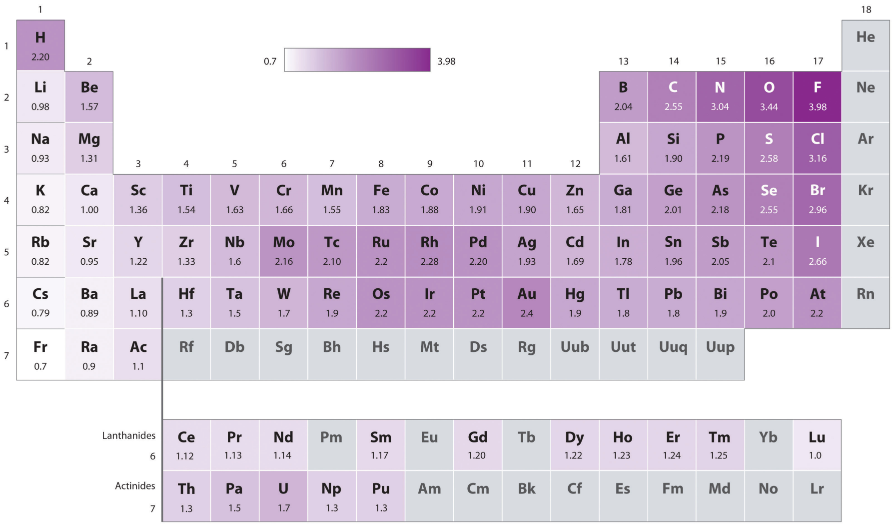


The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electronegativity increase from bottom to top and left to right.

Figure 8.4.2: *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

Linus Pauling (1901-1994)

When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school, but was later denied a high school degree, and had to work several jobs to put himself through college. Pauling would go on to become one of the most influential chemists of the century if not all time. He won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			

Lanthanides 6	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb	Lu 1.0
Actinides 7	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem, e.g., the Mulliken, Allred-Rochow, and Allen electronegativity scales. The Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity, showing the relationship between electronegativity and these other periodic properties.

Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity (χ ≥ 2.2 in Figure $8.4.2$) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities (χ ~ 2.0). These are the **metalloids** (or semimetals), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure $8.4.3$ shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

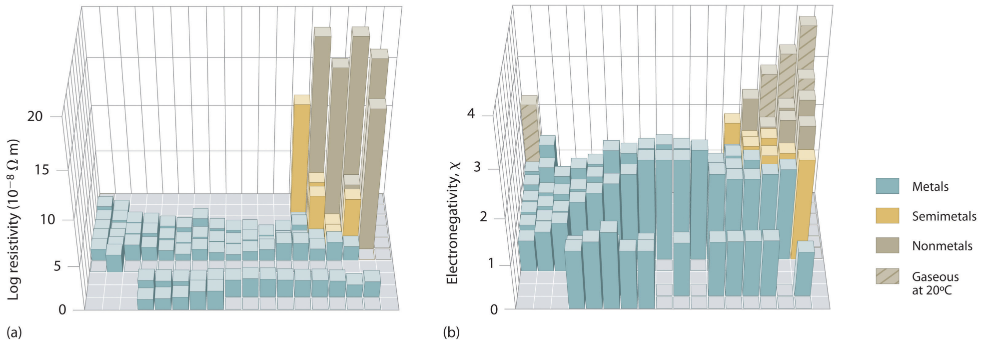


Figure 8.4.3: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

Metals are blue, semimetals are yellow, nonmetals are gray, gaseous at 20 degrees C are gray with dashed lines.

> Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states(opens in new window) are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

✓ Example 8.4.1: Increasing Electronegativity

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.
B. Arrange the elements in order of increasing electronegativity.
C. Classify each element as a metal, a nonmetal, or a metalloid according to its location about the diagonal belt of metalloids running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 8.4.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{\text{Cl}} > \chi_{\text{Se}}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{\text{Sr}} < \chi_{\text{Si}} < \chi_{\text{Se}} < \chi_{\text{Cl}}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of metalloids running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a metalloid, and Se and Cl are nonmetals.

? Exercise 8.4.1

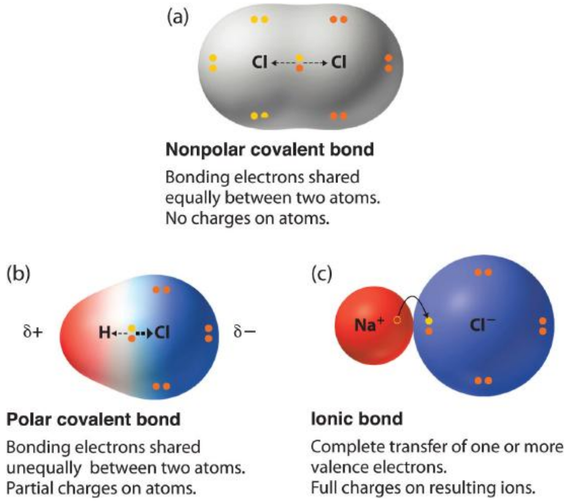
On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Answer

Rb < Zr < Ge < N < O; metals (Rb, Zr); metalloid (Ge); nonmetal (N, O)

Percent Ionic Character of a Covalent polar bond

The two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that electrons are shared unequally between the bonded atoms. Figure 8.4.4 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a polar bond.



Nonpolar covalent bond
Bonding electrons shared
equally between two atoms.
No charges on atoms.

Polar covalent bond
Bonding electrons shared
unequally between two atoms.
Partial charges on atoms.

Ionic bond
Complete transfer of one or more
valence electrons.
Full charges on resulting ions.

Figure 8.4.4: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{\textit{less electronegative}}{A}} \quad - \quad \underset{\delta^-}{\overset{\textit{more electronegative}}{B}} \tag{8.4.1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta^+}{H} \quad - \quad \overset{\delta^-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

> Bond polarity and ionic character **increase** with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge *Q* on the bonded atoms and the distance *r* between the partial charges:

$$\mu = Qr \tag{8.4.2}$$

where *Q* is measured in coulombs (C) and *r* in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot \cdot m \tag{8.4.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 8.4.4).

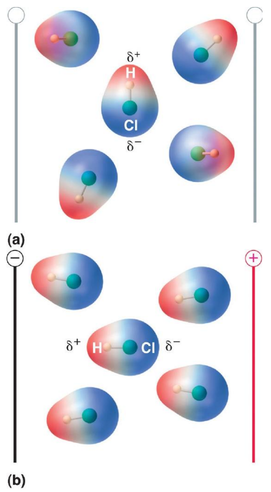


Figure 8.4.5: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field. In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 8.4.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$Q = \frac{\mu}{r} = 1.109\ \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{127.8\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 2.901 \times 10^{-20}\ C \tag{8.4.4}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901\times 10^{-20}\ \cancel{C}}{1.6022\times 10^{-19}\ \cancel{C}} = 0.1811\ e^{-} \tag{8.4.5}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta^+}{H} \quad - \quad \overset{\delta^-}{Cl}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta^+}{H} \quad - \quad \overset{0.18\delta^-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule. Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:

$$\overset{+\!\!\!\longrightarrow}{\mathrm{H{-}Cl}}$$

The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 8.4.6 shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure 8.4.6 show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 8.4.2.

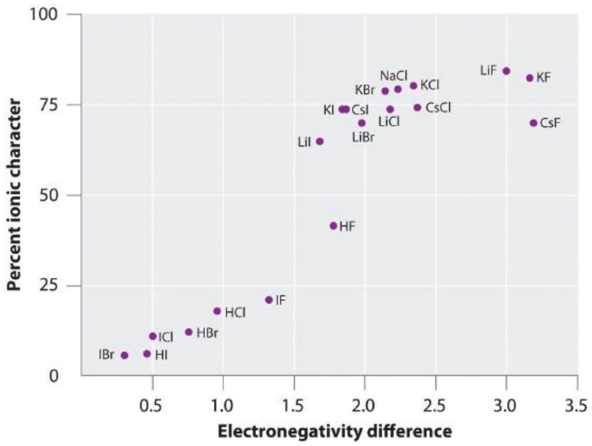


Figure 8.4.6: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

✓ Example 8.4.2

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 8.4.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r} = 9.001\ \cancel{D}\left(\frac{3.3356\times10^{-30}\ C\cdot\ \cancel{m}}{1\ \ \cancel{D}}\right)\left(\frac{1}{236.1\ \ \cancel{pm}}\right)\left(\frac{1\ \ \cancel{pm}}{10^{-12}\ \ \cancel{m}}\right) = 1.272\times10^{-19}\ C$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\%\ ionic\ character = \left(\frac{1.272\times10^{-19}\ \ \cancel{C}}{1.6022\times10^{-19}\ \ \cancel{C}}\right)(100) = 79.39\% \simeq 79\%$$

? Exercise 8.4.2

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer

55.5%

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity. The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

8.5: Bond Energies, Strengths, and Lengths

Learning Objectives

- The define Bond-dissociation energy (bond energy)
- To correlate bond strength with bond length
- To define and used *average bond energies*

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds. The stability of a molecule is a function of the strength of the covalent bonds holding the atoms together.

The Relationship between Bond Order and Bond Energy

Triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however. Table 8.5.1 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table 8.5.1: Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										**Multiple Bonds**	
H–H	432	C–C	346	N–N	≈167	O–O	≈142	F–F	155	C=C	602
H–C	411	C–Si	318	N–O	201	O–F	190	F–Cl	249	C≡C	835
H–Si	318	C–N	305	N–F	283	O–Cl	218	F–Br	249	C=N	615
H–N	386	C–O	358	N–Cl	313	O–Br	201	F–I	278	C≡N	887
H–P	≈322	C–S	272	N–Br	243	O–I	201	Cl–Cl	240	C=O	749
H–O	459	C–F	485	P–P	201	S–S	226	Cl–Br	216	C≡O	1072
H–S	363	C–Cl	327			S–F	284	Cl–I	208	N=N	418
H–F	565	C–Br	285			S–Cl	255	Br–Br	190	N≡N	942
H–Cl	428	C–I	213			S–Br	218	Br–I	175	N=O	607
H–Br	362	Si–Si	222					I–I	149	O=O	494
H–I	295	Si–O	452							S=O	532

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th ed. (1993).

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H–F bond is stronger than an H–I bond, H–C is stronger than H–Si, H–N is stronger than H–P, H–O is stronger than H–S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 8.11).
2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C–C single bond is stronger than the Si–Si single bond, which is stronger than the Ge–Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 8.11. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N–N, O–O, and F–F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore

$$\text{Cl–Cl} > \text{Br–Br} > \text{F–F} > \text{I–I}$$

   Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

> Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.

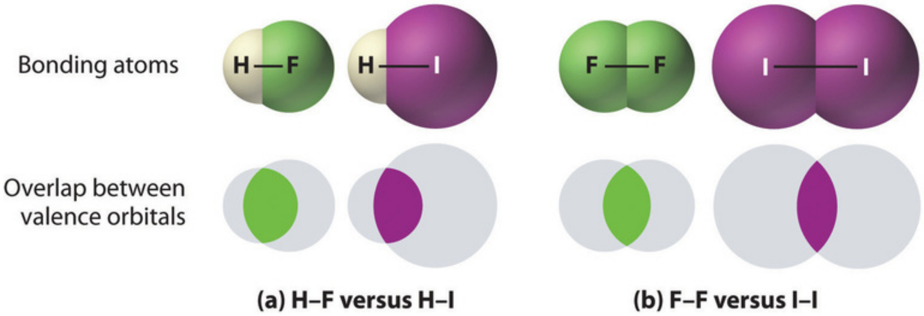


Figure 8.5.1: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space *relative to the size of the bonded atom* decreases; that is, the *percentage* of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, as we discussed for the SO_4^{2-} ion in Section 8.6. In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2.

> *Bond strengths increase as bond order* ***increases****, while bond distances* ***decrease****.*

The Relationship between Molecular Structure and Bond Energy

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table 8.5.2); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 8.5.1 are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table 8.5.2: Energies for the Dissociation of Successive C–H Bonds in Methane. Source: Data from CRC *Handbook of Chemistry and Physics* (2004).

Reaction	D (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	439
$CH_3(g) \rightarrow CH_2(g) + H(g)$	462
$CH_2(g) \rightarrow CH(g) + H(g)$	424
$CH(g) \rightarrow C(g) + H(g)$	338

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \tag{8.5.1}$$

The ≈ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn}.

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction that occurs during the combustion of gasoline:

$$CH_3(CH_2)_5CH_3(l) + 11\,O_2(g) \rightarrow 7\,CO_2(g) + 8\,H_2O(g) \tag{8.5.2}$$

In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

Binds Broken (kJ/mol) and Bonds Formed (kJ/mol)

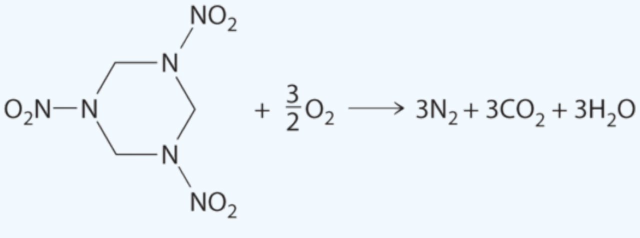
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately −4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481\,7 kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f^o values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

✓ Example 8.5.1: Explosives

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 8.5.1 to estimate the ΔH_{rxn} per mole of RDX.



RDX

Given: chemical reaction, structure of reactant, and Table 8.5.1.

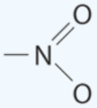
Asked for: ΔH_{rxn} per mole

Strategy:

A. List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.
B. Use Equation 8.5.1 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group ($–NO_2$) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)

Bonds Broken (kJ/mol)		**Bonds Broken (kJ/mol)**	
6 C–H	411 × 6 = 2466	6 C=O	799 × 6 = 4794
3 N–N	167 × 3 = 501	6 O–H	459 × 6 = 2754
3 N–O	201 × 3 = 603		**Total** = 10,374
3 N=O	607 × 3 = 1821		
1.5 O=O	494 × 1.5 = 741		
	Total = 7962		

B From Equation $8.5.1$, we have

$$\begin{aligned} \Delta H_{rxn} &\approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \\ &= 7962 \ kJ/mol - 10,374 \ kJ/mol \\ &= -2412 \ kJ/mol \end{aligned}$$

Thus this reaction is also highly exothermic

? Exercise $8.5.1$: Freon

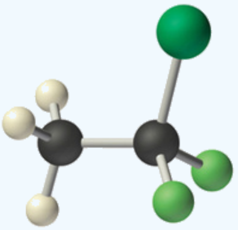
The molecule HCFC-142b is a hydrochlorofluorocarbon that is used in place of chlorofluorocarbons (CFCs) such as the Freons and can be prepared by adding HCl to 1,1-difluoroethylene:

1,1-difluoroethylene reacts with <span class=HCL to produce CH3Cf2Cl and HCFC142b." data-cke-saved-src="/@api/deki/files/129585/imageedit_31_2777381278.png" src="/@api/deki/files/129585/imageedit_31_2777381278.png" data-quail-id="371">

Use tabulated bond energies to calculate ΔH_{rxn}.

Answer

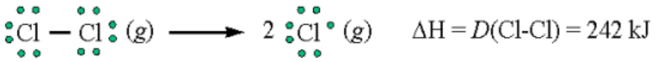
−54 kJ/mol



HCFC-142b

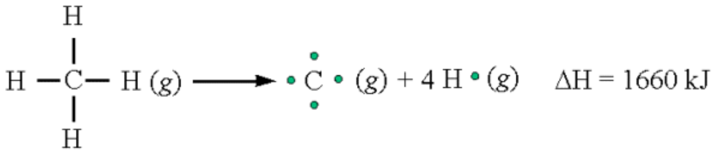
Bond Dissociation Energy

Bond Dissociation Energy (also referred to as Bond energy) is the enthalpy change (ΔH, heat input) required to break a bond (in 1 mole of a gaseous substance)



where "D(Cl-Cl)" represents the bond dissociation energy for the Cl-Cl bonc

What about when we have a compound which is not a diatomic molecule? Consider the dissociation of ***methane***:



There are four equivalent C-H bonds, thus we can that the dissociation energy for a single C-H bond would be:

$$\begin{aligned} D(C-H) &= (1660/4)\, kJ/mol \\ &= 415\, kJ/mol \end{aligned}$$

> The bond energy for a given bond is influenced by the rest of the molecule. However, this is a relatively small effect (suggesting that bonding electrons are localized between the bonding atoms). Thus, the bond energy for most bonds varies little from the average bonding energy for that type of bond

Bond energy is always a *positive* value - it takes energy to break a covalent bond (conversely energy is released during bond formation)

Table 8.5.4: Average bond energies:

Bond	**(kJ/mol)**
C-F	485
C-Cl	328
C-Br	276
C-I	240
C-C	348
C-N	293
C-O	358
C-F	485
C-C	348
C=C	614
C≡C	839

The more stable a molecule (i.e. the stronger the bonds) the less likely the molecule is to undergo a chemical reaction.

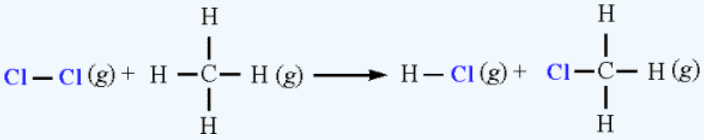
Bond Energies and the Enthalpy of Reactions

If we know which bonds are broken and which bonds are made during a chemical reaction, we can estimate the enthalpy change of the reaction (ΔH_{rxn}) even if we do not know the enthalpies of formation ((ΔH_f^o)for the reactants and products:

$$\Delta H = \sum \text{bond energies of broken bonds} - \sum \text{bond energies of formed bonds} \tag{8.5.3}$$

✓ Example 8.5.2: Chlorination of Methane

What is the enthalpy of reaction between 1 mol of chlorine and 1 mol methane?



$$Cl{-}Cl\,(g) + CH_4\,(g) \longrightarrow H{-}Cl\,(g) + CH_3Cl\,(g)$$

Solution

We use Equation 8.5.3, which requires tabulating bonds broken and formed.

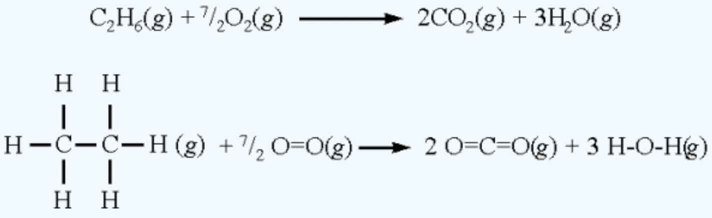
- **Bonds broken**: 1 mol of Cl-Cl bonds, 1 mol of C-H bonds
- **Bonds formed**: 1 mol of H-Cl bonds, 1 mol of C-Cl bonds

$$\begin{aligned}\Delta H &= [D(Cl-Cl) + D(C-H)] - [D(H-Cl) + D(C-Cl)] \\ &= [242 kJ + 413 kJ] - [431 kJ + 328 kJ] \\ &= -104\, kJ\end{aligned}$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

✓ Example 8.5.3: Combustion of Ethane

What is the enthalpy of reaction for the combustion of 1 mol of ethane?



$$C_2H_6(g) + {}^7/_2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$

$$H_3C{-}CH_3\,(g) + {}^7/_2\ O{=}O(g) \longrightarrow 2\ O{=}C{=}O(g) + 3\ H{-}O{-}H(g)$$

Solution

We use Equation 8.5.3, which requires tabulating bonds broken and formed.

- **bonds broken**: 6 moles C-H bonds, 1 mol C-C bonds, $^7/_2$ moles of O=O bonds

- **bonds formed**: 4 moles C=O bonds, 6 moles O-H bonds

$$\begin{aligned}\Delta H \quad &= [(6\times 413)+(348)+(\frac{7}{2}\times 495)]-[(4\times 799)+(6\times 463)]\\ &= 4558-5974\\ &= -1416\ kJ\end{aligned}$$

Therefor the reaction is exothermic.

Table 8.5.5: Bond strength and bond length

Bond	Bond Energy (kJ/mol)	Bond Length (Å)
C-C	348	1.54
C=C	614	1.34
C≡C	839	1.

As the number of bonds between two atoms increases, the bond grows shorter and stronger

Summary

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

The breakage and formation of bonds is similar to a relationship: you can either get married or divorced and it is more favorable to be married.

- Energy is always **released** to make bonds, which is why the enthalpy change for breaking bonds is always **positive**.
- Energy is always **required** to break bonds. Atoms are much happier when they are "married" and release energy because it is easier and more stable to be in a relationship (e.g., to generate *octet electronic configurations*). The enthalpy change is always **negative** because the system is releasing energy when forming bond.

CHAPTER OVERVIEW

9: Chemical Bonding II - Advanced Bonding Models

In 1912, Max von Laue, at the University of Munich in Germany, postulated that atoms in a crystal lattice had a regular, periodic structure with interatomic distances on the order of 1 A. Without having any evidence to support his claim on the periodic arrangements of atoms in a lattice, he further postulated that the crystalline structure can be used to diffract x-rays, much like a gradient in an infrared spectrometer can diffract infrared light. His postulate was based on the following assumptions: the atomic lattice of a crystal is periodic, x- rays are electromagnetic radiation, and the interatomic distance of a crystal are on the same order of magnitude as x- ray light. Laue's predictions were confirmed when two researchers: Friedrich and Knipping, successfully photographed the diffraction pattern associated with the x-ray radiation of crystalline copper (II) sulfate pentahydrate - and the science of x-ray crystallography was born. X-ray crystallography remains to this day the primary tool used by researchers in characterizing the structure and bonding of various compounds. In this Chapter, we will discuss the more advanced bonding models that predict molecular structures in three dimensions.

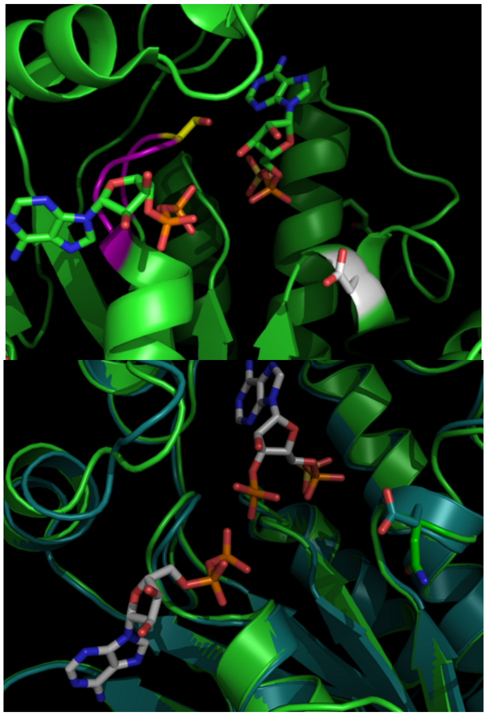


Figure 1: This is the structure of APS Kinase co-crystallized with ligands ADP and APS created via pymol by an undergrad working in the Structural Biology lab at UC Davis; Bottom right) This is the mutant overlay of APS kinase. The teal is the wild - type and the lime green is the mutant. D63 (from the wild-type) is mutated to asparagine. Images created by pymol by an undergrad working in the Structural Biology lab at UC Davis.

Chapter Sections

Contributors and Attributions

9.1: Valence Bond Theory - Bonds as Orbital Overlaps

Learning Objectives

- To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of H_2O and NH_3, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including SrF_2 and BaF_2, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

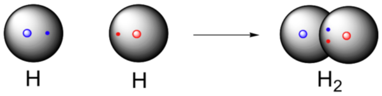
Introduction

As we have talked about using Lewis structures to depict the bonding in covalent compounds, we have been very vague in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the ‘sharing’ of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

The **valence bond theory** is introduced to describe bonding in covalent molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. To explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

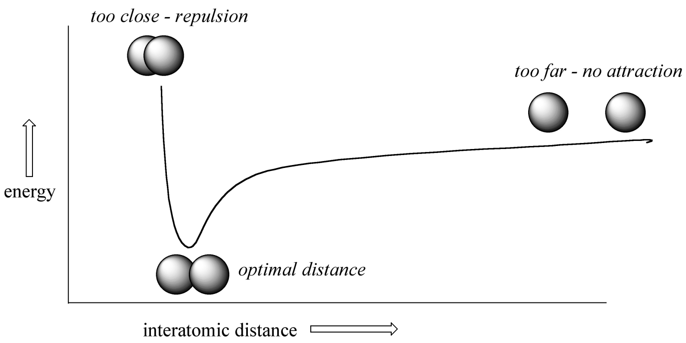
Example: The H_2 molecule

The simplest case to consider is the hydrogen molecule, H_2. When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1*s* orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals. In simple terms, we can say that both electrons now spend more time *between* the two nuclei and thus hold the atoms together. As we will see, the situation is not quite so simple as that, because the electron pair must still obey quantum mechanics - that is, the two electrons must now occupy a *shared orbital space*. This will be the essential principle of valence bond theory.



These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of ‘chemical glue’ holding the two nuclei together.

How far apart are the two nuclei? That is a very important issue to consider. If they are too far apart, their respective 1*s* orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second. However, something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.



Graph of increasing energy against increasing interatomic distance. If the two are too close there is repulsion, if the two are too far there is no attraction. There is an optimal distance.

At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have a very unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**. For the H_2 molecule, this distance is 74 x 10^{-12} meters, or 0.74 Å (Å means angstrom, or 10^{-10} meters). Likewise, the difference in potential energy between the lowest state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond energy**. For the hydrogen molecule, this energy is equal to about 104 kcal/mol.

Every covalent bond in a given molecule has a characteristic length and strength. In general, carbon-carbon single bonds are about 1.5 Å long (Å means angstrom, or 10^{-10} meters) while carbon-carbon double bonds are about 1.3 Å, carbon-oxygen double bonds are about 1.2 Å, and carbon-hydrogen bonds are in the range of 1.0 – 1.1 Å. Most covalent bonds in organic molecules range in strength from just under 100 kcal/mole (for a carbon-hydrogen bond in ethane, for example) up to nearly 200 kcal/mole. You can refer to tables in reference books such as the CRC Handbook of Chemistry and Physics for extensive lists of bond lengths, strengths, and many other data for specific organic compounds.

Balls and Springs

Although we tend to talk about "bond length" as a specific distance, it is not accurate to picture covalent bonds as rigid sticks of unchanging length - rather, it is better to picture them as *springs* which have a defined length when relaxed, but which can be compressed, extended, and bent. This 'springy' picture of covalent bonds will become very important, when we study the analytical technique known as infrared (IR) spectroscopy.

Valence Bond Theory: A Localized Bonding Approach

You learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm (Figure 9.1.1). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a *maximum of two electrons with opposite spin*, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1*s* atomic orbital of one hydrogen atom overlaps with the singly occupied 1*s* atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure 9.1.1).

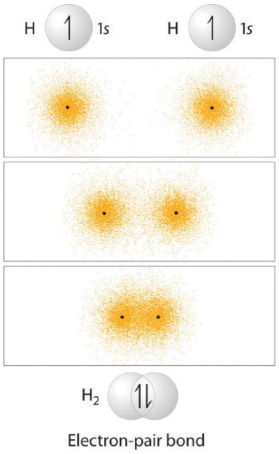


Figure 9.1.1: Overlap of Two Singly Occupied Hydrogen 1*s* Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1*s* orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory, which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure 9.1.2 shows an electron-pair bond formed by the overlap of two *ns* atomic orbitals, two *np* atomic orbitals, and an *ns* and an *np* orbital where $n = 2$. Notice that bonding overlap occurs when the interacting atomic orbitals have the correct orientation (are "pointing at" each other) and are *in phase* (represented by colors in Figure 9.1.2).

> Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

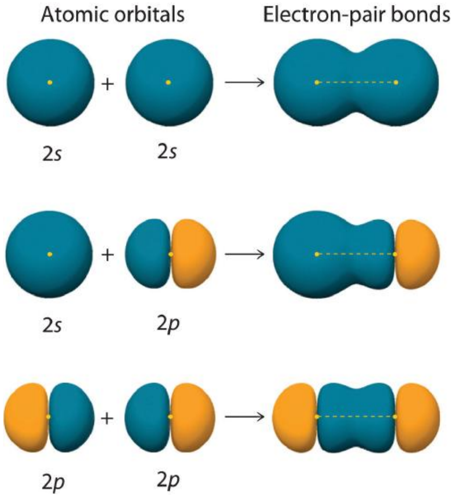


Figure 9.1.2 : Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two *ns* atomic orbitals (a), an *ns* and an *np* atomic orbital (b), and two *np* atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion:

The ground state of beryllium has one electron pair in the 2s orbital. The excited state of beryllium takes one of the electrons from the 2s orbital and moves it to the 2p orbital.

In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization.

Contributors and Attributions

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

9.2: Hybridization and Hybrid Orbitals in VBT

The localized **valence bond theory** uses a process called **hybridization**, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

Hybridization of *s* and *p* Orbitals

In BeH_2, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure $9.2.1$.

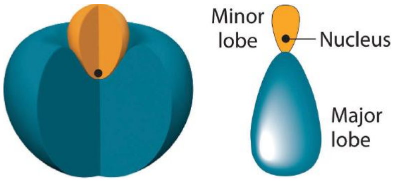


Figure $9.2.1$: The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference A − B can also be written as A + (−B), in Figure $9.2.2$ and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by −1 and adding. This gives us Equation 9.2.2, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{9.2.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{9.2.2}$$

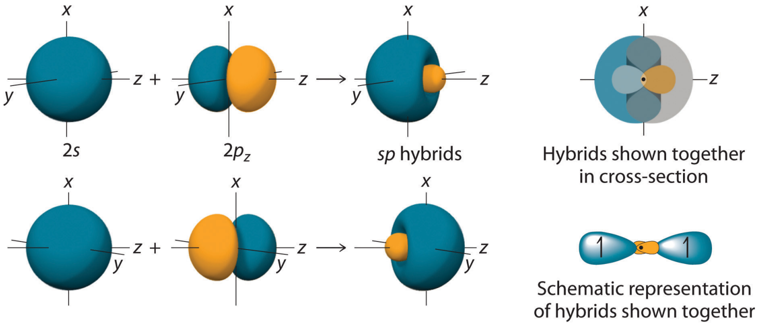


Figure $9.2.2$: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:

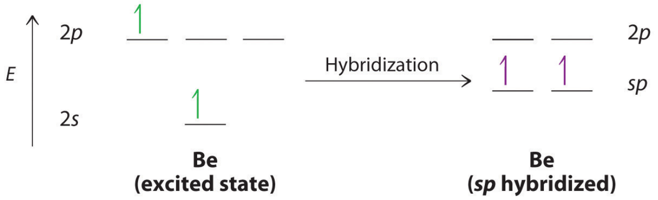


Figure 9.2.3. each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in BeH_2 are equivalent in energy and why BeH_2 has a linear geometry.

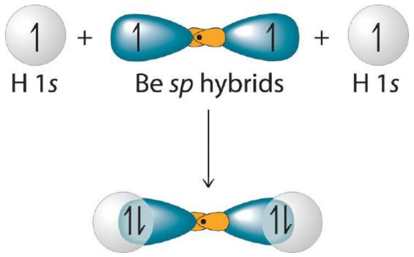


Figure 9.2.3: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1*s* orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule is linear.

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure 9.2.4). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

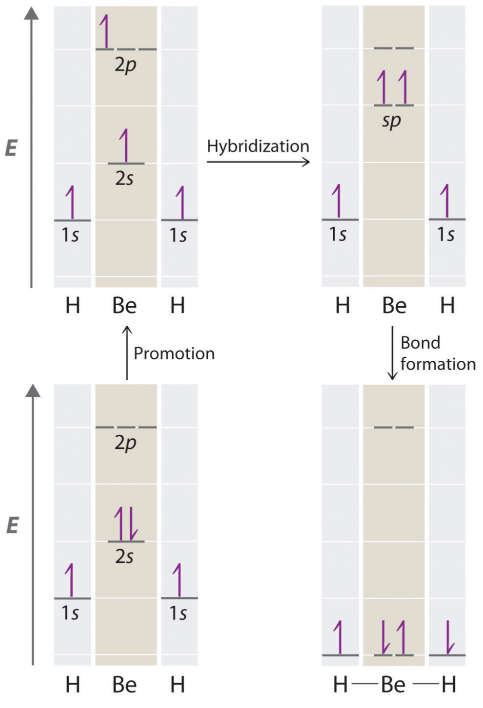


Figure 9.2.4: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable *only* if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.

The concept of hybridization also explains why boron, with a $2s^22p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2*s* electrons to an unoccupied 2*p* orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2*s* and two 2*p* orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:

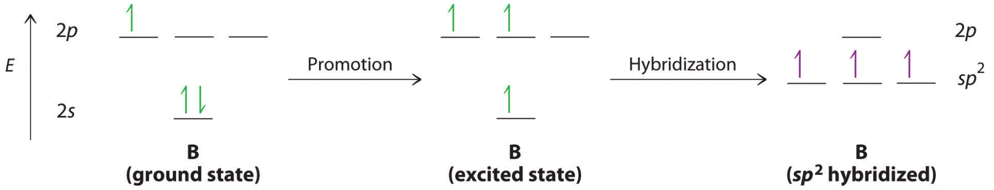


Figure 9.2.5). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced “s-p-two” or “s-p-squared”). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

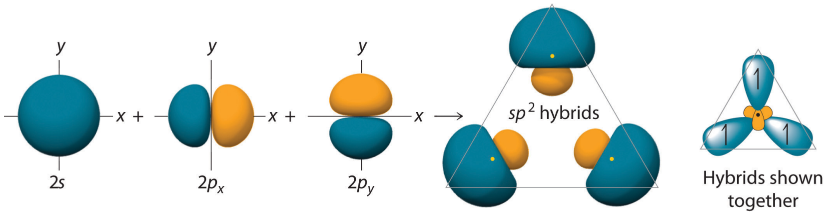


Figure 9.2.5: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

Looking at the $2s^22p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate sp^3 (“s-p-three” or “s-p-cubed”) hybrid orbitals, each with a single electron:

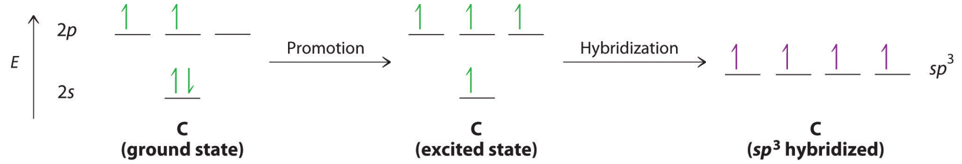


Figure 9.2.6). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy. Thus, methane (CH_4) is a tetrahedral molecule with four equivalent C-H bonds.

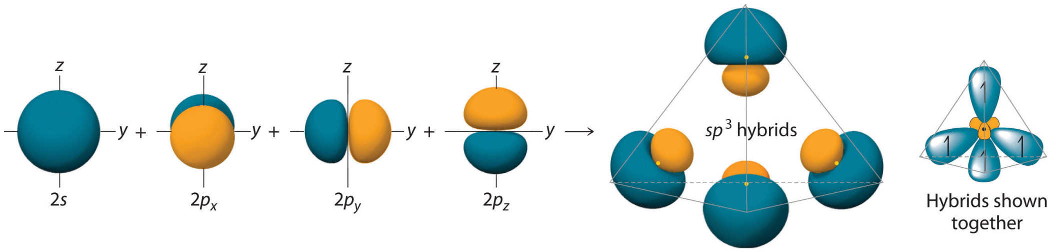


Figure 9.2.6: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that only form in certain chemical reactions.

> *Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.*

The bonding in molecules such as NH_3 or H_2O, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3, for example, N, with a $2s^22p^3$ valence electron configuration, can hybridize its 2*s* and 2*p* orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:

The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O. Unfortunately, however, recent experimental evidence indicates that in NH_3 and H_2O, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

✓ Example 9.2.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A. Using the VSEPR approach to determine the number of electron pairs and the molecular geometry of the molecule.
B. From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

1. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^23p^4$ valence electron configuration with six electrons, but by hybridizing its 3*s* and 3*p* orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^22p^2$ valence electron configuration. By hybridizing its 2*s* and 2*p* orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

? Exercise 9.2.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion
b. hydrazine ($H_2N–NH_2$)

Answer a

B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.

Answer b

Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

Hybridization Using d Orbitals

Hybridization is not restricted to the *ns* and *np* atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence $(n-1)d$ orbitals as well as its *ns* and *np* orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in PF_5 and SF_6). Using the *ns* orbital, all three *np* orbitals, and one $(n-1)d$ orbital gives a set of five sp^3d hybrid orbitals that point toward the vertices of a trigonal bipyramid (part (a) in Figure 9.2.7). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the *ns* orbital, all three *np* orbitals, and *two nd* orbitals gives a set of six equivalent sp^3d^2 hybrid orbitals oriented toward the vertices of an octahedron (part (b) in Figure 9.5.6). In the VSEPR model, PF_5 and SF_6 are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which sp^3d or sp^3d^2 hybrid orbitals are used for bonding.

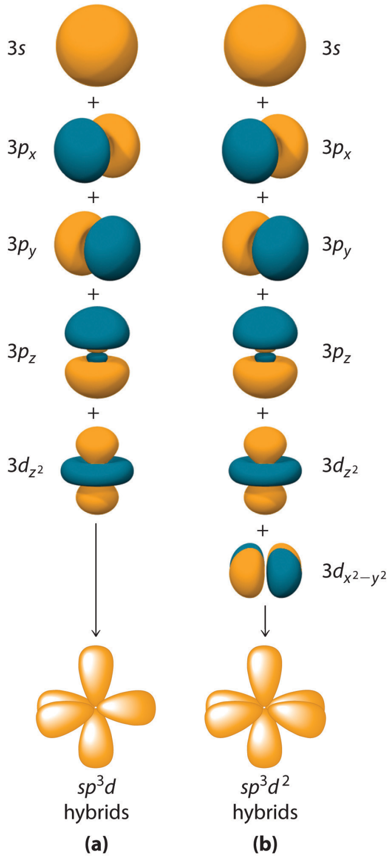


Figure 9.2.7: Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

✓ Example $9.2.2$

What is the hybridization of the central atom in each species? Describe the bonding in each species.

a. XeF_4
b. $SO_4{}^{2-}$
c. SF_4

Given: three chemical species

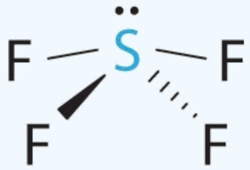
Asked for: hybridization of the central atom

Strategy:

A. Determine the geometry of the molecule using the strategy in Example $9.2.1$. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.
B. Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

Solution:

a. **A** Using the VSEPR model, we find that Xe in XeF_4 forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be sp^3d^2 hybridized. **B** With 12 electrons around Xe, four of the six sp^3d^2 hybrid orbitals form Xe–F bonds, and two are occupied by lone pairs of electrons.
b. **A** The S in the $SO_4{}^{2-}$ ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be sp^3 hybridized to generate four S–O bonds. **B** Filling the sp^3 hybrid orbitals with eight electrons from four bonds produces four filled sp^3 hybrid orbitals.
c. **A** The S atom in SF_4 contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:



To accommodate five electron pairs, the sulfur atom must be sp^3d hybridized. **B** Filling these orbitals with 10 electrons gives four sp^3d hybrid orbitals forming S–F bonds and one with a lone pair of electrons.

? Exercise $9.2.2$

What is the hybridization of the central atom in each species? Describe the bonding.

a. $PCl_4{}^+$
b. BrF_3
c. $SiF_6{}^{2-}$

Answer a

sp^3 with four P–Cl bonds

Answer a

sp^3d with three Br–F bonds and two lone pairs

Answer a

sp^3d^2 with six Si–F bonds

Hybridization using *d* orbitals allows chemists to explain the structures and properties of many molecules and ions. Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).

Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides (CF_4 and SiF_4), only SiF_4 reacts with F^- to give a stable hexafluoro dianion, SiF_6^{2-}. Because there are no 2*d* atomic orbitals, the formation of octahedral CF_6^{2-} would require hybrid orbitals created from 2*s*, 2*p*, and 3*d* atomic orbitals. The 3*d* orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp^3d^2 hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF_6^{2-} have never been prepared.

Example 9.2.3: OF_4

What is the hybridization of the oxygen atom in OF_4? Is OF_4 likely to exist?

Given: chemical compound

Asked for: hybridization and stability

Strategy:

A. Predict the geometry of OF_4 using the VSEPR model.
B. From the number of electron pairs around O in OF_4, predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

Solution:

A The VSEPR model predicts that OF_4 will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. **B** To accommodate five electron pairs, the O atom would have to be sp^3d hybridized. The only *d* orbital available for forming a set of sp^3d hybrid orbitals is a 3*d* orbital, which is *much* higher in energy than the 2*s* and 2*p* valence orbitals of oxygen. As a result, the OF_4 molecule is unlikely to exist. In fact, it has not been detected.

Exercise 9.2.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer a

sp^3d^2 hybridization; no

Summary

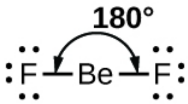
Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach. The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled ns^2 subshell to an empty np or $(n - 1)d$ valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an ns and an np orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of an ns and two or three np orbitals produces three equivalent **sp^2 hybrids** or four equivalent **sp^3 hybrids**, respectively. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two $(n - 1)d$ orbitals to give sets of five sp^3d or six **sp^3d^2 hybrid** orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

9.3: Valence Shell Electron-Pair Repulsion (VSEPR) Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure $9.3.2$) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure $9.3.2$).



A Lewis structure is shown. A fluorine atom with three lone pairs of electrons is single bonded to a beryllium atom which is single bonded to a fluorine atom with three lone pairs of electrons. The angle of the bonds between the two fluorine atoms and the beryllium atom is labeled, “180 degrees.”

Figure $9.3.2$: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure $9.3.3$ illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

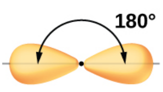
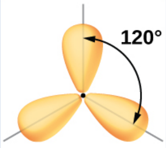
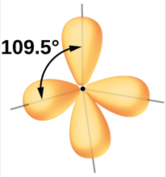
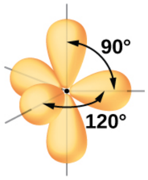
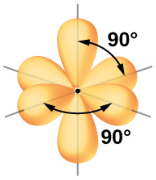
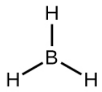
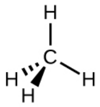
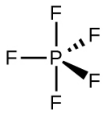
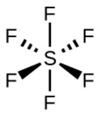
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	H—Be—H				
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 9.3.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

In this table summarizing the geometries proposed by VSPER Theory, the number of regions along with spatial arrangement, line-dash-wedge notation, and electron pair geometry are shown.

9.3.1: Lone Pairs and 3D Geometry

Learning Objectives

- To use the VSEPR model to predict molecular geometries.
- To predict whether a molecule has a dipole moment.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion** (VSEPR) model (pronounced “vesper”), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

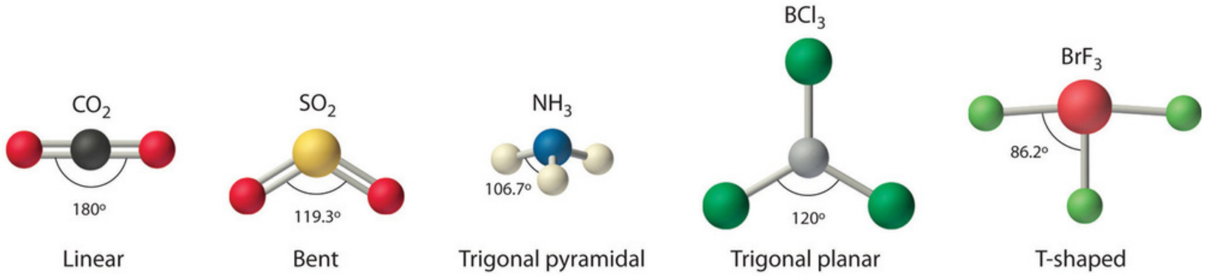
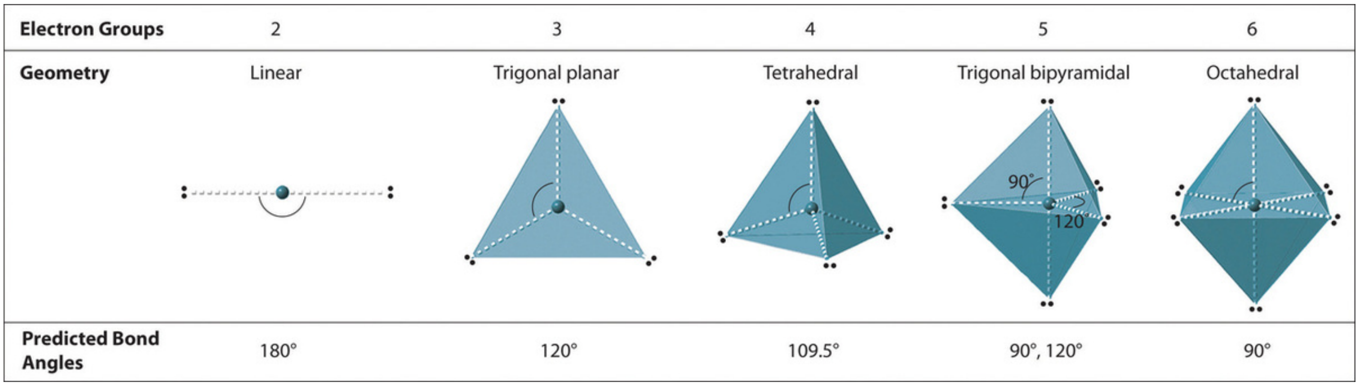


Figure 9.3.1.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figures $9.3.1.1$ and $9.3.1.2$



Electron Groups	2	3	4	5	6
Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Predicted Bond Angles	180°	120°	109.5°	90°, 120°	90°

Figure 9.3.1.2: Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions. (CC BY-NC-SA; anonymous)

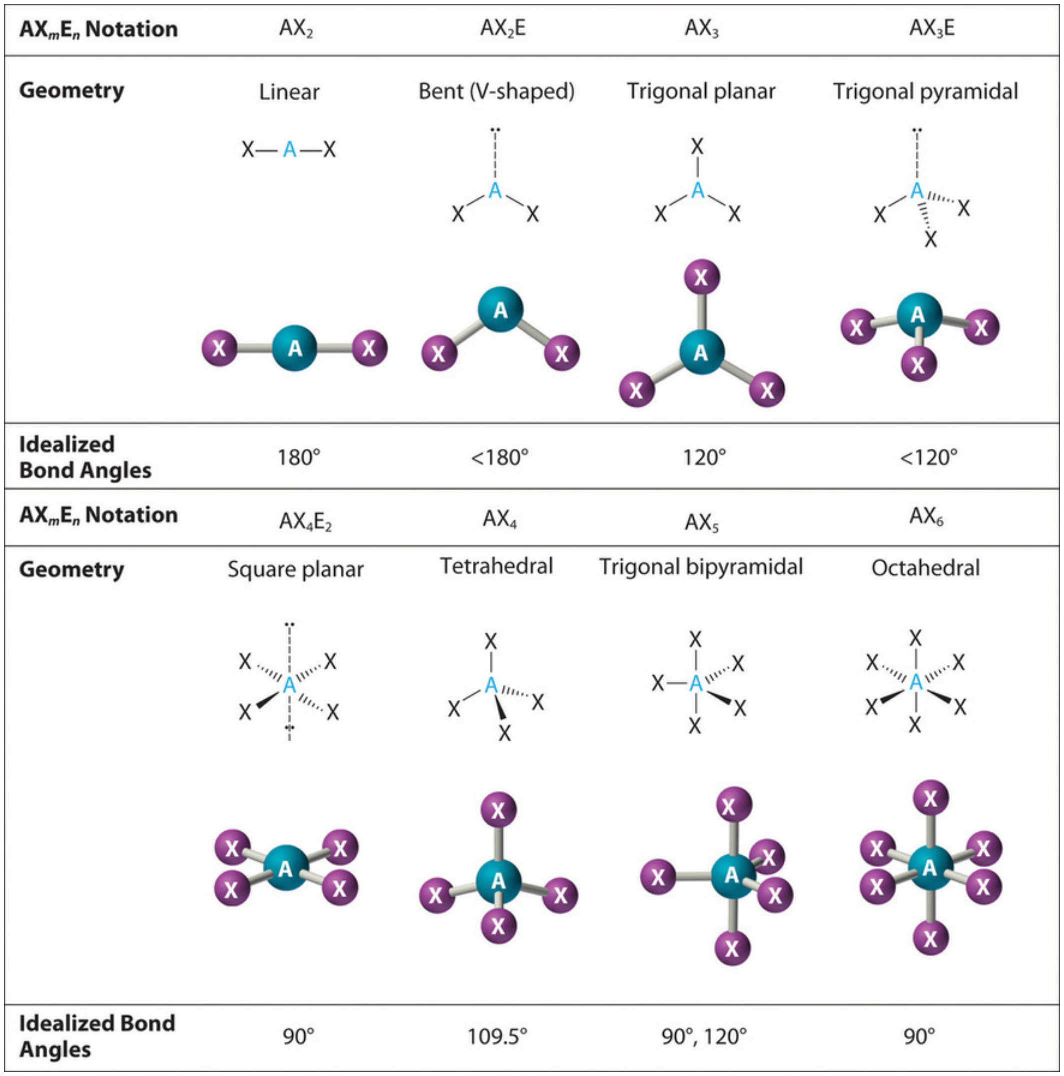
In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles. Using this information, we can describe the molecular geometry, the arrangement of the *bonded atoms* in a molecule or polyatomic ion.

VESPR Produce to predict Molecular geometry

This VESPR procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure 9.3.1.2 and Figure 9.3.1.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.



AX_mE_n Notation	AX_2	AX_2E	AX_3	AX_3E
Geometry	Linear	Bent (V-shaped)	Trigonal planar	Trigonal pyramidal
Idealized Bond Angles	180°	<180°	120°	<120°

AX_mE_n Notation	AX_4E_2	AX_4	AX_5	AX_6
Geometry	Square planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Idealized Bond Angles	90°	109.5°	90°, 120°	90°

Figure 9.3.1.3: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line. (CC BY-NC-SA; anonymous)

Linear, bent, trigonal planar, trigonal pyramidal, square planar, tetrahedral, trigonal bipyramidal, octahedral.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2 Molecules: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

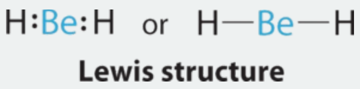


Figure 9.3.1.2 that the arrangement that minimizes repulsions places the groups 180° apart. (CC BY-NC-SA; anonymous)

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 9.3.1.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2 Molecules: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is

2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 9.3.1.3). The structure of CO_2 is shown in Figure 9.3.1.1.

Three Electron Groups

AX_3 Molecules: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is

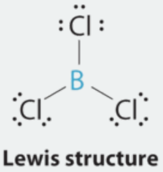


Figure 9.3.1.2): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 9.3.1.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 9.3.1.2

AX_3 Molecules: $CO_3{}^{2-}$

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as

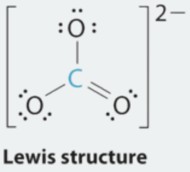
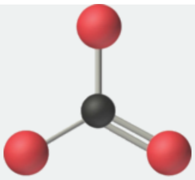


Figure 9.3.1.2).

The three oxygens are arranged in a triangular shape with carbon at the center. Two of the oxygens have three lone pairs. One ocht oxygens has 2 lone pairs and is double bonded to the carbon. The molecule has a minus 2 charge.

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure 9.3.1.3that the molecular geometry of $CO_3{}^{2-}$ is trigonal planar with bond angles of 120°.



In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX$_2$E Molecules: SO$_2$

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.

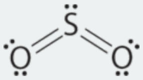


Figure 9.3.1.2): (CC BY-NC-SA; anonymous)

The two oxygens are double bonded to the sulfur. The oxygens have 2 lone pairs while sulfur had one lone pair.

3. There are two bonding pairs and one lone pair, so the structure is designated as AX$_2$E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 9.3.1.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO$_2$, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures 9.3.1.2and 9.3.1.3). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

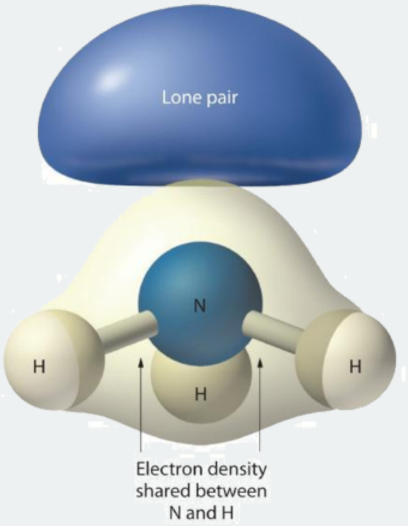
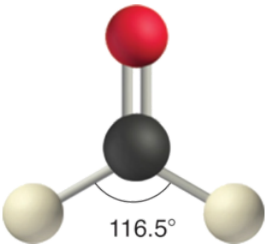


Figure 9.3.1.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair. (CC BY-NC-SA; anonymous)

As with SO$_2$, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH$_2$O (AX$_3$), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

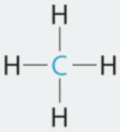


Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4 Molecules: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

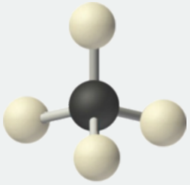


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 9.3.1.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

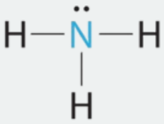
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 9.3.1.3).



Molecular geometry
(tetrahedral)

AX_3E Molecules: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the

angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 9.3.1.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 9.3.1.3and Figure 9.3.1.4).

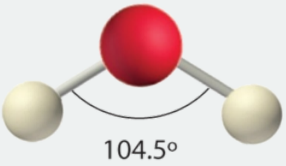
AX_2E_2 Molecules: H_2O

1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure

Figure 9.3.1.2: (CC BY-NC-SA; anonymous)

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.



Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5 Molecules: PCl_5

1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is

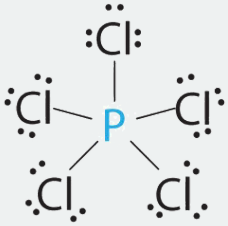
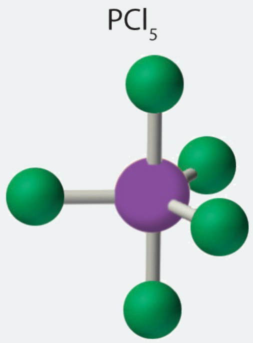


Figure 9.3.1.2): (CC BY-NC-SA; anonymous)

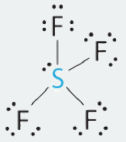
3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 9.3.1.3 The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



AX$_4$E Molecules: SF$_4$

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

Four fluorenes are bonded to a central sulfur. Each fluorine has three lone pairs. Sulfur has one lone pair.

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 9.3.1.2

3. We designate SF$_4$ as AX$_4$E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the axial position, we have three LP–BP repulsions at 90°. If we place it in the equatorial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the *equatorial position is more stable than the one with the lone pair in the axial position*. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

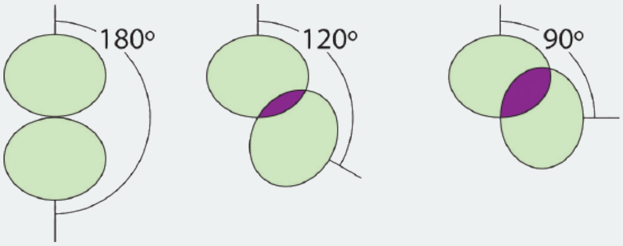
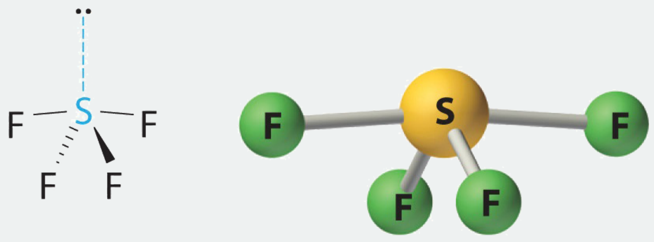


Figure 9.3.1.5: Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

180 degree angle has no shared space between teo electron pair, 120 degree angle has some shared area between two electron pairs. 90 degree angle has more shared space than 120.

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

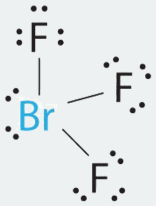
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F$_{axial}$–S–F$_{axial}$ angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX$_3$E$_2$ Molecules: BrF$_3$

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



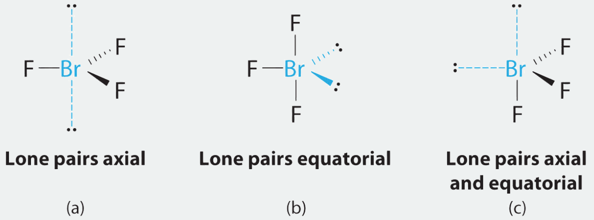
Lewis structure

Three fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has two lone pairs.

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX$_3$E$_2$ with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



Interactions	(a)	(b)	(c)
90° LP–LP	0	0	1
90° LP–BP	6	4	3

If the lone pairs are axiam, the 90 degree LP-LP interactions are o and the 90 degree LP-BP interaction is zero. If the Lone pares are equatorial there are zero 90 degree LP-LP interactions and four 90 degree LP-BP intereactions. If the lone pairs are axial and equatorial there is one 90 degree LP-LP interaction and three 90 degree LP-BP interaction.

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF$_3$ determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F$_{axial}$–Br–F$_{axial}$ angle is 172°, less than 180° because of LP–BP repulsions (Figure 9.3.1.21).

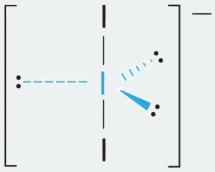
Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

AX$_2$E$_3$ Molecules: I$_3^-$

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is

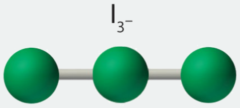
2. There are five electron groups about the central atom in I$_3^-$, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I$_3^-$ has a total of five electron pairs and is designated as AX$_2$E$_3$. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I$_3^-$ is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

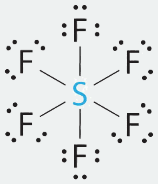


Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 9.3.1.2)

AX$_6$ Molecules: SF$_6$

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



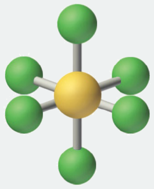
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 9.3.1.2 that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF$_6$ is designated as AX$_6$. All positions are chemically equivalent, so all electronic interactions are equivalent.

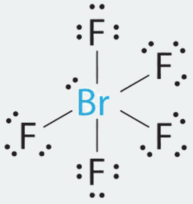
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX$_5$E Molecules: BrF$_5$

1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is

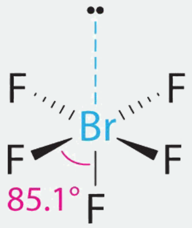


Lewis structure

Five fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has one lone pair.

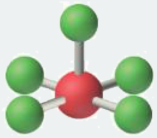
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

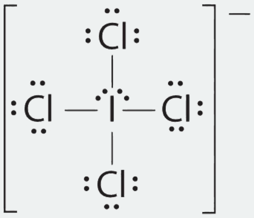
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



Molecular geometry
(square pyramidal)

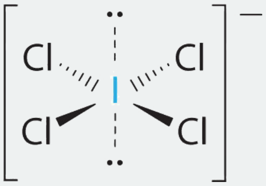
AX$_4$E$_2$ Molecules: ICl$_4^-$

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



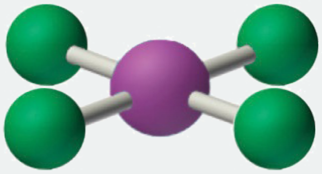
Four chlorines are bonded to a central iodine. Each chlorine has three electron pairs. The iodine has two electron pairs. The molecule is negatively charged.

2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is

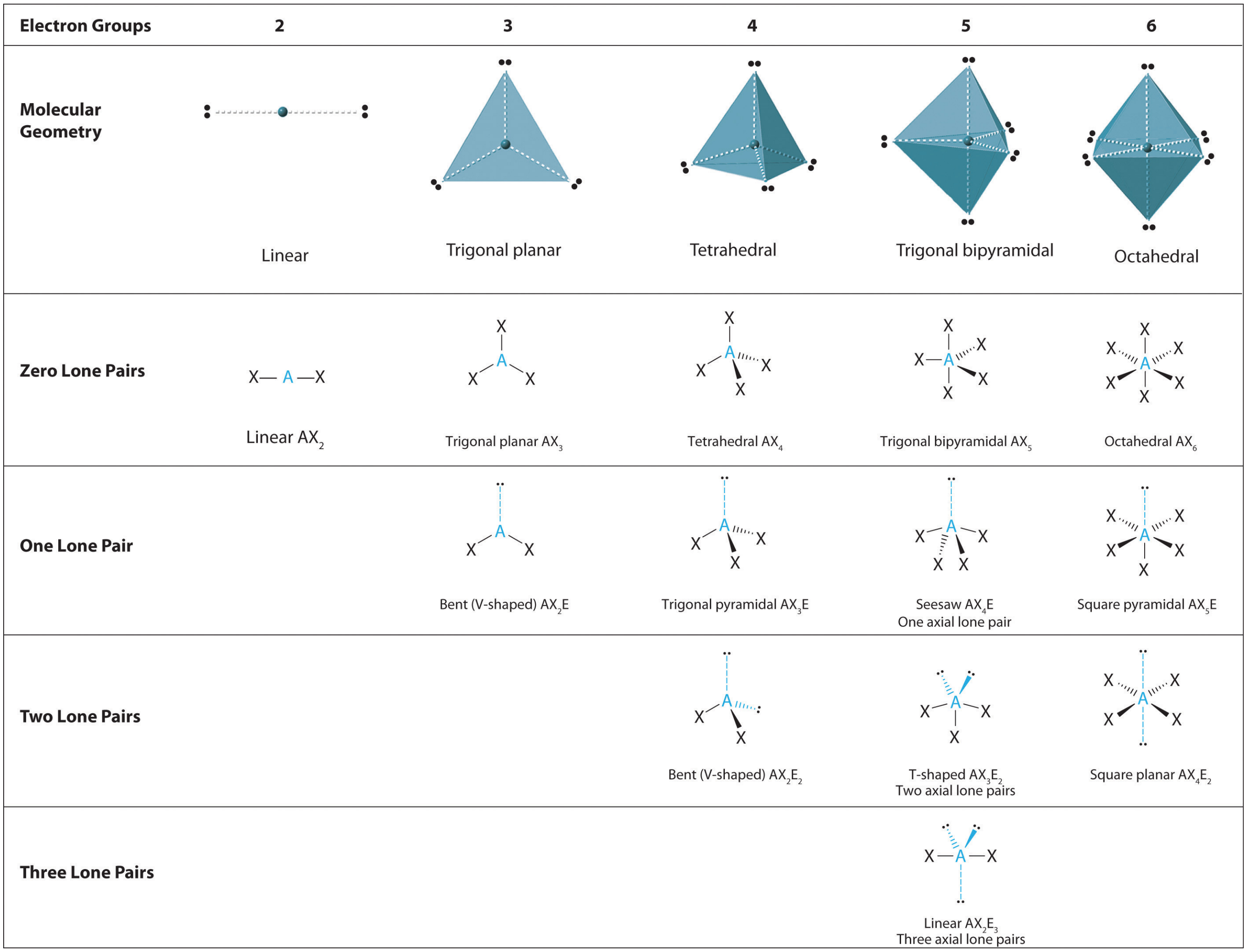


3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl4− ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure 9.3.1.6.



Electron Groups	2	3	4	5	6
Molecular Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Zero Lone Pairs	Linear AX_2	Trigonal planar AX_3	Tetrahedral AX_4	Trigonal bipyramidal AX_5	Octahedral AX_6
One Lone Pair		Bent (V-shaped) AX_2E	Trigonal pyramidal AX_3E	Seesaw AX_4E One axial lone pair	Square pyramidal AX_5E
Two Lone Pairs			Bent (V-shaped) AX_2E_2	T-shaped AX_3E_2 Two axial lone pairs	Square planar AX_4E_2
Three Lone Pairs				Linear AX_2E_3 Three axial lone pairs	

Figure 9.3.1.6: Overview of Molecular Geometries

Example 9.3.1.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A. Draw the Lewis electron structure of the molecule or polyatomic ion.
B. Determine the electron group arrangement around the central atom that minimizes repulsions.
C. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.
D. Describe the molecular geometry.

Solution:

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is

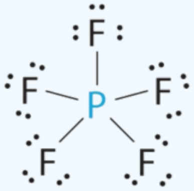
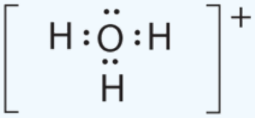


Figure 9.3.1.6): (CC BY-NC-SA; anonymous)

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.

2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is

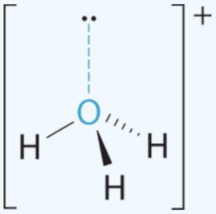


Three hydrogens are bonded to a central oxygen. The oxygen has two lone pairs. The molecule has a charge of plus one.

B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



Exercise 9.3.1.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer a

trigonal pyramidal

Answer b

octahedral

Answer c

linear

Example 9.3.1.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

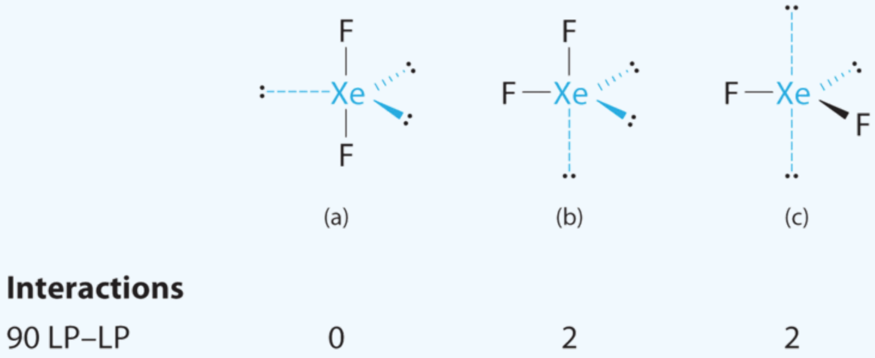
Use the strategy given in Example9.3.1.1

Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is

B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



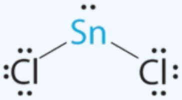
Interactions	(a)	(b)	(c)
90 LP–LP	0	2	2

If the two F atoms are axial ther are zero 90 LP-LP interactions. If the two F atoms are axial and equatorial or just equatorial, there are 2 90 LP-LP interactions.

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



Two chlorines are bonded to a central tin. Each chlorine has three lone pairs. Tin has one lone pair.

B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

? Exercise 9.3.1.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a

trigonal planar

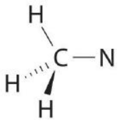
Answer b

square planar

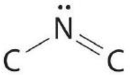
Molecules with No Single Central Atom

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4. We can therefore predict the CH_3–N portion of the molecule to be roughly tetrahedral, similar to methane:



The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



One carbon bonded to nitrogen and another carbon double bonded to the nitrogen. The nitrogen has one lone pair.

Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:

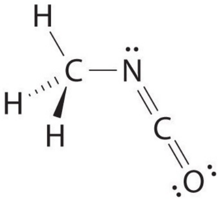


Figure 9.3.1.7).

Three hydrogens are bonded to a carbon. The carbon is also bonded to a nitrogen. The nitrogen is double bonded to another carbon. The second carbon is double bonded to an oxygen. The nitrogen has one lone pair. The oxygen has two lone pairs.

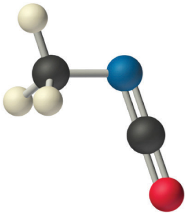


Figure 9.3.1.7: The Experimentally Determined Structure of Methyl Isocyanate

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

✓ Example 9.3.1.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C≡CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 9.3.1.3 to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

Exercise 9.3.1.3

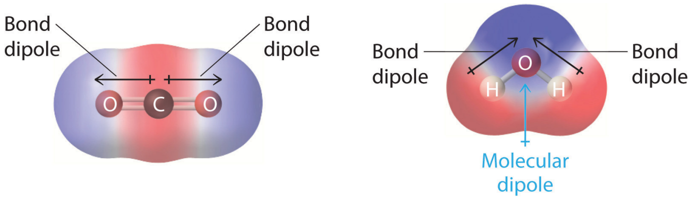
Predict the geometry of allene ($H_2C{=}C{=}CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

Molecular Dipole Moments

You previously learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (Figure 9.3.1.8a). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (Figure 9.3.1.8b); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.



(a) No net dipole moment (b) Net dipole moment

Figure 9.3.1.8: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.

Other examples of molecules with polar bonds are shown in Figure 9.3.1.9. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment. Molecules with asymmetrical charge distributions have a net dipole moment.

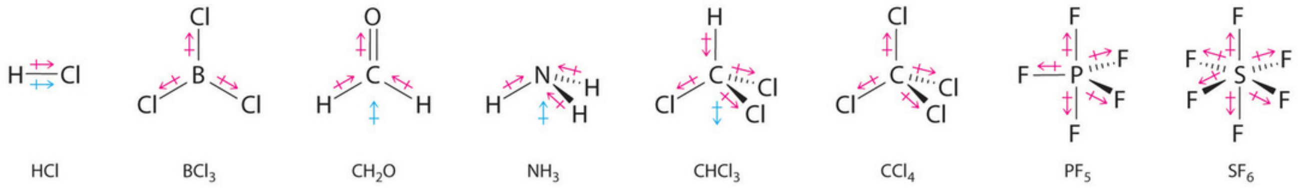


Figure $9.3.1.9$: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

✓ Example $9.3.1.4$

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

Given: three chemical compounds

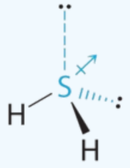
Asked for: net dipole moment

Strategy:

For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

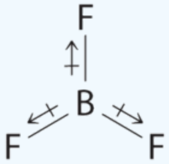
Solution:

1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure $9.3.1.6$). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



2. Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.

3. The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:



? Exercise 9.3.1.4

Which molecule(s) has a net dipole moment?

- CH_3Cl
- SO_3
- XeO_3

Answer

CH_3Cl and XeO_3

Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds. A combination of VSEPR and a bonding model, such as Lewis electron structures, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

9.4: Molecular Geometry and Polarity

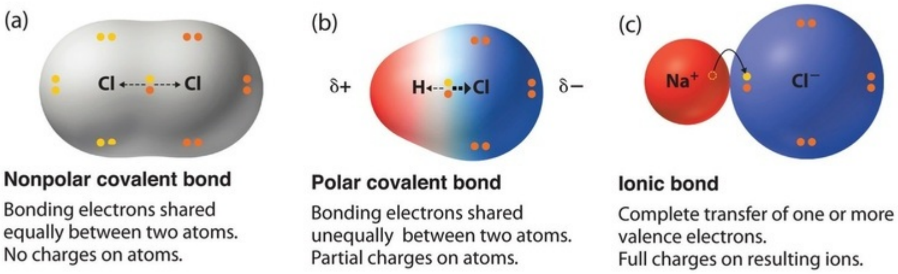
Learning Objectives

- To calculate the percent ionic character of a covalent polar bond

Previously, we described the two idealized extremes of chemical bonding:

- **ionic bonding**—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and
- **covalent bonding**, in which electrons are shared *equally* between two atoms.

Most compounds, however, have polar covalent bonds, which means that electrons are shared *unequally* between the bonded atoms. Figure $9.4.1$ compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a *polar bond*.



Nonpolar covalent bond
Bonding electrons shared equally between two atoms. No charges on atoms.

Polar covalent bond
Bonding electrons shared unequally between two atoms. Partial charges on atoms.

Ionic bond
Complete transfer of one or more valence electrons. Full charges on resulting ions.

Figure $9.4.1$: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. *Electronegativity* (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\begin{matrix} \textit{less electronegative} & & \textit{more electronegative} \\ A & - & B \\ \delta^{+} & & \delta^{-} \end{matrix} \tag{9.4.1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms:

$$\Delta\chi = \chi_B - \chi_A.$$

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms (Table A2): $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq\approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta^+}{H} \quad - \quad \overset{\delta^-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

> Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, $\mathrm{Cl_2}$, $\mathrm{ClF_5}$, and $\mathrm{HClO_4}$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a dipole moment where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr \tag{9.4.2}$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m \tag{9.4.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure $9.4.2$).

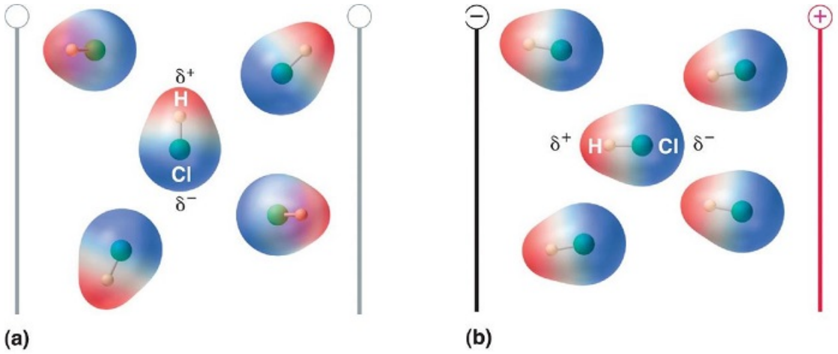


Figure $9.4.2$: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), theHClmolecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 9.4.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) \\ &= 2.901 \times 10^{-20}\ C \end{aligned}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution inHCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} = 0.1811\ e^- \tag{9.4.4}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta^+}{H} \quad - \quad \overset{\delta^-}{Cl}$$

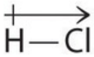
we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta^+}{H} \quad - \quad \overset{0.18\delta^-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine ($\chi_H = 2.20$ and $\chi_{Cl} = 3.16$) so

$$\chi_{Cl} - \chi_H = 0.96$$

This is a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule.Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

A warning about Dipole Moment arrows

As the figure above shows, we represent dipole moments by an arrow with a length proportional to μ and pointing from the positive charge to the negative charge. However, the **opposite** convention is still widely used especially among physicists.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure $9.4.2$ shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as $NaCl_{(g)}$ and $CsF_{(g)}$ is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure $9.4.2$ show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example $9.4.1$.

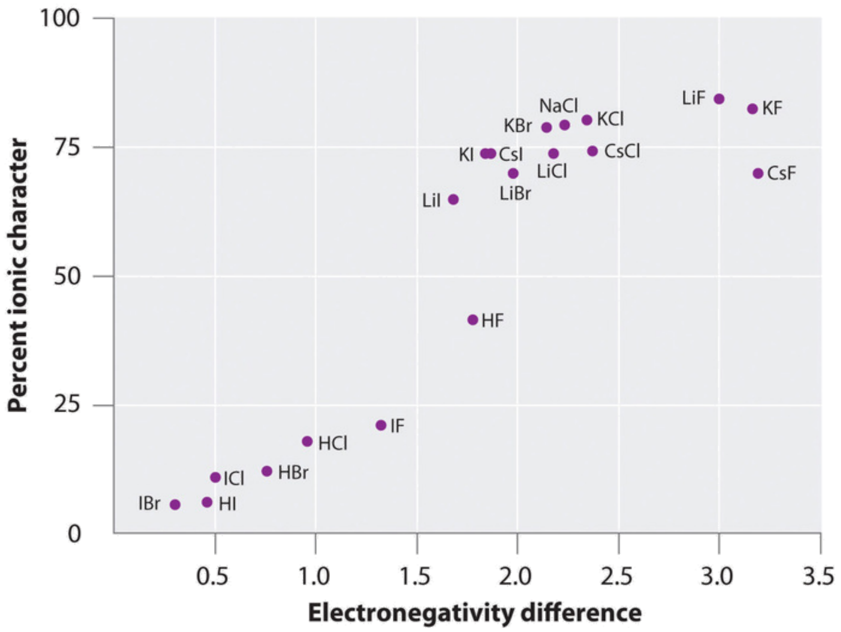


Figure 9.4.2: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms. In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

✓ Example 9.4.1: percent ionic character

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A. Compute the charge on each atom using the information given and Equation 9.4.2

B. Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 9.001\ \cancel{D}\left(\frac{3.3356\times 10^{-30}\ C\cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{236.1\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) \\ &= 1.272\times 10^{-19}\ C \end{aligned}$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\begin{aligned} \text{ionic character} &= \left(\frac{1.272\times 10^{-19}\ \cancel{C}}{1.6022\times 10^{-19}\ \cancel{C}}\right)(100) \\ &= 79.39\% \simeq 79\% \end{aligned}$$

? Exercise 9.4.1

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer

55.5%

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity.

$$\mu = Qr$$

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

Contributors and Attributions

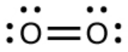
- Modified by Joshua Halpern (Howard University)

9.5: Molecular Orbital Theory

Learning Objectives

- Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
- Describe traits of bonding and antibonding molecular orbitals
- Calculate bond orders based on molecular electron configurations
- Write molecular electron configurations for first- and second-row diatomic molecules
- Relate these electron configurations to the molecules' stabilities and magnetic properties

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



A Lewis structure is shown. It is made up of two oxygen atoms, each with two lone pairs of electrons, bonded together with a double bond.

This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called paramagnetism, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure 9.5.1), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

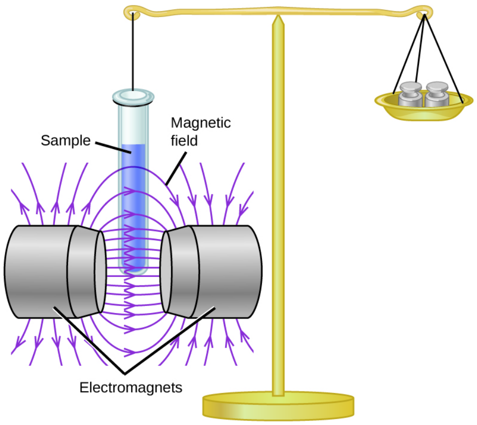


Figure 9.5.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.

Video 9.5.1: Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more (levitating frog [www.youtube.com])

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are delocalized over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table 9.5.1 summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Table \(\PageIndex{1}\): Comparison of Bonding Theories

Valence Bond Theory	**Molecular Orbital Theory**
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, Ψ, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a molecular orbital (Ψ^2). Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2, for example). Such molecules are called homonuclear diatomic molecules. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the linear combination of atomic orbitals (LCAO). The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (Figure 9.5.2). In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.

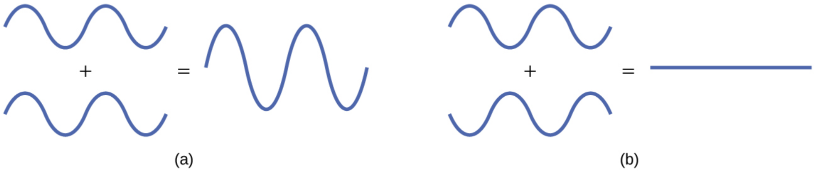


Figure 9.5.2: (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

A pair of diagrams are shown and labeled, “a” and “b.” Diagram a shows two identical waves with two crests and two troughs. They are drawn one above the other with a plus sign in between and an equal sign to the right. To the right of the equal sign is a much taller wave with a same number of troughs and crests. Diagram b shows two waves with two crests and two troughs, but they are mirror images of one another rotated over a horizontal axis. They are drawn one above the other with a plus sign in between and an equal sign to the right. To the right of the equal sign is a flat line.

There are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms. The two types are illustrated in Figure 9.5.3. The in-phase combination produces a lower energy σ_s molecular orbital (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy σ_s^* molecular orbital (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals bonding orbitals. Electrons in the σ_s^* orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

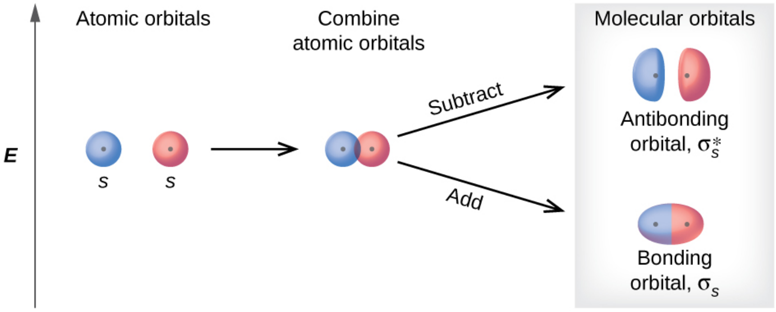
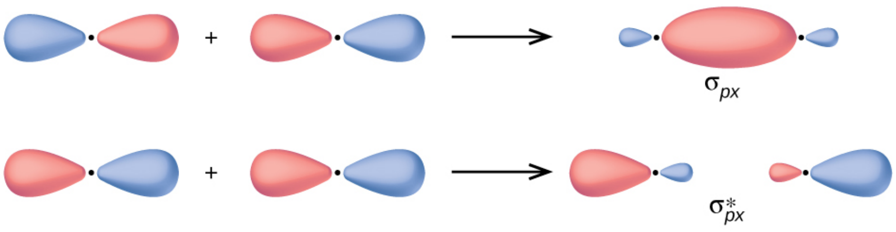


Figure 9.5.3: Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.

A diagram is shown that depicts a vertical upward-facing arrow that lies to the left of all the other portions of the diagram and is labeled, “E.” To the immediate right of the midpoint of the arrow are two circles each labeled with a positive sign, the letter S, and the phrase, “Atomic orbitals.” These are followed by a right-facing horizontal arrow that points to the same two circles labeled with plus signs, but they are now touching and are labeled, “Combine atomic orbitals.” Two right-facing arrows lead to the last portion of the diagram, one facing upward and one facing downward. The upper arrow is labeled, “Subtract,” and points to two oblong ovals labeled with plus signs, and the phrase, “Antibonding orbitals sigma subscript s superscript asterisk.” The lower arrow is labeled, “Add,” and points to an elongated oval with two plus signs that is labeled, “Bonding orbital sigma subscript s.” The heading over the last section of the diagram are the words, “Molecular orbitals.”

In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When *p* orbitals overlap end to end, they create σ and σ* orbitals (Figure 9.5.4). If two atoms are located along the *x*-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and σ_{px}^* (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with *s*-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.



Two horizontal rows of diagrams are shown. The upper diagram shows two equally-sized peanut-shaped orbitals with a plus sign in between them connected to a merged orbital diagram by a right facing arrow. The merged diagram has a much larger oval at the center and much smaller ovular orbitals on the edge. It is labeled, “sigma subscript p x.” The lower diagram shows two equally-sized peanut-shaped orbitals with a plus sign in between them connected to a split orbital diagram by a right facing arrow. The split diagram has a much larger oval at the outer ends and much smaller ovular orbitals on the inner edges. It is labeled, “sigma subscript p x superscript asterisk”.

Figure $9.5.4$: Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σp and σ^*_p.

The side-by-side overlap of two *p* orbitals gives rise to a pi (π) bonding molecular orbital and a \(π^*\) antibonding molecular orbital, as shown in Figure $9.5.5$. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.

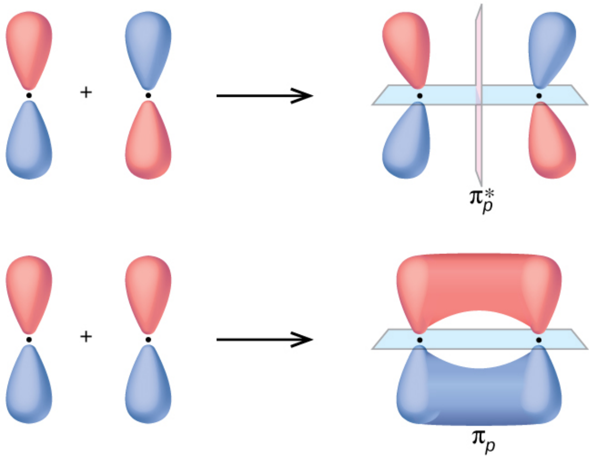


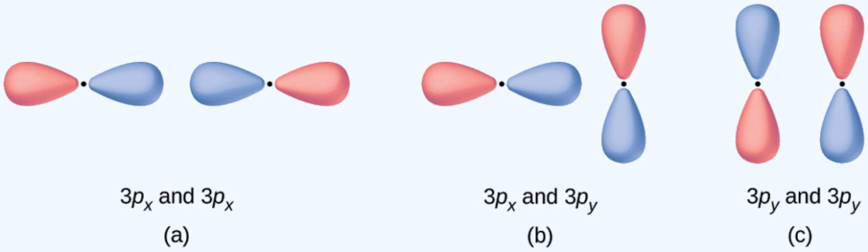
Figure $9.5.5$: Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue plane) containing the internuclear axis with the two lobes of the orbital located above and below this node.

Two horizontal rows of diagrams are shown. The upper and lower diagrams both begin with two vertical peanut-shaped orbitals with a plus sign in between followed by a right-facing arrow. The upper diagram shows the same vertical peanut orbitals bending slightly away from one another and separated by a dotted line. It is labeled, “pi subscript p superscript asterisk.” The lower diagram shows the horizontal overlap of the two orbitals and is labeled, “pi subscript p.”

In the molecular orbitals of diatomic molecules, each atom also has two sets of *p* orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π^* orbitals. The π_{py} and π^*_{py} orbitals are oriented at right angles to the π_{pz} and π^*_{pz} orbitals. Except for their orientation, the $π_{py}$ and $π_{pz}$ orbitals are identical and have the same energy; they are degenerate orbitals. The π^*_{py} and π^*_{pz} antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic *p* orbitals in two atoms: σ_{px} and σ^*_{px}, π_{py} and π^*_{py}, π_{pz} and π^*_{pz}.

✓ Example 9.5.1: Molecular Orbitals

Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.


$3p_x$ and $3p_x$
(a)
$3p_x$ and $3p_y$
(b)
$3p_y$ and $3p_y$
(c)

Three diagrams are shown and labeled “a,” “b,” and “c.” Diagram a shows two horizontal peanut-shaped orbitals laying side-by-side. They are labeled, “3 p subscript x and 3 p subscript x.” Diagram b shows one vertical and one horizontal peanut-shaped orbital which are at right angles to one another. They are labeled, “3 p subscript x and 3 p subscript y.” Diagram c shows two vertical peanut-shaped orbitals laying side-by-side and labeled, “3 p subscript y and 3 p subscript y.”

Solution

a. This is an in-phase combination, resulting in a σ_{3p} orbital
b. This will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.
c. This is an out-of-phase combination, resulting in a π^*_{3p} orbital.

? Exercise 9.5.1

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.

Two orbitals are shown lying end-to-end. Each has one enlarged and one small side. The small sides are facing one another

Answer

The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.

Two orbitals are shown lying end-to-end. Each has one enlarged and one small side. The small sides are facing one another and are separated by a vertical dotted line.

Application: Computational Chemistry in Drug Design

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (Figure 9.5.6). Thousands of potential candidates can be narrowed down to a few of the most promising candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.

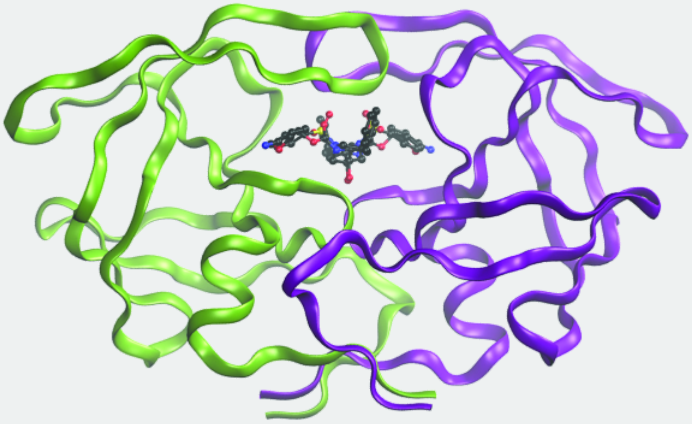


Figure $9.5.6$: The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

A diagram of a molecule is shown. The image shows a tangle of ribbon-like, intertwined, pink and green curling lines with a complex ball and stick model in the center.

9.5.1: Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure $9.5.7$). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2*p* atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

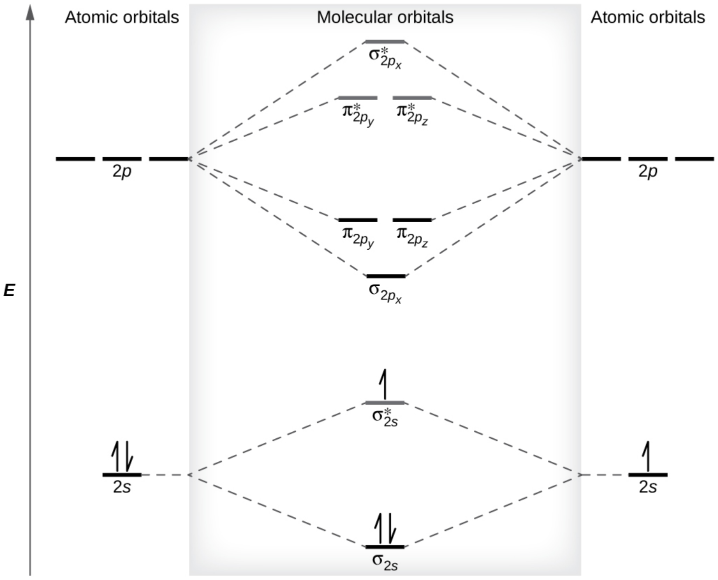


Figure 9.5.7: This is the molecular orbital diagram for the homonuclear diatomic Be_2^+, showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled, "E." At the bottom center of the diagram is a horizontal line labeled, "sigma subscript 2 s," that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, "2 s." The line on the left has two vertical half arrows drawn on it, one facing up and one facing down while the line of the right has one half arrow facing up drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but further up from the first. It is labeled, "sigma subscript 2 s superscript asterisk." This horizontal line has one upward-facing vertical half-arrow drawn on it. Moving farther up the center of the diagram is a long horizontal line labeled, "sigma subscript 2 p subscript x," which lies below two horizontal lines. These two horizontal lines lie side-by-side, and labeled, "pi subscript 2 p subscript y," and, "pi subscript 2 p subscript z." Both the bottom and top lines are connected to the right and left by upward-facing, dotted lines to three more horizontal lines, each labeled, "2 p." These sets of lines are connected by upward-facing dotted lines to another single line and then pair of double lines in the center of the diagram, but farther up from the lower lines. They are labeled, "sigma subscript 2 p subscript x superscript asterisk," and, ""pi subscript 2 p subscript y superscript asterisk," and, "pi subscript 2 p subscript z superscript asterisk," respectively. The left and right sides of the diagram have headers that read, "Atomic orbitals," while the center is header reads "Molecular orbitals".

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (Figure 9.5.7). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as Be_2^+) would have the molecular electron configuration $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^1$. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

9.5.2: Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the bond order that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2}$$

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases. If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

9.5.3: Bonding in Diatomic Molecules

A dihydrogen molecule (H_2) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital. A dihydrogen molecule, H_2, readily forms because the energy of a H_2 molecule is lower than that of two H atoms. The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1*s* atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (Figure $9.5.8$) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

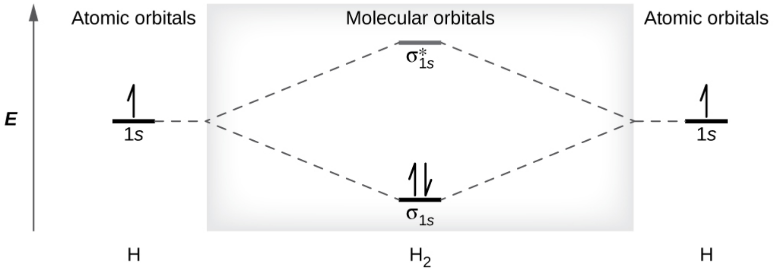


Figure $9.5.8$: The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled “E.” At the bottom center of the diagram is a horizontal line labeled, “sigma subscript 1 s,” that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, “1 s,” and each with one vertical half-arrow facing up drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but farther up from the first, and labeled, “sigma subscript 1 s superscript asterisk.” The left and right sides of the diagram have headers that read, ”Atomic orbitals,” while the center header reads, “Molecular orbitals.” The bottom left and right are labeled “H” while the center is labeled “H subscript 2.”

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in } H_2 = \frac{(2-0)}{2} = 1$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

A helium atom has two electrons, both of which are in its 1*s* orbital. Two helium atoms do not combine to form a dihelium molecule, He_2, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He_2 as $(\sigma_{1s})^2(\sigma^*_{1s})^2$ as in Figure $9.5.9$. The net energy change would be zero, so there is no driving force for helium atoms to form the diatomic molecule. In fact, helium exists as discrete atoms rather than as diatomic molecules. The bond order in a hypothetical dihelium molecule would be zero.

$$\text{bond order in } He_2 = \frac{(2-2)}{2} = 0$$

A bond order of zero indicates that no bond is formed between two atoms.

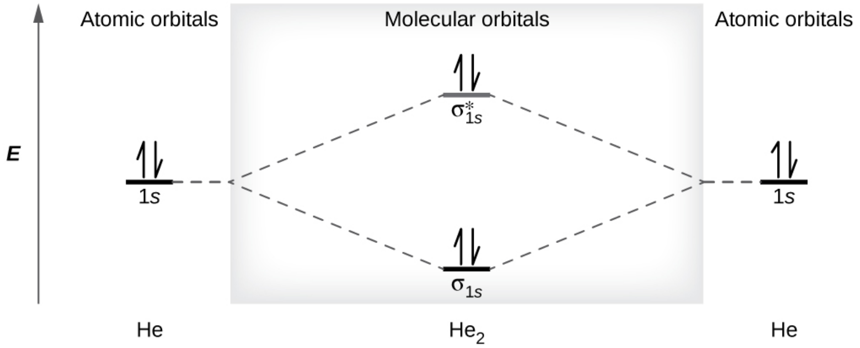


Figure 9.5.9: The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled, “E.” At the bottom center of the diagram is a horizontal line labeled, “sigma subscript 1 s,” that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, “1 s,” and each with one vertical half-arrow facing up and one facing down drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but farther up from the first, and labeled, “sigma subscript 1 s superscript asterisk.” This line has one upward-facing and one downward-facing vertical arrow drawn on it. The left and right sides of the diagram have headers that read, “Atomic orbitals,” while the center header reads, “Molecular orbitals.” The bottom left and right are labeled, “H e,” while the center is labeled, “H e subscript 2.”

9.5.4: The Diatomic Molecules of the Second Period

Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, and Ne_2. However, we can predict that the Be_2 molecule and the Ne_2 molecule would not be stable. We can see this by a consideration of the molecular electron configurations (Table 9.5.1).

Table 9.5.1: Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements

Molecule	Electron Configuration	Bond Order
Li_2	$(\sigma_{2s})^2$	1
Be_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2$	0
B_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^2$	1
C_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4$	2
N_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4(\sigma_{2px})^2$	3
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\pi^*_{2pz})^2$	2
F_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\ \pi^*_{2pz})^4$	1
Ne_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\pi^*_{2pz})^4(\sigma^*_{2px})^2$	0

We predict valence molecular orbital electron configurations just as we predict electron configurations of atoms. Valence electrons are assigned to valence molecular orbitals with the lowest possible energies. Consistent with Hund’s rule, whenever there are two or more degenerate molecular orbitals, electrons fill each orbital of that type singly before any pairing of electrons takes place.

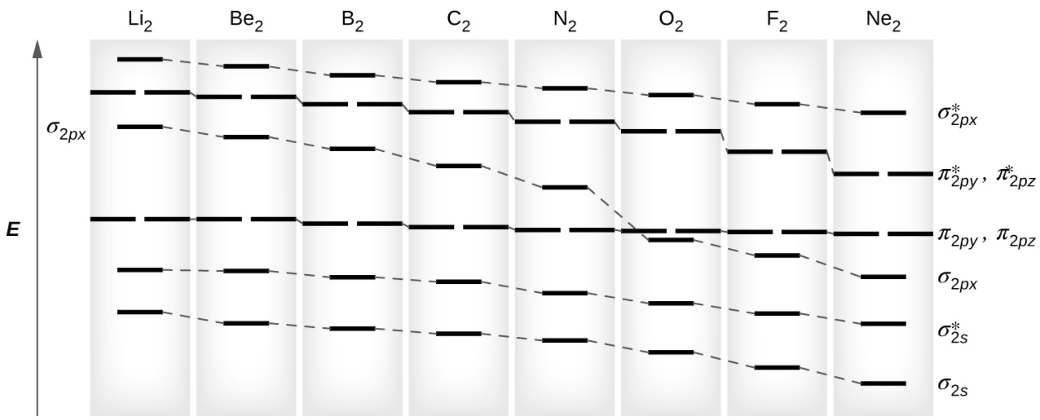


Figure 9.5.10: This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes.

A graph is shown in which the y-axis is labeled, “E,” and appears as a vertical, upward-facing arrow. Across the top, the graph reads, “L i subscript 2,” “B e subscript 2,” “B subscript 2,” “C subscript 2,” “N subscript 2,” “O subscript 2,” “F subscript 2,” and “Ne subscript 2.” Directly below each of these element terms is a single pink line, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled, “sigma subscript 2 p x superscript asterisk”. Directly below each of these lines is a set of two pink lines, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. It is consistently lower than the first line. This line is labeled, “pi subscript 2 p y superscript asterisk,” and, “pi subscript 2 p z superscript asterisk.” Directly below each of these double lines is a single pink line, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. It has a distinctive drop at the label, “O subscript 2.” This line is labeled, “sigma subscript 2 p x.” Directly below each of these lines is a set of two pink lines, and all lines are connected to one another by a dashed line to create an overall line that decreases very slightly in height as it moves from left to right across the graph. It is consistently lower than the third line until it reaches the point labeled, “O subscript 2.” This line is labeled, “pi subscript 2 p y,” and, “pi subscript 2 p z.” Directly below each of these lines is a single blue line, and all lines are connected to one another by a dashed line to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled, “sigma subscript 2 s superscript asterisk.” Finally, directly below each of these lines is a single blue line, and all lines are connected to one another by a dashed line to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled. “sigma subscript 2 s.”

As we saw in valence bond theory, σ bonds are generally more stable than π bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in Figure 9.5.10. Looking at Ne_2 molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the *p* orbitals (Li through N) we observe a different pattern, in which the σ_p orbital is higher in energy than the π_p set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.

This switch in orbital ordering occurs because of a phenomenon called s-p mixing. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σ_s wavefunction mathematically combines with the σ_p wavefunction, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable (Figure 9.5.11). Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.

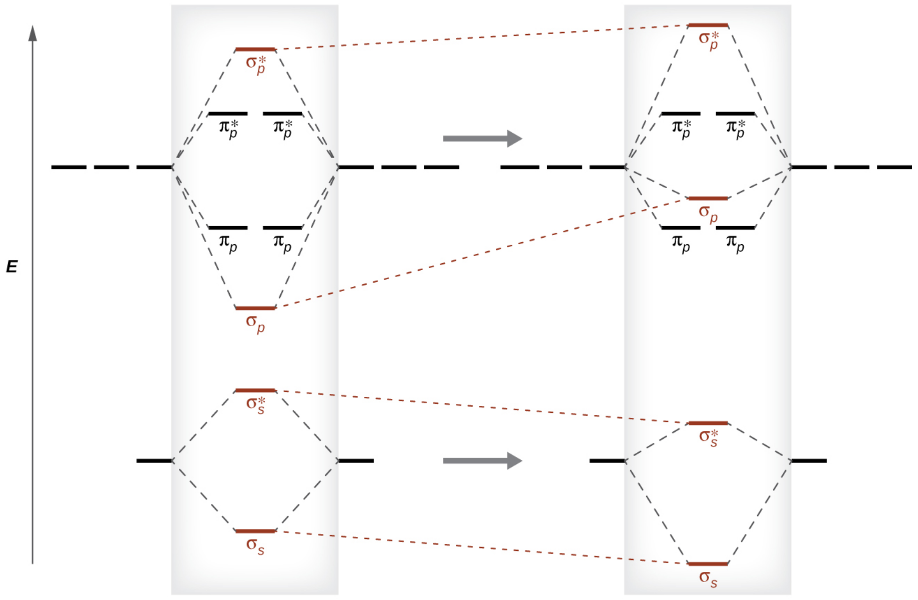


Figure 9.5.11: Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the σ_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

A diagram is shown. At the bottom left of the diagram is a horizontal line that is connected to the right and left by upward-facing, dotted lines to two more horizontal lines. Those two lines are connected by upward-facing dotted lines to another line in the center of the diagram but farther up from the first. Each of the bottom two central lines has a vertical downward-facing arrow. Above this structure is a horizontal line that is connected to the right and left by upward-facing, dotted lines to two sets of three horizontal lines and those two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but further up from the first. In between the horizontal lines of this structure are two pairs of horizontal lines that are above the first line but below the second and connected by dotted lines to the side horizontal lines. The bottom and top central lines each have an upward-facing vertical arrow. These two structures are redrawn on the right side of the diagram, but this time, the central lines of the bottom structure are moved downward in relation to the side lines. The upper portion of the structure has its central lines shifted upward in relation to the side lines. This structure also shows the bottom line appearing above the set of two lines.

s-p mixing occurs when the *s* and *p* orbitals have similar energies. The energy difference between 2*s* and 2*p* orbitals in O, F, and Ne is greater than that in Li, Be, B, C, and N. Because of this, O_2, F_2, and Ne exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in Figure 9.5.7. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

Using the MO diagrams shown in Figure 9.5.11, we can add in the electrons and determine the molecular electron configuration and bond order for each of the diatomic molecules. As shown in Table 9.5.1, Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

The combination of two lithium atoms to form a lithium molecule, Li_2, is analogous to the formation of H_2, but the atomic orbitals involved are the valence 2*s* orbitals. Each of the two lithium atoms has one valence electron. Hence, we have two valence electrons available for the σ_{2s} bonding molecular orbital. Because both valence electrons would be in a bonding orbital, we would predict the Li_2 molecule to be stable. The molecule is, in fact, present in an appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in Table 9.5.1 with a bond order greater than zero are also known.

The O_2 molecule has enough electrons to half fill the $(\pi^*_{2py}, \pi^*_{2pz})$ level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O_2 is in accord with the fact that the oxygen molecule has two unpaired electrons (Figure 9.5.10). The presence of two unpaired electrons has proved to be difficult to explain using Lewis structures, but the molecular orbital theory explains it quite well. In fact, the unpaired electrons of the oxygen molecule provide a strong piece of support for the molecular orbital theory.

Application: Band Theory in Extended Systems

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (e.g., H_2 in Figure 9.5.8). The bonding orbital is lower in energy than the original atomic orbitals because the atomic orbitals are in-phase in the molecular orbital. The antibonding orbital is higher in energy than the original atomic orbitals because the atomic orbitals are out-of-phase.

In a solid, similar things happen, but on a much larger scale. Remember that even in a small sample there are a huge number of atoms (typically > 10^{23} atoms), and therefore a huge number of atomic orbitals that may be combined into molecular orbitals. When N valence atomic orbitals, all of the same energy and each containing one (1) electron, are combined, $N/2$ (filled) bonding orbitals and $N/2$ (empty) antibonding orbitals will result. Each bonding orbital will show an energy lowering as the atomic orbitals are *mostly* in-phase, but each of the bonding orbitals will be a little different and have slightly different energies. The antibonding orbitals will show an increase in energy as the atomic orbitals are *mostly* out-of-phase, but each of the antibonding orbitals will also be a little different and have slightly different energies. The allowed energy levels for all the bonding orbitals are so close together that they form a band, called the valence band. Likewise, all the antibonding orbitals are very close together and form a band, called the conduction band. Figure $9.5.12$) shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

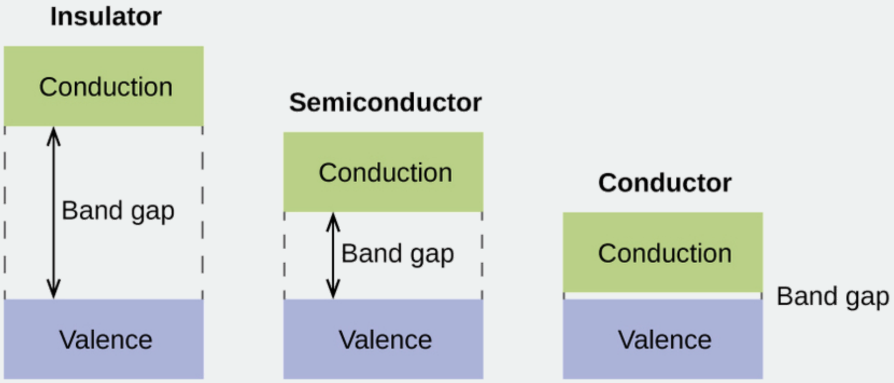


Figure $9.5.12$: Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the “band gap” between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.

This figure shows three diagrams. The first is labeled, “Insulator,” and it consists of two boxes. The “conduction” box is above and the “valence” box is below. A large gap marked by 4 dashed lines contains a double-headed arrow. One head pointing towards the “conduction box” and the other towards the “valence” box. The arrow is labeled, “Band gap.” The second diagram is similar to the first, but the band gap is about half as large. This diagram is labeled, “Semiconductor.” The third diagram is similar to the other two, but the band gap is about a fifth that of the “Semiconductor” diagram. This diagram is labeled, “Conductor.”

In order to conduct electricity, electrons must move from the filled valence band to the empty conduction band where they can move throughout the solid. The size of the band gap, or the energy difference between the top of the valence band and the bottom of the conduction band, determines how easy it is to move electrons between the bands. Only a small amount of energy is required in a conductor because the band gap is very small. This small energy difference is “easy” to overcome, so they are good conductors of electricity. In an insulator, the band gap is so “large” that very few electrons move into the conduction band; as a result, insulators are poor conductors of electricity. Semiconductors conduct electricity when “moderate” amounts of energy are provided to move electrons out of the valence band and into the conduction band. Semiconductors, such as silicon, are found in many electronics.

Semiconductors are used in devices such as computers, smartphones, and solar cells. Solar cells produce electricity when light provides the energy to move electrons out of the valence band. The electricity that is generated may then be used to power a light or tool, or it can be stored for later use by charging a battery. As of December 2014, up to 46% of the energy in sunlight could be converted into electricity using solar cells.

✓ Example $9.5.2$: Molecular Orbital Diagrams, Bond Order, and Number of Unpaired Electrons

Draw the molecular orbital diagram for the oxygen molecule, O_2. From this diagram, calculate the bond order for O_2. How does this diagram account for the paramagnetism of O_2?

Solution

We draw a molecular orbital energy diagram similar to that shown in Figure 9.5.7. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 9.5.7.

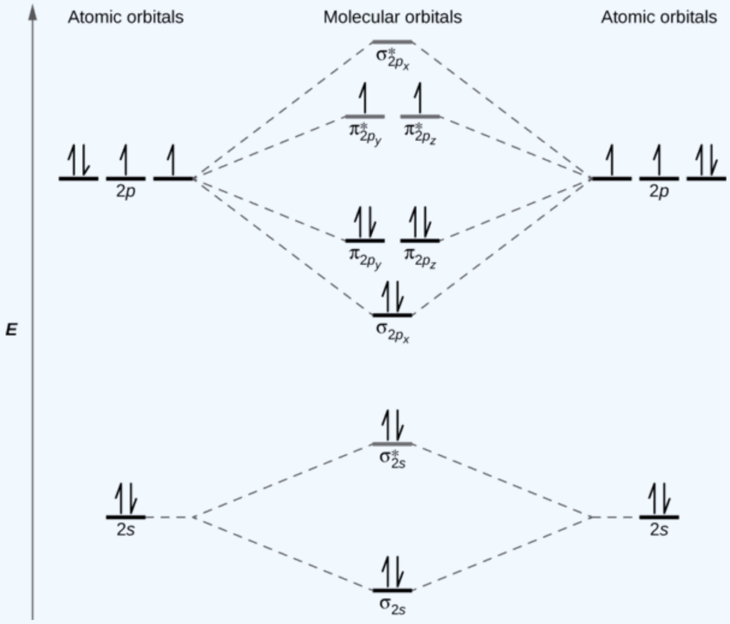


Figure 9.5.13: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

We calculate the bond order as

$$O_2 = \frac{(8-4)}{2} = 2$$

Oxygen's paramagnetism is explained by the presence of two unpaired electrons in the $(\pi_{2py}, \pi_{2pz})^*$ molecular orbitals.

? Exercise 9.5.2

The main component of air is N_2. From the molecular orbital diagram of N_2, predict its bond order and whether it is diamagnetic or paramagnetic.

Answer

N_2 has a bond order of 3 and is diamagnetic.

✓ Example 9.5.3: Ion Predictions with MO Diagrams

Give the molecular orbital configuration for the valence electrons in C_2^{2-}. Will this ion be stable?

Solution

Looking at the appropriate MO diagram, we see that the π orbitals are lower in energy than the σ_p orbital. The valence electron configuration for C_2 is

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4.$$

Adding two more electrons to generate the C_2^{2-} anion will give a valence electron configuration of

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4(\sigma_{2px})^2$$

Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.

? Exercise 9.5.3

How many unpaired electrons would be present on a Be_2^{2-} ion? Would it be paramagnetic or diamagnetic?

Answer

two, paramagnetic

9.5.5: Key Concepts and Summary

Molecular orbital (MO) theory describes the behavior of electrons in a molecule in terms of combinations of the atomic wave functions. The resulting molecular orbitals may extend over all the atoms in the molecule. Bonding molecular orbitals are formed by in-phase combinations of atomic wave functions, and electrons in these orbitals stabilize a molecule. Antibonding molecular orbitals result from out-of-phase combinations of atomic wave functions and electrons in these orbitals make a molecule less stable. Molecular orbitals located along an internuclear axis are called σ MOs. They can be formed from *s* orbitals or from *p* orbitals oriented in an end-to-end fashion. Molecular orbitals formed from *p* orbitals oriented in a side-by-side fashion have electron density on opposite sides of the internuclear axis and are called π orbitals.

We can describe the electronic structure of diatomic molecules by applying molecular orbital theory to the valence electrons of the atoms. Electrons fill molecular orbitals following the same rules that apply to filling atomic orbitals; Hund’s rule and the Aufbau principle tell us that lower-energy orbitals will fill first, electrons will spread out before they pair up, and each orbital can hold a maximum of two electrons with opposite spins. Materials with unpaired electrons are paramagnetic and attracted to a magnetic field, while those with all-paired electrons are diamagnetic and repelled by a magnetic field. Correctly predicting the magnetic properties of molecules is in advantage of molecular orbital theory over Lewis structures and valence bond theory.

9.5.1: The Predictive Power of MO Theory - The Case of Oxygen

Learning Objectives

- To describe the connection between bond order, bond length and bond energy in diatomic molecules
- To explain the observed paramagnetic properties of molecular oxygen with Molecular Orbital theory

In general chemistry courses, students learn that covalent bonds can come as either single, double or triple bonds, which are identifies by their bond order. Both bond length and bond energy changes as the bond order increases and as the number of electrons shared between two atoms in a molecule increases, the bond order of a bond increases, the strength of the bond increases and the distance between nuclei decreases (Table 9.10.1).

Table 9.10.1 : General Correlation between Bond Strength, length and order in Covalent bonds

Bond	Bond Order	Bond Enthalpy (kJ/mol)	Bond Length (Å)
$C-C$	1	348	1.54
$C=C$	2	614	1.34
$C\equiv C$	3	839	1.20
$N-N$	1	163	1.47
$N=N$	2	418	1.24
$N\equiv N$	3	941	1.10

The above trend can be observed in the first row diatomics in Figure 9.10.1 . The bond order can be determined directly form the molecular orbital electron configurations. For diatomics, the occupations can correlate to bond length, bond energies (Figure 9.10.1).

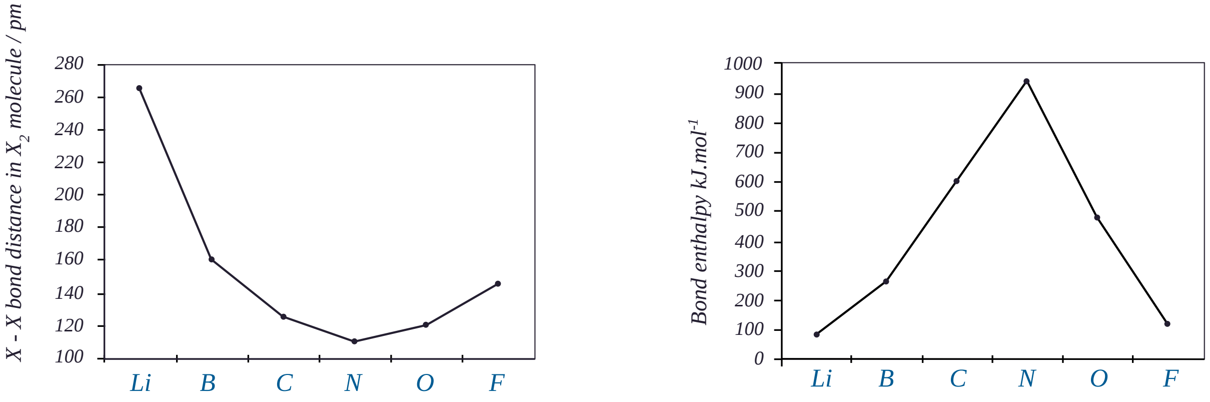


Figure 9.10.1 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

The trends in Figure 9.10.1 and Table 9.10.1 extend to molecular ions.

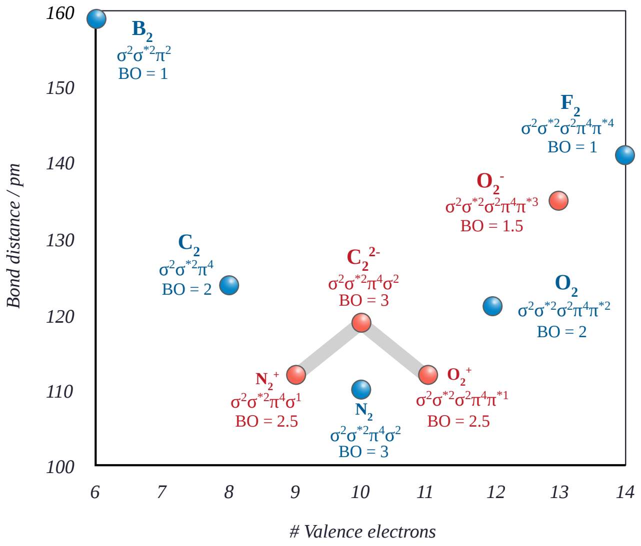


Figure 9.10.2 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

✓ Example 9.10.1 : Molecular Oxygen

Arrange the following four molecular oxygen species in order of increasing bond length: O_2^+, O_2, O_2^-, and O_2^{2-}.

Solution

The bond length in the oxygen species can be explained by the positions of the electrons in molecular orbital theory. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in Figure 9.10.1 . We again fill the orbitals according to Hund's rules and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and $\sigma_{2s}*$ orbitals, two more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^\star_{2p_x}$ and $\pi^\star_{2p_y}$ orbitals. According to Hund's first rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving a multiplicity of 3 (a triplet state) with two unpaired electrons. This leads to a predicted bond order of

$$\frac{8-4}{2} = 2$$

which corresponds to a double bond, in agreement with experimental data: the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

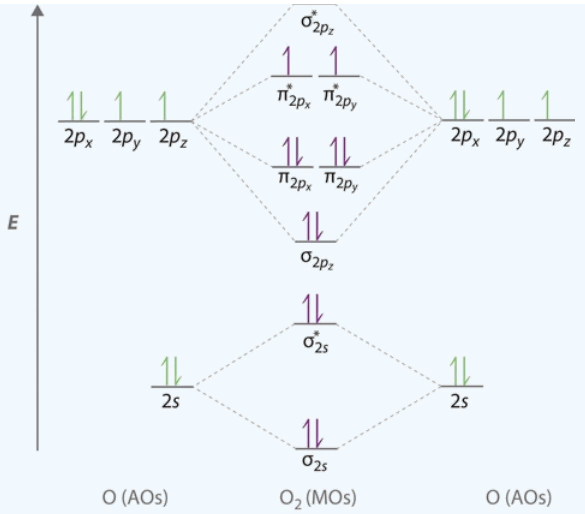


Figure 9.10.3 : Molecular Orbital Energy-Level Diagrams for O_2. With 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^\star_{np_x}, \pi^\star_{np_y}\right)$ pair of orbitals. Hund's first rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; Anonymous by request).

The bond order is determined from the the electron configurations. The electron configurations for the four species are contrasted below.

- O_2:

$$\sigma^2_{1s}\sigma^*_{1s}{}^2\sigma^2_{2s}\sigma^*_{2s}{}^2\sigma^2_{2p}\pi^2_{2p_y}\pi^*_{2p_y}{}^2\pi^1_{2p_x}\pi^*_{2p_y}{}^1$$

  From Equation ???, the bond order for O_2 is 2 (i.e., a double bond).

- O_2^+:

$$\sigma^2_{1s}\sigma^*_{1s}{}^2\sigma^2_{2s}\sigma^*_{2s}{}^2\sigma^2_{2p}\pi^2_{2p_y}\pi^*_{2p_y}{}^2\pi^1_{2p_x}\pi^*_{2p_y}{}^0$$

  From Equation ???, the bond order for O_2^+ is 2.5. An alternative and equally valid configuration is

$$\sigma^2_{1s}\sigma^*_{1s}{}^2\sigma^2_{2s}\sigma^*_{2s}{}^2\sigma^2_{2p}\pi^2_{2p_y}\pi^*_{2p_y}{}^2\pi^0_{2p_x}\pi^*_{2p_y}{}^1$$

- O_2^-:

$$\sigma^2_{1s}\sigma^*_{1s}{}^2\sigma^2_{2s}\sigma^*_{2s}{}^2\sigma^2_{2p}\pi^2_{2p_y}\pi^*_{2p_y}{}^2\pi^2_{2p_x}\pi^*_{2p_y}{}^1$$

  From Equation ???, the bond order for O_2^- is 1.5. An alternative and equally valid configuration is

$$\sigma^2_{1s}\sigma^*_{1s}{}^2\sigma^2_{2s}\sigma^*_{2s}{}^2\sigma^2_{2p}\pi^2_{2p_y}\pi^*_{2p_y}{}^2\pi^1_{2p_x}\pi^*_{2p_y}{}^2$$

- O_2^{2-}:

$$\sigma^2_{1s}\sigma^*_{1s}{}^2\sigma^2_{2s}\sigma^*_{2s}{}^2\sigma^2_{2p}\pi^2_{2p_y}\pi^*_{2p_y}{}^2\pi^2_{2p_x}\pi^*_{2p_y}{}^2$$

  From Equation ???, the bond order for O_2^{2-} is 1.

The bond order decreases and the bond length increases in the order. The predicted order of increasing bondlength then is $O_2^+ < O_2 < O_2^- < O_2^{2-}$. This trend is confirmed experimentally with O_2^+ (112.2 pm), O_2 (121 pm), O_2^- (128 pm) and O_2^{2-} (149 pm).

9.5.1.1: Molecular Oxygen is Paramagnetic

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. None of the other bonding models (e.g., Valence Bond theory or Lewis bonding) can predict the presence of two unpaired electrons in O_2.

Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Video 9.10.1 , it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches.

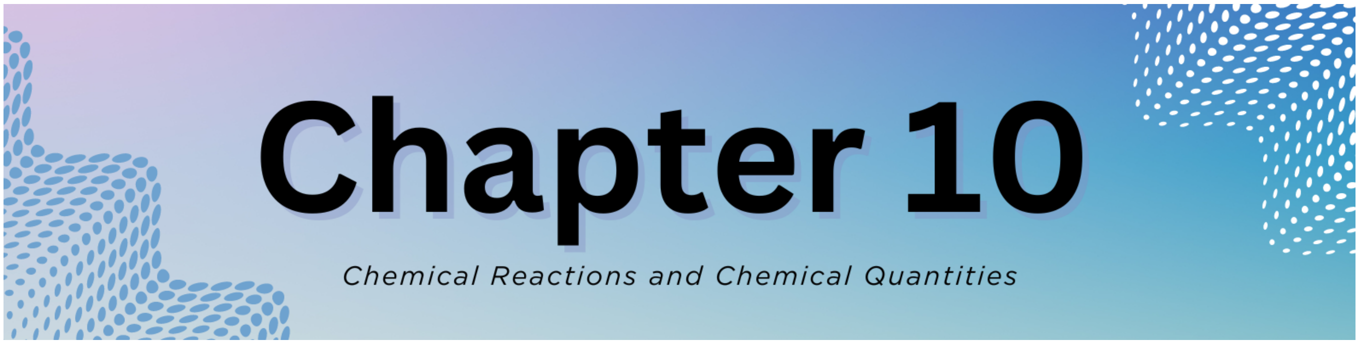
Video 9.10.1 : Liquid O_2 Suspended between the Poles of a Magnet. Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

Advanced: Spin Barriers

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth’s atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*.

CHAPTER OVERVIEW

10: Chemical Reactions and Chemical Quantities



In this paragraph from the *Elements of Chemistry*, Antoine Lavoisier (1743–94) is explaining an experiment in which he was trying to demonstrate that water is not an element but instead is composed of hydrogen (the gas “capable of being burnt”) and oxygen. This is a historical account of a groundbreaking experiment and illustrates the importance of *amounts* in chemistry. Lavoisier was pointing out that the initial total mass of water and charcoal, 85.7 g plus 28 g, equals the final total mass of carbonic acid and the particular gas, 100 g plus 13.7 g. In this way, he was illustrating the law of conservation of matter - another way of saying that *amounts matter*.

Amounts do matter and in a variety of circumstances. For example, a nurse who mistakenly read “2–3 mg” as “23 mg” and administered the higher and potentially fatal dose of morphine to a child. Food scientists who work in test kitchens must keep track of specific amounts of ingredients as they develop new products for us to eat. Quality control technicians measure amounts of substances in manufactured products to ensure that the products meet company or government standards. Supermarkets routinely weigh meat and produce and charge consumers by the ounce or the pound.

In the lab, we look at changes in matter that deal with billions of atoms at a time. How can we keep track of so many atoms (and molecules) during the reaction process? In this chapter, we will be describing and quantifying chemical changes via **stoichiometry** - or "element counting".

5.01: Prelude to Introduction to Chemical Reactions

Chapter Sections

References

1. https://saylordotorg.github.io/text_...l-reactio.html

10.1: Chemical Reactions and Balanced Chemical Equations

Learning Objectives

- Explain the roles of subscripts and coefficients in chemical equations.
- Balance a chemical equation when given the unbalanced equation.

Even though chemical compounds are broken up and new compounds are formed during a chemical reaction, atoms in the reactants do not disappear, nor do new atoms appear to form the products. In chemical reactions, atoms are never created or destroyed. The same atoms that were present in the reactants are present in the products—they are merely reorganized into different arrangements. In a complete chemical equation, the two sides of the equation must be present on the reactant and the product sides of the equation.

Coefficients and Subscripts

There are two types of numbers that appear in chemical equations. There are subscripts, which are part of the chemical formulas of the reactants and products; and there are coefficients that are placed in front of the formulas to indicate how many molecules of that substance is used or produced.

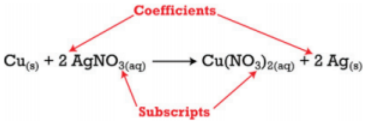
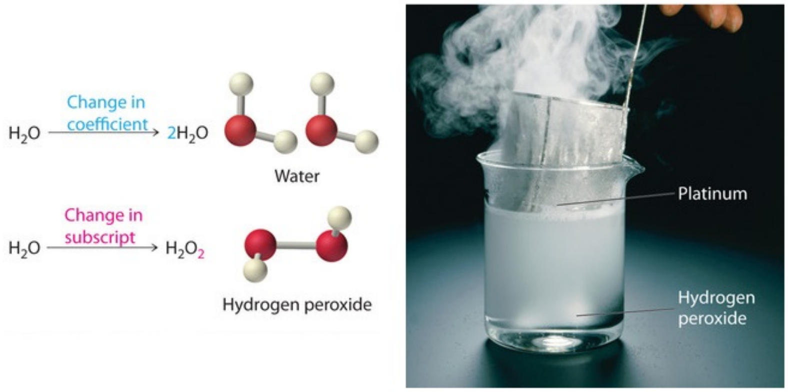


Figure 10.1.1: Balancing Equations. *You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water* (H_2O) *and hydrogen peroxide* (H_2O_2) *are chemically distinct substances.* H_2O_2 *decomposes to* H_2O *and* O_2 *gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.*

The **subscripts** are part of the formulas and once the formulas for the reactants and products are determined, the subscripts may not be changed. The **coefficients** indicate the number of each substance involved in the reaction and may be changed in order to balance the equation. The equation above indicates that one mole of solid copper is reacting with two moles of aqueous silver nitrate to produce one mole of aqueous copper (II) nitrate and two atoms of solid silver.

Balancing a Chemical Equation

Because the identities of the reactants and products are fixed, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure 10.1.1.



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

Steps in Balancing a Chemical Equation

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

Example 10.1.1: Combustion of Heptane

Balance the chemical equation for the combustion of Heptane (C_7H_{16}).

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

Solution

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is C_7H_{16}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients.**	a. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which contains 1 carbon atom, on the right side: $$\mathrm{C_7H_{16}(l) + O_2(g) \rightarrow \underline{7}CO_2(g) + H_2O(g)}$$ - 7 carbon atoms on both reactant and product sides b. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H_2O molecules, each of which contains 2 hydrogen atoms, on the right side: $$\mathrm{C_7H_{16}(l) + O_2(g) \rightarrow 7\,CO_2(g) + \underline{8}H_2O(g)}$$ - 16 hydrogen atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.**	The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O_2, on the reactant side: $$\mathrm{C_7H_{16}(l) + \underline{11}O_2(g) \rightarrow 7\,CO_2(g) + 8\,H_2O(g)}$$ - 22 oxygen atoms on both reactant and product sides
5. **Check your work.**	The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. Always check to be sure that a chemical equation is balanced.

Example 10.1.2: Combustion of Isooctane

Combustion of Isooctane (C_8H_{18})

$$\mathrm{C_8H_{18}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)}$$

Solution

The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start. The combustion of any hydrocarbon with oxygen produces carbon dioxide and water.

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is C_8H_{18}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients.**	a. The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that there must be 8 CO_2 molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow \underline{8}CO_2(g) + H_2O(g)$$ - 8 carbon atoms on both reactant and product sides b. 18 hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow 8\,CO_2(g) + \underline{9}H_2O(g)$$ - 18 hydrogen atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.**	The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 molecule, we must use a fractional coefficient ($\frac{25}{2}$) to balance the oxygen atoms: $$C_8H_{18}(l) + \underline{\frac{25}{2}}O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(g)$$ - 25 oxygen atoms on both reactant and product sides The equation is now balanced, but we usually write equations with whole number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by **2**: $$\underline{2}C_8H_{18}(l) + \underline{25}O_2(g) \longrightarrow \underline{16}CO_2(g) + \underline{18}H_2O(g)$$
5. **Check your work.**	The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side. Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

✓ Example 10.1.3: Precipitation of Lead (II) Chloride

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

Solution

Steps	Example

Steps	**Example**
1. **Identify the most complex substance.**	The most complex substance is lead (II) chloride. $Pb(NO_3)_2(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + PbCl_2(s)$
2. **Adjust the coefficients.**	There are twice as many chloride ions in the reactants than in the products. Place a 2 in front of the NaCl in order to balance the chloride ions. $Pb(NO_3)_2(aq) + \underline{2}NaCl(aq) \rightarrow NaNO_3(aq) + PbCl_2(s)$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on reactant side, 1 Na atom on product side • 2 Cl atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	The nitrate ions are still unbalanced. Place a 2 in front of the $NaNO_3$. The result is: $Pb(NO_3)_2(aq) + 2\,NaCl(aq) \rightarrow \underline{2}NaNO_3(aq) + PbCl_2(s)$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on both reactant and product sides • 2 Cl atoms on both reactant and product sides • 2 NO_3^- atoms on both reactant and product sides
4. **Balance the remaining atoms.**	There is no need to balance the remaining atoms because they are already balanced.
5. **Check your work.**	$Pb(NO_3)_2(aq) + 2\,NaCl(aq) \rightarrow 2\,NaNO_3(aq) + PbCl_2(s)$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on both reactant and product sides • 2 Cl atoms on both reactant and product sides • 2 NO_3^- atoms on both reactant and product sides

? Exercise 10.1.1

Is each chemical equation balanced?

a. $2\,Hg(\ell) + O_2(g) \rightarrow 2\,HgO(s)$
b. $C_2H_4(g) + 2\,O_2(g) \rightarrow 2\,CO_2(g) + 2\,H_2O(g)$
c. $Mg(NO_3)_2(s) + 2\,Li(s) \rightarrow Mg(s) + 2\,LiNO_3(s)$

Answer a

yes

Answer b

no

Answer c

yes

? Exercise 10.1.2

Balance the following chemical equations.

a. $N_2(g) + O_2(g) \rightarrow NO_2(g)$
b. $Pb(NO_3)_2(aq) + FeCl_3(aq) \rightarrow Fe(NO_3)_3(aq) + PbCl_2(s)$
c. $C_6H_{14}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

Answer a

N_2 (g) + $2O_2$ (g) → $2NO_2$ (g)

Answer b

$3Pb(NO_3)_2$(aq) + $2FeCl_3$(aq) → $2Fe(NO_3)_3$(aq) + $3PbCl_2$(s)

Answer c

$2C_6H_{14}$(l) + $19O_2$(g)→ $12CO_2$(g) + $14H_2O$(g)

Summary

- To be useful, chemical equations must always be balanced. Balanced chemical equations have the same number and type of each atom on both sides of the equation.
- The coefficients in a balanced equation must be the simplest whole number ratio. Mass is always conserved in chemical reactions.

Vocabulary

- Chemical reaction: The process in which one or more substances are changed into one or more new substances.
- Reactants: The starting materials in a reaction.
- Products: Materials present at the end of a reaction.
- Balanced chemical equation: A chemical equation in which the number of each type of atom is equal on the two sides of the equation.
- Subscripts: Part of the chemical formulas of the reactants and products that indicate the number of atoms of the preceding element.
- Coefficient: A small whole number that appears in front of a formula in a balanced chemical equation.

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10.1.1: Coefficients and Mole Ratios

Learning Objectives

- Balance a chemical equation in terms of moles.
- Use the balanced equation to construct conversion factors in terms of moles.
- Calculate moles of one substance from moles of another substance using a balanced chemical equation.

Consider this balanced chemical equation:

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

We interpret this as "two molecules of hydrogen react with one molecule of oxygen to make two molecules of water." The chemical equation is balanced as long as the coefficients are in the ratio 2:1:2. For instance, this chemical equation is also balanced:

$$100\,H_2 + 50\,O_2 \rightarrow 100\,H_2O$$

This equation is not conventional—because convention says that we use the lowest ratio of coefficients—but it is balanced. So is this chemical equation:

$$5,000\,H_2 + 2,500\,O_2 \rightarrow 5,000\,H_2O$$

Again, this is not conventional, but it is still balanced. Suppose we use a much larger number:

$$12.044 \times 10^{23} H_2 + 6.022 \times 10^{23} O_2 \rightarrow 12.044 \times 10^{23} H_2O$$

These coefficients are also in the ratio of 2:1:2. But these numbers are related to the number of things in a mole: the first and last numbers are two times Avogadro's number, while the second number is Avogadro's number. That means that the first and last numbers represent 2 mol, while the middle number is just 1 mol. Well, why not just use the number of moles in balancing the chemical equation?

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

is the same balanced chemical equation we started with! What this means is that chemical equations are not just balanced in terms of molecules; *they are also balanced in terms of moles*. We can just as easily read this chemical equation as "two moles of hydrogen react with one mole of oxygen to make two moles of water." All balanced chemical reactions are balanced in terms of moles.

✓ Example 10.1.1.1

Interpret this balanced chemical equation in terms of moles.

$$P_4 + 5\,O_2 \rightarrow P_4O_{10}$$

Solution

The coefficients represent the number of moles that react, not just molecules. We would speak of this equation as "one mole of molecular phosphorus reacts with five moles of elemental oxygen to make one mole of tetraphosphorus decoxide."

? Exercise 10.1.1.1

Interpret this balanced chemical equation in terms of moles.

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

Answer

One mole of elemental nitrogen reacts with three moles of elemental hydrogen to produce two moles of ammonia.

In Section 4.1, we stated that a chemical equation is simply a recipe for a chemical reaction. As such, chemical equations also give us equivalents—equivalents between the reactants and the products. However, now we understand that *these equivalents are expressed in terms of moles*. Consider the chemical equation

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

This chemical reaction gives us the following equivalents:

$$2 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } H_2O$$

Any two of these quantities can be used to construct a conversion factor that lets us relate the number of moles of one substance to an equivalent number of moles of another substance. If, for example, we want to know how many moles of oxygen will react with 17.6 mol of hydrogen, we construct a conversion factor between 2 mol of H_2 and 1 mol of O_2 and use it to convert from moles of one substance to moles of another:

$$17.6\ mol\,\cancel{H_2} \times \frac{1\,mol\,O_2}{2\ mol\,\cancel{H_2}} = 8.80\,mol\,O_2$$

Note how the mol H_2 unit cancels, and mol O_2 is the new unit introduced. This is an example of a **mole-mole calculation,** when you start with moles of one substance and convert to moles of another substance by using the balanced chemical equation. The example may seem simple because the numbers are small, but numbers won't always be so simple!

✓ Example 10.1.1.2

For the balanced chemical equation

$$2\,C_4H_{10}(g) + 13\,O_2 \rightarrow 8\,CO_2(g) + 10\,H_2O(\ell)$$

if 154 mol of O_2 are reacted, how many moles of CO_2 are produced?

Solution

We are relating an amount of oxygen to an amount of carbon dioxide, so we need the equivalence between these two substances. According to the balanced chemical equation, the equivalence is

$$13 \text{ mol } O_2 \Leftrightarrow 8 \text{ mol } CO_2$$

We can use this equivalence to construct the proper conversion factor. We start with what we are given and apply the conversion factor:

$$154\ mol\,\cancel{O_2} \times \frac{8\,mol\,CO_2}{13\ mol\,\cancel{O_2}} = 94.8\,mol\,CO_2$$

The mol O_2 unit is in the denominator of the conversion factor so it cancels. Both the 8 and the 13 are exact numbers, so they do not contribute to the number of significant figures in the final answer.

? Exercise 10.1.1.2

Using the above equation, how many moles of H_2O are produced when 154 mol of O_2 react?

Answer

118 mol

It is important to reiterate that balanced chemical equations are balanced in terms of *moles*. Not grams, kilograms, or liters—but moles. Any stoichiometry problem will likely need to work through the mole unit at some point, especially if you are working with a balanced chemical reaction.

Summary

Balanced chemical reactions are balanced in terms of moles. A balanced chemical reaction gives equivalents in moles that allow stoichiometry calculations to be performed.

10.2: General Types of Chemical Reactions

Learning Objectives

- To classify a given chemical reaction into a variety of types.

Although there are untold millions of possible chemical reactions, most can be classified into a small number of general reaction types. Classifying reactions has two purposes: it helps us to recognize similarities among them, and it enables us to predict the products of certain reactions. A particular reaction may fall into more than one of the categories that we will define in this book.

Combination (composition) Reactions

A combination (composition) reaction is a chemical reaction that makes a single substance from two or more reactants. There may be more than one molecule of product in the balanced chemical equation, but there is only one substance produced. For example, the equation

$$4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3 \tag{10.2.1}$$

is a combination reaction that produces Fe_2O_3 from its constituent elements—Fe and O_2. Combination reactions do not have to combine elements, however. The chemical equation

$$Fe_2O_3 + 3\,SO_3 \rightarrow Fe_2(SO_4)_3 \tag{10.2.2}$$

shows a combination reaction in which Fe_2O_3 combines with three molecules of SO_3 to make $Fe_2(SO_4)_3$.

Example 10.2.1

Which equations are combination reactions?

a. $Co(s) + Cl_2(g) \rightarrow CoCl_2(s)$
b. $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$
c. $N_2H_4(\ell) + O_2(g) \rightarrow N_2(g) + 2H_2O(\ell)$

Solution

a. This is a combination reaction.
b. This is a combination reaction. (The compound $COCl_2$ is called phosgene and, in the past, was used as a gassing agent in chemical warfare.)
c. This is not a combination reaction.

Exercise 10.2.1

Which equations are combination reactions?

a. $P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(g)$
b. $SO_3(\ell) + H_2O(\ell) \rightarrow H_2SO_4(\ell)$
c. $NaOH(s) + HCl(g) \rightarrow NaCl(s) + H_2O(\ell)$

Decomposition Reactions

A decomposition reaction is the reverse of a combination reaction. In a decomposition reaction, a single substance is converted into two or more products. There may be more than one molecule of the reactant, but there is only one substance initially. For example, the equation

$$2\,NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(\ell) \tag{10.2.3}$$

is a decomposition reaction that occurs when $NaHCO_3$ is exposed to heat. Another example is the decomposition of $KClO_3$:

$$2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g) \tag{10.2.4}$$

This reaction was once commonly used to generate small amounts of oxygen in the chemistry lab.

> The decomposition reaction of $NaHCO_3$ is the reaction that occurs when baking soda is poured on a small kitchen fire. The intent is that the H_2O and CO_2 produced by the decomposition will smother the flames.

Combustion Reactions

A combustion reaction occurs when a substance combines with molecular oxygen to make oxygen-containing compounds of other elements in the reaction. One example is the burning of acetylene (C_2H_2) in torches:

$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O \tag{10.2.5}$$

Oxygen (in its elemental form) is a crucial reactant in combustion reactions, and it is also present in the products.

> *Energy in the form of heat is usually given off as a product in a combustion reaction as well.*

✓ Example 10.2.2

Identify each type of reaction.

a. $2K(s) + S(s) + 2O_2(g) \rightarrow K_2SO_4(s)$
b. $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(\ell)$
c. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$

Solution

a. Multiple reactants are combining to make a single product, so this reaction is a combination reaction.
b. A single substance reacts to make several products, so we have a decomposition reaction.
c. Oxygen reacts with a compound to make carbon dioxide (an oxide of carbon) and water (an oxide of hydrogen). This is a combustion reaction.

? Exercise 10.2.2

Identify each type of reaction.

a. $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
b. $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$
c. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Summary

There are several recognizable types of chemical reactions: combination, decomposition, and combustion reactions are examples.

Concept Review Exercises

1. What is the difference between a combination reaction and a combustion reaction?
2. Give the distinguishing characteristic(s) of a decomposition reaction.
3. How do we recognize a combustion reaction?

Answers

1. A combination reaction produces a certain substance; a combustion reaction is a vigorous reaction, usually a combination with oxygen, that is accompanied by the production of light and/or heat.
2. In a decomposition reaction, a single substance reacts to make multiple substances as products.
3. A combustion reaction is typically a vigorous reaction accompanied by light and/or heat, usually because of reaction with oxygen.

Exercises

1. Identify each type of reaction.
    a. $C_6H_5CH_3 + 9O_2 \rightarrow 7CO_2 + 4H_2O$

   b. $2NaHCO_3$ → $Na_2CO_3 + H_2O + CO_2$
   c. $C + 2H_2$ → CH_4

2. Identify each type of reaction.

   a. $P_4O_{10} + 6H_2O$ → $4H_3PO_4$
   b. $FeO + SO_3$ → $FeSO_4$
   c. $CaCO_3(s)$ → $CO_2(g) + CaO(s)$

3. Identify each type of reaction.

   a. $2NH_4NO_3(s)$ → $2N_2(g) + 4H_2O(g) + O_2(g)$
   b. $Hg(\ell) + ½O_2\ (g)$ → $HgO(s)$
   c. $CH_2CH_2(g) + Br_2(\ell)$ → CH_2BrCH_2Br

4. Identify each type of reaction.

   a. $Ti(s) + O_2(g)$ → $TiO_2(s)$
   b. $H_2SO_3(aq)$ → $H_2O(\ell) + SO_2(g)$
   c. $3O_2(g)$ → $2O_3(g)$

Answers

1. a. combustion
   b. decomposition
   c. combination

3. a. decomposition
   b. combustion or combination
   c. combination

10.3: Mole Quantities

Learning Objectives

- Express amounts of substances in g, kg, or mL, or L.
- Express amounts of substances in moles (mol).
- Convert amounts of substances from mass units (g, kg etc) to the unit mole.

Amounts of Substances in Various Units

Amounts of substances are measured in units of mass (g or kg), volume (L) and mole (mol). Unit interconversions are based on the definitions of the units, and converting amounts from g or kg into mol is based on atomic masses of the elements.

Atomic masses are the masses of one mole of elements. A **mole** of any element has an Avogadro's number of atoms (= 6.02x10^{23} atoms per mole).

The natural units of substances are **molecules**, which are groups of atoms bonded together, except monatomic molecules of inert gases, He, Ne, Ar, Kr, Xe, and Rn. For example, molecules of oxygen, water, and phosphorous are $\mathrm{O_2}$, $\mathrm{H_2O}$, and $\mathrm{P_4}$ respectively. These molecules have 2, 3, and 4 atoms respectively. Masses of one mole of substances are called **molecular weights**. Atomic and molecular weights are called **molar masses**.

Molecules of Ne, O_2, H_2O and P_4

The above illustrates only a very small number of examples. There are millions of compounds in the world. Please think of some other compounds you know of, and write down their formulas. Then figure out the number of atoms in each mole of your compounds.

Different substances have different molecular masses. Thus, equal masses have different numbers of atoms, molecules, or moles. On the other hand, equal numbers of moles of different substances have different masses. The stoichiometric relationships among reactants and products may be complicated in units of g, but much simpler relationships are seen if we deal with units of moles or natural units of atoms and molecules.

Moles (mol) represent amounts of substances in the unit of **Avogadro's number** (6.022x10^{23}) of atoms and molecules. Since empirical formulas such as $\mathrm{Fe^{2+}}$ ions and $\mathrm{Fe_2O_3}$ are used for ionic compounds, a mole represent Avogadro's number of ions or per formula as written. A mole of $\mathrm{Fe^{2+}}$ has 6.022x10^{23} ions, and a mole of $\mathrm{Fe_2O_3}$ has 1.204x10^{24} Fe and 1.8066x10^{24} O atoms, a total of 3.0x10^{24} Fe and O atoms.

The mole unit is very important for chemical reactions, as is the skill to convert masses in g to mol. The number of moles of a substance in a sample is the mass in g divided by the **molar mass**, which gives the amount in moles.

$$\mathrm{mole} = \dfrac{\mathrm{mass\ (g)}}{\mathrm{molar\ mass\ (g/mol)}}$$

Another common measure of substances is volume. Since density is the mass divided by its volume, conversion between volume and mass is accomplished by the formula:

$$\mathrm{density} = \dfrac{\mathrm{mass\ (g)}}{\mathrm{volume\ (cm^3)}}$$

$$\mathrm{mass} = \mathrm{density\ (g\ cm^{-3})} \times \mathrm{volume\ (cm^3)}$$

These fundamental formulas are results of the definition of these terms.

Key Concepts

- Atoms, atomic weights, masses
- Molecules, molecular weights

- Empirical formula, ionic compounds
- Avogadro's number, mole, molar masses

Skill Developing Questions

1. **What are the molar masses of the elements hydrogen (H), oxygen (O), iron (Fe) and gold (Au)?**

   Know where to find: 1.0, 16.0, 55.9, 197

   Skill: know where to find molar masses of elements.

2. **The element gold is a precious metal. How many moles of gold are present in a mass of 1.0 kg?**

   1000/197 = ?

   Skill: to convert mass in g into moles.

3. **A liter of water has a mass of 1.0 kg. How many moles of water are 1.0 kg?**

   1000 g / 18 g = 55.6 mol

   Skill: calculate molar masses of molecular compounds

4. **At standard temperature and pressure, a mole of gas occupies 22.4 L. If 20% of air is oxygen, how many moles of oxygen are contained in 1.0 L?**

   0.20 mol / 22.4 L = 8.93e-3 mol/L

   Skill: express amount in volume.

5. **How many grams are there in 8.93e-3 mol of oxygen O_2 (molar mass 32.0)?**

   32 g/mol * 8.93e-3 mol = 0.286 g

   Skill: convert amounts in moles to mass in g or kg.

6. **How many moles of Fe_2O_3 are present in 1000 kg of the oxide? Atomic weights: Fe, 55.8, O, 16.0.**

   1000000 g/(159.6 g/mol) = 6265 mol

   Skill: convert amounts between moles and kg of compounds represented by chemical formulas.

Contributors and Attributions

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10.4: Stoichiometry

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

Balancing

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

Reactants to Products

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

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

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

Stoichiometric Coefficients

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

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

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

✓ Example 1

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

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

Solution

Start by counting the number of atoms of each element.

UNBALANCED

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

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

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

BALANCED

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

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

A balanced equation ultimately has to satisfy two conditions.

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

Stoichiometry and Balanced Equations

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

✓ Example 2

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

Solution

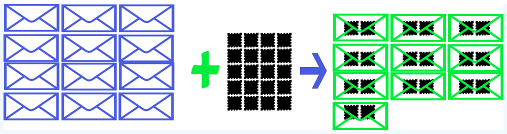
The equation for this can be written as

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

where

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

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



Invitations Stamps Party Invitations Sent

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

Example 3

What is the limiting reagent in this example?

Solution

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

$$12 \text{ I x } (1IS_2/1I) = 12 \text{ } IS_2 \text{ possible}$$

$$20 \text{ S x } (1IS_2/2S) = 10 \text{ } IS_2 \text{ possible}$$

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

Types of Reactions

There are 6 basic types of reactions.

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

Molar Mass

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

Example 4

What is the molar mass of H_2O?

Solution

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

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

✓ Example 5: Combustion of Propane

Propane ($\mathrm{C_3H_8}$) burns in this reaction:

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

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

Solution

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

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

Variation in Stoichiometric Equations

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

Density

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

Volume x (Mass/Volume) = Mass

Mass x (Volume/Mass) = Volume

Percent Mass

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

✓ Example 6

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

Solution

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

0.5g carbon x (1 mol carbon/12.011g carbon) = 0.0416 mol carbon

Molarity

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

✓ Example 7

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

Solution

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

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

Determining Empirical Formulas

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

✓ Example 8: Combustion of Organic Molecules

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

Solution

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

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

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

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

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

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

Moles of oxygen in CO_2:

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

Moles of oxygen in H_2O:

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

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

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

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

Moles of oxygen in O_2

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

Moles of oxygen in unknown

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

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

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

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

Determining Molecular Formulas

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

✓ Example 9

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

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

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

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

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

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

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

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

$$CH_2O * 4 = ?$$

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

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

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

$$CH_2O * 4 = C_4H_8O_4$$

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

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

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

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

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

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

✓ Example 10: Complex Stoichiometry Problem

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

Solution

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

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

Step 2: Write down all the given information

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

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

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

1 liter alloy = 1000cm^3 alloy

alloy sample = 1.203cm^3 alloy

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

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

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

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

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

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

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

Step 5: Check units

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

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

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

Problems

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

1) Why are the following equations not considered balanced?

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

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

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

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

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

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

Weblinks for further reference

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

References

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10.5: The Limiting Reactant, Theoretical Yield, and Percent Yield

Learning Objectives

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

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

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

$$1 \text{ box mix} + 2 \text{ eggs} \rightarrow 1 \text{ batch brownies} \tag{10.5.1}$$

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

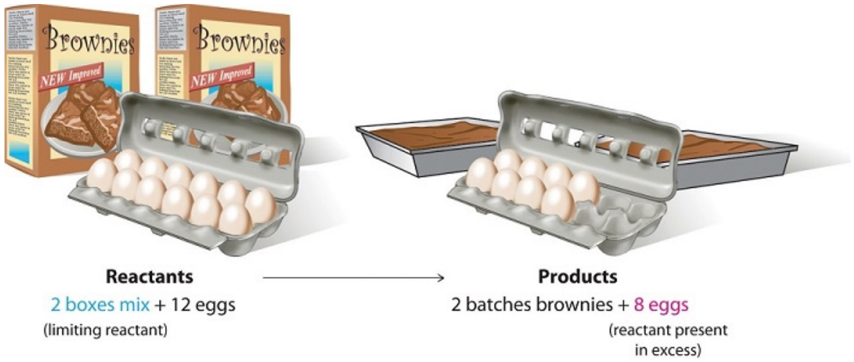


Figure 10.5.1: The Concept of a Limiting Reactant in the Preparation of Brownies

Reactants: 2 boxes of brownie mix + 12 eggs produces 2 batches of brownies + 8 eggs. Brownie mix is the limiting reactant. Eggs are the reactant present in excess.

Introduction to Limiting Reactant Problems: Introduction to Limiting Reactant Problems, YouTube(opens in new window) [youtu.be]

Now consider a chemical example of a limiting reactant: the production of pure titanium. This metal is fairly light (45% lighter than steel and only 60% heavier than aluminum) and has great mechanical strength (as strong as steel and twice as strong as aluminum). Because it is also highly resistant to corrosion and can withstand extreme temperatures, titanium has many applications in the aerospace industry. Titanium is also used in medical implants and portable computer housings because it is light and resistant to corrosion. Although titanium is the ninth most common element in Earth's crust, it is relatively difficult to extract from its ores. In the first step of the extraction process, titanium-containing oxide minerals react with solid carbon and chlorine gas to form titanium tetrachloride ($\mathrm{TiCl_4}$) and carbon dioxide.

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

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

$$\mathrm{TiCl_4(g) + 2\ Mg(l) \rightarrow Ti(s) + 2\ MgCl_2(l)} \tag{10.5.2}$$

Because titanium ores, carbon, and chlorine are all rather inexpensive, the high price of titanium (about $100 per kilogram) is largely due to the high cost of magnesium metal. Under these circumstances, magnesium metal is the limiting reactant in the production of metallic titanium.

Figure 10.5.2: Medical use of titanium. Here is an example of its successful use in joint replacement implants. An A-P X-ray of a pelvis showing a total hip joint replacement. The right hip joint (on the left in the photograph) has been replaced. A metal prostheses is cemented in the top of the right femur and the head of the femur has been replaced by the rounded head of the prosthesis. Figure courtesy of NIH (NIADDK) 9AO4 (Connie Raab)

With 1.00 kg of titanium tetrachloride and 200 g of magnesium metal, how much titanium metal can be produced according to Equation 10.5.2?

Solving this type of problem requires that you carry out the following steps

1. Determine the number of moles of each reactant.
2. Compare the mole ratio of the reactants with the ratio in the balanced chemical equation to determine which reactant is limiting.
3. Calculate the number of moles of product that can be obtained from the limiting reactant.
4. Convert the number of moles of product to mass of product.

Step 1: To determine the number of moles of reactants present, calculate or look up their molar masses: 189.679 g/mol for titanium tetrachloride and 24.305 g/mol for magnesium. The number of moles of each is calculated as follows:

$$\begin{aligned} \text{moles } \mathrm{TiCl_4} &= \frac{\text{mass } \mathrm{TiCl_4}}{\text{molar mass } \mathrm{TiCl_4}} \\ &= 1000 \ \cancel{g}\ \mathrm{TiCl_4} \times \frac{1\, mol\ TiCl_4}{189.679 \ \cancel{g}\ \mathrm{TiCl_4}} \\ &= 5.272\, mol\ \mathrm{TiCl_4} \end{aligned} \tag{10.5.3}$$

$$\begin{aligned} \text{moles Mg} &= \frac{\text{mass Mg}}{\text{molar mass Mg}} \\ &= 200 \ \cancel{g}\ \mathrm{Mg} \times \frac{1\ mol\ \mathrm{Mg}}{24.305 \ \cancel{g}\ \mathrm{Mg}} \\ &= 8.23\ \mathrm{mol\ Mg} \end{aligned} \tag{10.5.4}$$

Step 2: There are more moles of magnesium than of titanium tetrachloride, but the ratio is only the following:

$$\frac{mol\ \mathrm{Mg}}{mol\ \mathrm{TiCl_4}} = \frac{8.23\ mol}{5.272\ mol} = 1.56$$

Because the ratio of the coefficients in the balanced chemical equation is,

$$\frac{2\ mol\ \mathrm{Mg}}{1\ mol\ \mathrm{TiCl_4}} = 2$$

there is not have enough magnesium to react with all the titanium tetrachloride. If this point is not clear from the mole ratio, calculate the number of moles of one reactant that is required for complete reaction of the other reactant. For example, there are 8.23 mol of Mg, so (8.23 ÷ 2) = 4.12 mol of $\mathrm{TiCl_4}$ are required for complete reaction. Because there are 5.272 mol of $\mathrm{TiCl_4}$, titanium tetrachloride is present in excess. Conversely, 5.272 mol of $\mathrm{TiCl_4}$ requires 2 × 5.272 = 10.54 mol of Mg, but there are only 8.23 mol. Therefore, magnesium is the limiting reactant.

Step 3: Because magnesium is the limiting reactant, the number of moles of magnesium determines the number of moles of titanium that can be formed:

$$mol\ \mathrm{Ti} = 8.23\ mol\ \mathrm{Mg} = \frac{1\ mol\ \mathrm{Ti}}{2\ mol\ \mathrm{Mg}} = 4.12\ mol\ \mathrm{Ti}$$

Thus only 4.12 mol of Ti can be formed.

Step 4. To calculate the mass of titanium metal that can obtain, multiply the number of moles of titanium by the molar mass of titanium (47.867 g/mol):

$$\begin{aligned} \text{moles Ti} &= \text{mass Ti} \times \text{molar mass Ti} \\ &= 4.12\ mol\ \mathrm{Ti} \times \frac{47.867\ g\ \mathrm{Ti}}{1\ mol\ \mathrm{Ti}} \\ &= 197\ g\ \mathrm{Ti} \end{aligned}$$

Here is a simple and reliable way to identify the limiting reactant in any problem of this sort:

1. Calculate the number of moles of each reactant present: 5.272 mol of $\mathrm{TiCl_4}$ and 8.23 mol of Mg.
2. Divide the actual number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation:

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

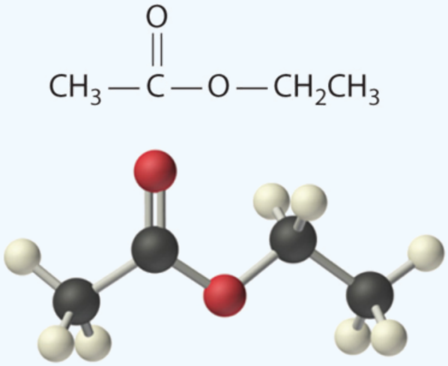
$$Mg : \frac{8.23\ mol\ (actual)}{2\ mol\ (stoich)} = 4.12$$

3. The reactant with the smallest mole ratio is limiting. Magnesium, with a calculated stoichiometric mole ratio of 4.12, is the limiting reactant.

Density is the mass per unit volume of a substance. If we are given the density of a substance, we can use it in stoichiometric calculations involving liquid reactants and/or products, as Example 10.5.1 demonstrates.

Example 10.5.1: Fingernail Polish Remover

Ethyl acetate ($CH_3CO_2C_2H_5$) is the solvent in many fingernail polish removers and is used to decaffeinate coffee beans and tea leaves. It is prepared by reacting ethanol (C_2H_5OH) with acetic acid (CH_3CO_2H); the other product is water. A small amount of sulfuric acid is used to accelerate the reaction, but the sulfuric acid is not consumed and does not appear in the balanced chemical equation. Given 10.0 mL each of acetic acid and ethanol, how many grams of ethyl acetate can be prepared from this reaction? The densities of acetic acid and ethanol are 1.0492 g/mL and 0.7893 g/mL, respectively.



Ethyl acetate

Given: reactants, products, and volumes and densities of reactants

Asked for: mass of product

Strategy:

A. Balance the chemical equation for the reaction.
B. Use the given densities to convert from volume to mass. Then use each molar mass to convert from mass to moles.
C. Using mole ratios, determine which substance is the limiting reactant. After identifying the limiting reactant, use mole ratios based on the number of moles of limiting reactant to determine the number of moles of product.
D. Convert from moles of product to mass of product.

Solution:

A Always begin by writing the balanced chemical equation for the reaction:

$$C_2H_5OH(l) + CH_3CO_2H(aq) \rightarrow CH_3CO_2C_2H_5(aq) + H_2O(l)$$

B We need to calculate the number of moles of ethanol and acetic acid that are present in 10.0 mL of each. Recall that the density of a substance is the mass divided by the volume:

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

Rearranging this expression gives mass = (density)(volume). We can replace mass by the product of the density and the volume to calculate the number of moles of each substance in 10.0 mL (remember, 1 mL = 1 cm^3):

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

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

C The number of moles of acetic acid exceeds the number of moles of ethanol. Because the reactants both have coefficients of 1 in the balanced chemical equation, the mole ratio is 1:1. We have 0.171 mol of ethanol and 0.175 mol of acetic acid, so ethanol is the limiting reactant and acetic acid is in excess. The coefficient in the balanced chemical equation for the product (ethyl acetate) is also 1, so the mole ratio of ethanol and ethyl acetate is also 1:1. This means that given 0.171 mol of ethanol, the amount of ethyl acetate produced must also be 0.171 mol:

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

D The final step is to determine the mass of ethyl acetate that can be formed, which we do by multiplying the number of moles by the molar mass:

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

Thus 15.1 g of ethyl acetate can be prepared in this reaction. If necessary, you could use the density of ethyl acetate (0.9003 g/cm3) to determine the volume of ethyl acetate that could be produced:

$$\begin{aligned}
\text{volume of ethyl acetate } &= 15.1 \, g \, \mathrm{CH_3CO_2C_2H_5} \times \frac{1 \, ml \ \mathrm{CH_3CO_2C_2H_5}}{0.9003 \, g \ \mathrm{CH_3CO_2C_2H_5}} \\
&= 16.8 \, ml \, \mathrm{CH_3CO_2C_2H_5}
\end{aligned}$$

? Exercise 10.5.1

Under appropriate conditions, the reaction of elemental phosphorus and elemental sulfur produces the compound P_4S_{10}. How much P_4S_{10} can be prepared starting with 10.0 g of $\mathrm{P_4}$ and 30.0 g of S_8?

Answer

35.9 g

Determining the Limiting Reactant and Theoretical Yield for a Reaction: Determining the Limiting Reactant and Theoretical Yield for a Reaction, YouTube(opens in new window) [youtu.be]

Limiting Reactants in Solutions

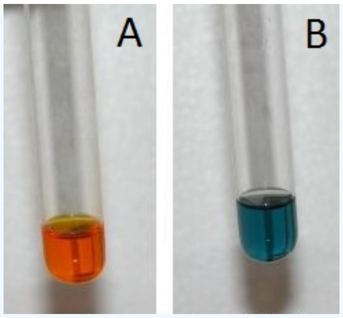
The concept of limiting reactants applies to reactions carried out in solution as well as to reactions involving pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example $10.5.2$

Example $10.5.2$: Breathalyzer reaction

Because the consumption of alcoholic beverages adversely affects the performance of tasks that require skill and judgment, in most countries it is illegal to drive while under the influence of alcohol. In almost all US states, a blood alcohol level of 0.08% by volume is considered legally drunk. Higher levels cause acute intoxication (0.20%), unconsciousness (about 0.30%), and even death (about 0.50%). The Breathalyzer is a portable device that measures the ethanol concentration in a person’s breath, which is directly proportional to the blood alcohol level. The reaction used in the Breathalyzer is the oxidation of ethanol by the dichromate ion:

$$3\,\mathrm{CH_3CH_2OH(aq)} + \underset{yellow-orange}{2\,\mathrm{Cr_2O_7^{2\,-}}\,(aq)} + 16\,\mathrm{H^+(aq)} \xrightarrow[\mathrm{H_2SO_4(aq)}]{\mathrm{Ag^+}} 3\,\mathrm{CH_3CO_2H(aq)} + \underset{green}{4\,\mathrm{Cr^{3\,+}}}(aq) + 11\,\mathrm{H_2O(l)}$$

When a measured volume (52.5 mL) of a suspect’s breath is bubbled through a solution of excess potassium dichromate in dilute sulfuric acid, the ethanol is rapidly absorbed and oxidized to acetic acid by the dichromate ions. In the process, the chromium atoms in some of the $\mathrm{Cr_2O_7^{2\,-}}$ ions are reduced from Cr^{6+} to Cr^{3+}. In the presence of Ag^+ ions that act as a catalyst, the reaction is complete in less than a minute. Because the $\mathrm{Cr_2O_7^{2\,-}}$ ion (the reactant) is yellow-orange and the Cr^{3+} ion (the product) forms a green solution, the amount of ethanol in the person’s breath (the limiting reactant) can be determined quite accurately by comparing the color of the final solution with the colors of standard solutions prepared with known amounts of ethanol.



A Breathalyzer reaction with a test tube before (a) and after (b) ethanol is added. When a measured volume of a suspect's breath is bubbled through the solution, the ethanol is oxidized to acetic acid, and the solution changes color from yellow-orange to green. The intensity of the green color indicates the amount of ethanol in the sample.

A typical Breathalyzer ampul contains 3.0 mL of a 0.25 mg/mL solution of $K_2Cr_2O_7$ in 50% H_2SO_4 as well as a fixed concentration of $AgNO_3$ (typically 0.25 mg/mL is used for this purpose). How many grams of ethanol must be present in 52.5 mL of a person's breath to convert all the Cr^{6+} to Cr^{3+}?

Given: volume and concentration of one reactant

Asked for: mass of other reactant needed for complete reaction

Strategy:

A. Calculate the number of moles of $\mathrm{Cr_2O_7^{2-}}$ ion in 1 mL of the Breathalyzer solution by dividing the mass of $K_2Cr_2O_7$ by its molar mass.
B. Find the total number of moles of $\mathrm{Cr_2O_7^{2-}}$ ion in the Breathalyzer ampul by multiplying the number of moles contained in 1 mL by the total volume of the Breathalyzer solution (3.0 mL).
C. Use the mole ratios from the balanced chemical equation to calculate the number of moles of C_2H_5OH needed to react completely with the number of moles of $\mathrm{Cr_2O_7^{2-}}$ ions present. Then find the mass of C_2H_5OH needed by multiplying the number of moles of C_2H_5OH by its molar mass.

Solution:

A In any stoichiometry problem, the first step is always to calculate the number of moles of each reactant present. In this case, we are given the mass of $K_2Cr_2O_7$ in 1 mL of solution, which can be used to calculate the number of moles of $K_2Cr_2O_7$ contained in 1 mL:

$$\frac{moles\ K_2Cr_2O_7}{1\ mL} = \frac{(0.25\ \cancel{mg}\ K_2Cr_2O_7)}{mL}\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{294.18\ \cancel{g}\ K_2Cr_2O_7}\right) = 8.5\times10^{-7}\ moles$$

B Because 1 mol of $K_2Cr_2O_7$ produces 1 mol of $\mathrm{Cr_2O_7^{2-}}$ when it dissolves, each milliliter of solution contains 8.5×10^{-7} mol of $Cr_2O_7^{2-}$. The total number of moles of $Cr_2O_7^{2-}$ in a 3.0 mL Breathalyzer ampul is thus

$$moles\ Cr_2O_7^{2-} = \left(\frac{8.5\times10^{-7}\ mol}{1\ \cancel{mL}}\right)(3.0\ \cancel{mL}) = 2.6\times10^{-6}\ mol\ Cr_2O_7^{2-}$$

C The balanced chemical equation tells us that 3 mol of C_2H_5OH is needed to consume 2 mol of $\mathrm{Cr_2O_7^{2-}}$ ion, so the total number of moles of C_2H_5OH required for complete reaction is

$$moles\ of\ \mathrm{C_2H_5OH} = (2.6\times10^{-6}\ \ mol\ \cancel{\mathrm{Cr_2O_7^{2-}}})\left(\frac{3\ mol\ \mathrm{C_2H_5OH}}{2\ \ mol\ \cancel{\mathrm{Cr_2O_7^{2-}}}}\right) = 3.9\times10^{-6}\ mol\ \mathrm{C_2H_5OH}$$

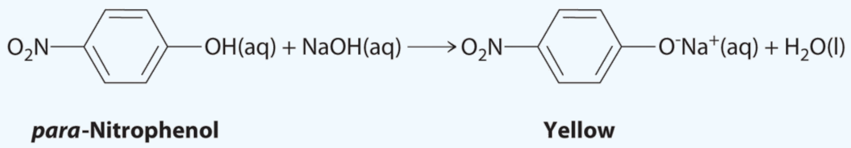
As indicated in the strategy, this number can be converted to the mass of C_2H_5OH using its molar mass:

$$mass\ \mathrm{C_2H_5OH} = (3.9\times10^{-6}\ \ mol\ \cancel{\mathrm{C_2H_5OH}})\left(\frac{46.07\ g}{mol\ \cancel{\mathrm{C_2H_5OH}}}\right) = 1.8\times10^{-4}\ g\ \mathrm{C_2H_5OH}$$

Thus 1.8×10^{-4} g or 0.18 mg of C_2H_5OH must be present. Experimentally, it is found that this value corresponds to a blood alcohol level of 0.7%, which is usually fatal.

? Exercise 10.5.2

The compound *para*-nitrophenol (molar mass = 139 g/mol) reacts with sodium hydroxide in aqueous solution to generate a yellow anion via the reaction



Chemical equation showing conversion of para-nitrophenol to its yellow-colored form with aqueous sodium hydroxide.

Because the amount of *para*-nitrophenol is easily estimated from the intensity of the yellow color that results when excess NaOH is added, reactions that produce *para*-nitrophenol are commonly used to measure the activity of enzymes, the catalysts in biological systems. What volume of 0.105 M NaOH must be added to 50.0 mL of a solution containing 7.20×10^{-4} g of *para*-nitrophenol to ensure that formation of the yellow anion is complete?

Answer

4.93×10^{-5} L or 49.3 μL

In Examples 10.5.1 and 10.5.2, the identities of the limiting reactants are apparent: $[Au(CN)_2]^-$, $LaCl_3$, ethanol, and *para*-nitrophenol. When the limiting reactant is not apparent, it can be determined by comparing the molar amounts of the reactants with their coefficients in the balanced chemical equation. The only difference is that the volumes and concentrations of solutions of reactants, rather than the masses of reactants, are used to calculate the number of moles of reactants, as illustrated in Example 10.5.3.

✓ Example 10.5.3

When aqueous solutions of silver nitrate and potassium dichromate are mixed, an exchange reaction occurs, and silver dichromate is obtained as a red solid. The overall chemical equation for the reaction is as follows:

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

What mass of $Ag_2Cr_2O_7$ is formed when 500 mL of 0.17 M $K_2Cr_2O_7$ are mixed with 250 mL of 0.57 M $AgNO_3$?

Given: balanced chemical equation and volume and concentration of each reactant

Asked for: mass of product

Strategy:

A. Calculate the number of moles of each reactant by multiplying the volume of each solution by its molarity.
B. Determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation.
C. Use mole ratios to calculate the number of moles of product that can be formed from the limiting reactant. Multiply the number of moles of the product by its molar mass to obtain the corresponding mass of product.

Solution:

A The balanced chemical equation tells us that 2 mol of $AgNO_3$(aq) reacts with 1 mol of $K_2Cr_2O_7$(aq) to form 1 mol of $Ag_2Cr_2O_7$(s) (Figure 8.3.2). The first step is to calculate the number of moles of each reactant in the specified volumes:

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

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

B Now determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

$$K_2Cr_2O_7 : \frac{0.085\ mol}{1\ mol} = 0.085$$

$$AgNO_3 : \frac{0.14\ mol}{2\ mol} = 0.070$$

Because 0.070 < 0.085, we know that $AgNO_3$ is the *limiting reactant*.

C Each mole of $Ag_2Cr_2O_7$ formed requires 2 mol of the limiting reactant ($AgNO_3$), so we can obtain only 0.14/2 = 0.070 mol of $Ag_2Cr_2O_7$. Finally, convert the number of moles of $Ag_2Cr_2O_7$ to the corresponding mass:

$$mass\ of\ Ag_2Cr_2O_7 = 0.070\ \cancel{mol} \left(\frac{431.72\ g}{1\ \cancel{mol}}\right) = 30\ g\ Ag_2Cr_2O_7$$

The Ag^+ and $Cr_2O_7^{2-}$ ions form a red precipitate of solid $Ag_2Cr_2O_7$, while the K^+ and NO_3^- ions remain in solution. (Water molecules are omitted from molecular views of the solutions for clarity.)

? Exercise 10.5.3

Aqueous solutions of sodium bicarbonate and sulfuric acid react to produce carbon dioxide according to the following equation:

$$2\,NaHCO_3(aq) + H_2SO_4(aq) \rightarrow 2\,CO_2(g) + Na_2SO_4(aq) + 2\,H_2O(l)$$

If 13.0 mL of 3.0 M H_2SO_4 are added to 732 mL of 0.112 M $NaHCO_3$, what mass of CO_2 is produced?

Answer

3.4 g

Limiting Reactant Problems Using Molarities: Limiting Reactant Problems Using Molarities, YouTube(opens in new window) [youtu.be]eOXTliL-gNw (opens in new window)

Theoretical Yields

When reactants are not present in stoichiometric quantities, the limiting reactant determines the maximum amount of product that can be formed from the reactants. The amount of product calculated in this way is the theoretical yield, the amount obtained if the reaction occurred perfectly and the purification method were 100% efficient.

In reality, less product is always obtained than is theoretically possible because of mechanical losses (such as spilling), separation procedures that are not 100% efficient, competing reactions that form undesired products, and reactions that simply do not run to completion, resulting in a mixture of products and reactants; this last possibility is a common occurrence. Therefore, the actual yield, the measured mass of products obtained from a reaction, is almost always less than the theoretical yield (often much less). The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, multiplied by 100 to give a percentage:

$$\text{percent yield} = \frac{\text{actual yield } (g)}{\text{theoretical yield } (g)} \times 100\% \tag{10.5.5}$$

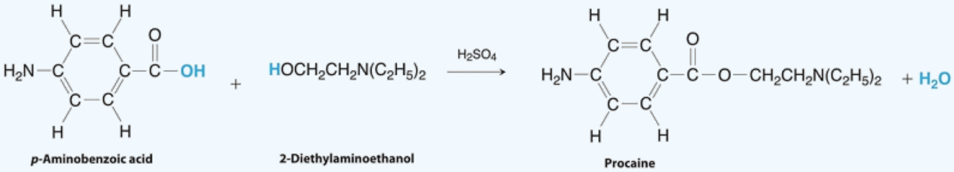
The method used to calculate the percent yield of a reaction is illustrated in Example $10.5.4$

Example $10.5.4$: Novocain

Procaine is a key component of Novocain, an injectable local anesthetic used in dental work and minor surgery. Procaine can be prepared in the presence of H2SO4 (indicated above the arrow) by the reaction

$$\underset{\text{p-amino benzoic acid}}{C_7H_7NO_2} + \underset{\text{2-diethylaminoethanol}}{C_6H_{15}NO} \xrightarrow{H_2SO_4} \underset{\text{procaine}}{C_{13}H_{20}N_2O_2} + H_2O$$

If this reaction were carried out with 10.0 g of p-aminobenzoic acid and 10.0 g of 2-diethylaminoethanol, and 15.7 g of procaine were isolated, what is the percent yield?



The preparation of procaine. A reaction of p-aminobenzoic acid with 2-diethylaminoethanol yields procaine and water.

Given: masses of reactants and product

Asked for: percent yield

Strategy:

A. Write the balanced chemical equation.
B. Convert from mass of reactants and product to moles using molar masses and then use mole ratios to determine which is the limiting reactant. Based on the number of moles of the limiting reactant, use mole ratios to determine the theoretical yield.
C. Calculate the percent yield by dividing the actual yield by the theoretical yield and multiplying by 100.

Solution:

A From the formulas given for the reactants and the products, we see that the chemical equation is balanced as written. According to the equation, 1 mol of each reactant combines to give 1 mol of product plus 1 mol of water.

B To determine which reactant is limiting, we need to know their molar masses, which are calculated from their structural formulas: p-aminobenzoic acid ($C_7H_7NO_2$), 137.14 g/mol; 2-diethylaminoethanol ($C_6H_{15}NO$), 117.19 g/mol. Thus the reaction used the following numbers of moles of reactants:

$$mol \text{ p-aminobenzoic acid} = 10.0\, g \times \frac{1\, mol}{137.14\, g} = 0.0729\, mol \text{ p-aminbenzoic acid}$$

$$mol \text{ 2-diethylaminoethanol} = 10.0\, g \times \frac{1\, mol}{117.19\, g} = 0.0853\, mol \text{ 2-diethylaminoethanol}$$

The reaction requires a 1:1 mole ratio of the two reactants, so p-aminobenzoic acid is the limiting reactant. Based on the coefficients in the balanced chemical equation, 1 mol of p-aminobenzoic acid yields 1 mol of procaine. We can therefore obtain only a maximum of 0.0729 mol of procaine. To calculate the corresponding mass of procaine, we use its structural formula (C13H20N2O2) to calculate its molar mass, which is 236.31 g/mol.

$$\text{theoretical yield of procaine} = 0.0729\, mol \times \frac{236.31\, g}{1\, mol} = 17.2\, g$$

C The actual yield was only 15.7 g of procaine, so the percent yield (via Equation 10.5.5) is

$$\text{percent yield} = \frac{15.7\, g}{17.2\, g} \times 100 = 91.3\%$$

(If the product were pure and dry, this yield would indicate very good lab technique!)

? Exercise 10.5.4: Extraction of Lead

Lead was one of the earliest metals to be isolated in pure form. It occurs as concentrated deposits of a distinctive ore called galena (PbS), which is easily converted to lead oxide (PbO) in 100% yield by roasting in air via the following reaction:

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

The resulting PbO is then converted to the pure metal by reaction with charcoal. Because lead has such a low melting point (327°C), it runs out of the ore-charcoal mixture as a liquid that is easily collected. The reaction for the conversion of lead oxide to pure lead is as follows:

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

If 93.3 kg of PbO is heated with excess charcoal and 77.3 kg of pure lead is obtained, what is the percent yield?

Electrolytically refined pure (99.989 %) superficially oxidized lead nodules and a high purity (99.989 %) 1 cm^3 lead cube for comparison. Figure used with permission from Wikipedia.

Answer

89.2%

Percent yield can range from 0% to 100%. In the laboratory, a student will occasionally obtain a yield that appears to be greater than 100%. This usually happens when the product is impure or is wet with a solvent such as water. If this is not the case, then the student must have made an error in weighing either the reactants or the products. The law of conservation of mass applies even to undergraduate chemistry laboratory experiments. A 100% yield means that everything worked perfectly, and the chemist obtained all the product that could have been produced. Anyone who has tried to do something as simple as fill a salt shaker or add oil to a car's engine without spilling knows the unlikelihood of a 100% yield. At the other extreme, a yield of 0% means that no product was obtained. A percent yield of 80%–90% is usually considered good to excellent; a yield of 50% is only fair. In part because of the problems and costs of waste disposal, industrial production facilities face considerable pressures to optimize the yields of products and make them as close to 100% as possible.

Summary

The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained. The stoichiometry of a reaction describes the relative amounts of reactants and products in a balanced chemical equation. A stoichiometric quantity of a reactant is the amount necessary to react completely with the other reactant(s). If a quantity of a reactant remains unconsumed after complete reaction has occurred, it is in excess. The reactant that is consumed first and limits the amount of product(s) that can be obtained is the limiting reactant. To identify the limiting reactant, calculate the number of moles of each reactant present and compare this ratio to the mole ratio of the reactants in the balanced chemical equation. The maximum amount of product(s) that can be obtained in a reaction from a given amount of reactant(s) is the theoretical yield of the reaction. The actual yield is the amount of product(s) actually obtained in the reaction; it cannot exceed the theoretical yield. The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, expressed as a percentage.

CHAPTER OVERVIEW

11: Solutions, Concentration, and Dilution

Solutions are all around us. Air, for example, is a solution. If you live near a lake, a river, or an ocean, that body of water is not pure H_2O but most probably a solution. Much of what we drink—for example, soda, coffee, tea, and milk—is at least in part a solution. Solutions are a large part of everyday life. A lot of the chemistry occurring around us happens in solution. In fact, much of the chemistry that occurs in our own bodies takes place in solution, and many solutions—such as the Ringer’s lactate IV solution—are important for our health. In our understanding of chemistry, we need to understand a little bit about solutions. In this chapter, you will learn about the special characteristics of solutions, how solutions are characterized, and some of their properties.

Chapter Sections

11.1: Solutes and Solvents

Learning Objectives

- To understand what causes solutions to form.

A solution is another name for a homogeneous mixture. A *mixture* as a material composed of two or more substances. In a solution, the combination is so intimate that the different substances cannot be differentiated by sight, even with a microscope. Compare, for example, a mixture of salt and pepper and another mixture consisting of salt and water. In the first mixture, we can readily see individual grains of salt and the flecks of pepper. A mixture of salt and pepper is not a solution. However, in the second mixture, no matter how carefully we look, we cannot see two different substances. Salt dissolved in water is a solution.

The major component of a solution, called the **solvent**, is typically the same phase as the solution itself. Each minor component of a solution (and there may be more than one) is called the **solute**. In most of the solutions we will describe in this textbook, there will be no ambiguity about whether a component is the solvent or the solute. For example, in a solution of salt in water, the solute is salt, and solvent is water.

Solutions come in all phases, and the solvent and the solute do not have to be in the same phase to form a solution (such as salt and water). For example, air is a gaseous solution of about 80% nitrogen and about 20% oxygen, with some other gases present in much smaller amounts. An alloy is a solid solution consisting of a metal (like iron) with some other metals or nonmetals dissolved in it. Steel, an alloy of iron and carbon and small amounts of other metals, is an example of a solid solution. Table 11.1.1 lists some common types of solutions, with examples of each.

Table 11.1.1: Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	saltwater
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

What causes a solution to form? The simple answer is that the solvent and the solute must have similar intermolecular interactions. When this is the case, the individual particles of solvent and solute can easily mix so intimately that each particle of solute is surrounded by particles of solvent, forming a solution. However, if two substances have very different intermolecular interactions, large amounts of energy are required to force their individual particles to mix intimately, so a solution does not form. Thus two alkanes like *n*-heptane, C_7H_{16}, and *n*-hexane, C_6H_{14}, are completely miscible in all proportions. The C_7H_{16} and C_6H_{14} molecules are so similar (recall Section 4.6) that there are only negligible differences in intermolecular forces.

For a similar reason, methanol, CH_3OH, is completely miscible with water. In this case both molecules are polar and can form hydrogen bonds among themselves, and so there are strong intermolecular attractions within each liquid. However, CH_3OH dipoles can align with H_2O dipoles, and CH_3OH molecules can hydrogen bond to H_2O molecules, and so the attractions among unlike molecules in the solution are similar to those among like molecules in each pure liquid.

This process leads to a simple rule of thumb: *like dissolves like*. Solvents that are very polar will dissolve solutes that are very polar or even ionic. Solvents that are nonpolar will dissolve nonpolar solutes. Thus water, being polar, is a good solvent for ionic compounds and polar solutes like ethanol (C_2H_5OH). However, water does not dissolve nonpolar solutes, such as many oils and greases (Figure 11.1.1).

Figure 11.1.1: A beaker holds water with blue food dye (upper liquid layer) and a much more dense perfluoroheptane (a fluorocarbon) lower liquid layer. The two fluids cannot mix and the dye cannot dissolve in fluorocarbon. A goldfish and a crab have been introduced into the water. The goldfish cannot penetrate the dense fluorocarbon. The crab floats at the liquid boundary with only parts of his legs penetrating the fluorocarbon fluid, unable to sink to the bottom of the beaker. Quarter coins rest on the bottom of the beaker. Animals were rescued from their predicament after the photo was taken. Figure used with permission from Wikipedia (Sbharris (Steven B. Harris)).

We use the word soluble to describe a solute that dissolves in a particular solvent, and the word insoluble for a solute that does not dissolve in a solvent. Thus, we say that sodium chloride is soluble in water but insoluble in hexane (C_6H_{14}). If the solute and the solvent are both liquids and soluble in any proportion, we use the word miscible, and the word immiscible if they are not.

Example 11.1.1

Water is considered a polar solvent. Which substances should dissolve in water?

1. methanol (CH_3OH)
2. sodium sulfate (Na_2SO_4)
3. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

1. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
2. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
3. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

Exercise 11.1.1

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Answer

Octane only.

Example 11.1.2

Predict which of the following compounds will be most soluble in water:

a. $\underset{\text{Ethanol}}{\mathrm{CH_3CH_2OH}}$
b. $\underset{\text{Hexanol}}{\mathrm{CH_3CH_2CH_2CH_2CH_2CH_2OH}}$

Solution

Since ethanol contains an **OH** group, it can hydrogen bond to water. Although the same is true of hexanol, the OH group is found only at one end of a fairly large molecule. The rest of the molecule can be expected to behave much as though it were a nonpolar alkane. This substance should thus be much less soluble than the first. Experimentally we find that ethanol is completely miscible with water, while only 0.6 g hexanol dissolves in 100 g water.

cise

Would I_2 be more soluble in CCl_4 or H_2O?

Answer

> I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

Key Takeaway

- Solutions form because a solute and a solvent experience similar intermolecular interactions.

11.2: Aqueous Solutions and Dissolution

Learning Outcomes

- Define a solution and describe the parts of a solution.
- Describe how an aqueous solution is formed from both ionic compounds and molecular compounds.
- Recognize that some compounds are insoluble in water.
- Describe the differences among strong electrolytes, weak electrolytes, and nonelectrolytes.

Forming a Solution

When one substance dissolves into another, a solution is formed. A **solution** *is a homogenous mixture consisting of a solute dissolved into a solvent.* The **solute** *is the substance that is being dissolved*, while the **solvent** *is the dissolving medium.* Solutions can be formed with many different types and forms of solutes and solvents. In this chapter, we will focus on solution where the solvent is water. An **aqueous solution** *is water that contains one or more dissolved substance.* The dissolved substances in an aqueous solution may be solids, gases, or other liquids.

In order to be a true solution, a mixture must be stable. When sugar is fully dissolved into water, it can stand for an indefinite amount of time, and the sugar will not settle out of the solution. Further, if the sugar-water solution is passed through a filter, it will remain with the water. This is because the dissolved particles in a solution are very small, usually less than 1 nm in diameter. Solute particles can be atoms, ions, or molecules, depending on the type of substance that has been dissolved.

Figure 11.2.1: When a colored solution is passed through a filter, the entire solution, both solute and solvent, pass through unchanged.

The Dissolving Process

Water typically dissolves most ionic compounds and polar molecules. Nonpolar molecules, such as those found in grease or oil, do not dissolve in water. We will first examine the process that occurs when an ionic compound, such as table salt (sodium chloride), dissolves in water.

Water molecules move about continuously due to their kinetic energy. When a crystal of sodium chloride is placed into water, the water's molecules collide with the crystal lattice. Recall that the crystal lattice is composed of alternating positive and negative ions. Water is attracted to the sodium chloride crystal because water is polar; it has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see figure below).

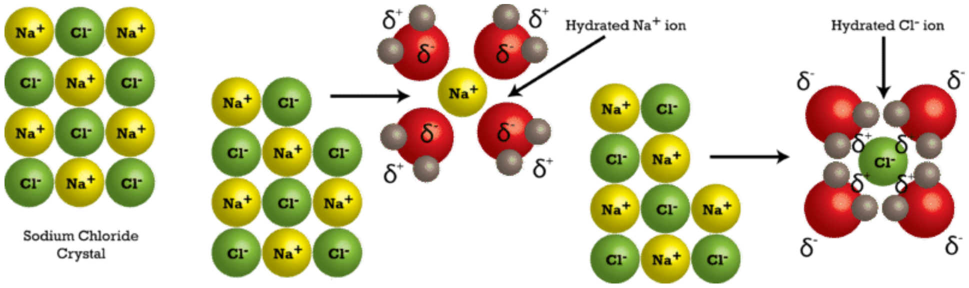


Figure 11.2.2: The process of an ionic sodium chloride crystal being dissolved and hydrated by water.

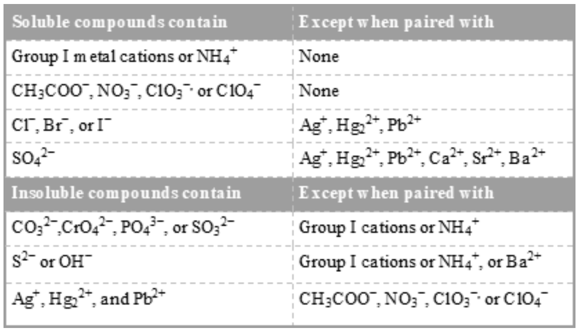
After coming apart from the crystal, *the individual ions are then surrounded by solvent particles in a process called* **solvation**. Note in the figure above that the individual Na^+ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration** *is the process of solute particles being surrounded by water molecules arranged in a specific manner*. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is made of the molecular compound sucrose $(C_{12}H_{22}O_{11})$. Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but it *does not break the covalent bonds* between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated. The hydration shell around a molecule of sucrose is arranged so that its partially negative oxygen atoms are near the partially positive hydrogen atoms in the solvent, and vice versa.

Insoluble Compounds

Not all compounds dissolve well in water. Some ionic compounds, such as calcium carbonate $\left(CaCO_3\right)$ and silver chloride $(AgCl)$, are nearly insoluble. This is because the attractions between the ions in the crystal lattice are stronger than the attraction that the water molecules have for the ions. As a result, the crystal remains intact. The solubility of ionic compounds can be predicted using the solubility rules as shown in Table $11.2.1$.

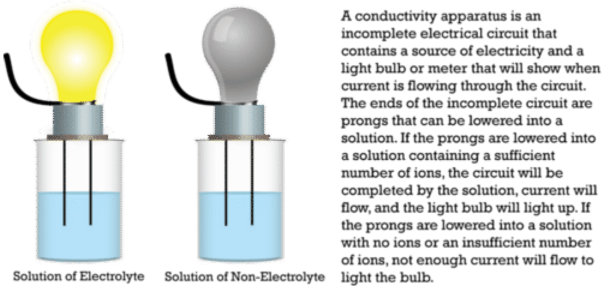
Table* $\mathbf{11.2.1}$*: *Solubility rules for ionic compounds in water.*



Soluble compounds contain	Except when paired with
Group I metal cations or NH_4^+	None
CH_3COO^-, NO_3^-, ClO_3^- or ClO_4^-	None
Cl^-, Br^-, or I^-	Ag^+, Hg_2^{2+}, Pb^{2+}
SO_4^{2-}	Ag^+, Hg_2^{2+}, Pb^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}
Insoluble compounds contain	**Except when paired with**
CO_3^{2-}, CrO_4^{2-}, PO_4^{3-}, or SO_3^{2-}	Group I cations or NH_4^+
S^{2-} or OH^-	Group I cations or NH_4^+, or Ba^{2+}
Ag^+, Hg_2^{2+}, and Pb^{2+}	CH_3COO^-, NO_3^-, ClO_3^- or ClO_4^-

Electrolytes and Nonelectrolytes

An **electrolyte** *is a compound that conducts an electric current when it is dissolved in water or melted.* In order to conduct a current, a substance must contain mobile ions that can move from one electrode to the other. All ionic compounds are electrolytes. When ionic compounds dissolve, they break apart into ions, which are then able to conduct a current. Even insoluble ionic compounds, such as $CaCO_3$, are considered electrolytes because they can conduct a current in the molten (melted) state.



A conductivity apparatus is an incomplete electrical circuit that contains a source of electricity and a light bulb or meter that will show when current is flowing through the circuit. The ends of the incomplete circuit are prongs that can be lowered into a solution. If the prongs are lowered into a solution containing a sufficient number of ions, the circuit will be completed by the solution, current will flow, and the light bulb will light up. If the prongs are lowered into a solution with no ions or an insufficient number of ions, not enough current will flow to light the bulb.

Figure 11.2.4: An apparatus for testing the conductivity of a solution.

A **nonelectrolyte** *is a compound that does not conduct an electric current in either aqueous solution or in the molten state.* Many molecular compounds, such a sugar or ethanol, are nonelectrolytes. When these compounds dissolve in water, they do not produce ions. Illustrated below is the difference between an electrolyte and a nonelectrolyte.

Dissociation

Earlier, you saw how an ionic crystal lattice breaks apart when it is dissolved in water. **Dissociation** *is the separation of ions that occurs when a solid ionic compound dissolves*. Simply undo the crisscross method that you learned when writing chemical formulas for ionic compounds, and you are left with the components of an ionic dissociation equation. The subscripts for the ions in the chemical formulas become the coefficients of the respective ions on the product side of the equations. Shown below are dissociation equations for $NaCl$, $Ca(NO_3)_2$, and $(NH_4)_3PO_4$.

$$\mathrm{NaCl}\,(s) \rightarrow \mathrm{Na}^+\,(aq) + \mathrm{Cl}^-\,(aq) \tag{11.2.1}$$

$$\mathrm{Ca(NO_3)_2}\,(s) \rightarrow \mathrm{Ca}^{2+}\,(aq) + 2\mathrm{NO_3^-}\,(aq) \tag{11.2.2}$$

$$\mathrm{(NH_4)_3PO_4}\,(s) \rightarrow 3\mathrm{NH_4^+}\,(aq) + \mathrm{PO_4^{3-}}\,(aq) \tag{11.2.3}$$

One formula unit of sodium chloride dissociates into one sodium ion and one chloride ion. The calcium nitrate formula unit dissociates into one calcium ion and two nitrate ions, because the $2+$ charge of each calcium ion requires two nitrate ions (each with a charge of $1-$) to form an electrically neutral compound. The ammonium phosphate formula unit dissociates into three ammonium ions and one phosphate ion.

Do not confuse the subscripts of the atoms within the polyatomic ion for the subscripts that result from the crisscrossing of the charges that make the original compound neutral. The 3 subscript of the ntirate ion and the 4 subscript of the ammonium ion are part of the polyatomic ion and remain a part of the ionic formula after the compound dissociates. Notice that the compounds are solids (s) that become ions when dissolved in water, producing an aqueous solution (aq).

Figure 11.2.5: Calcium nitrate is a typical ionic compound. In an aqueous solution, it dissociates into calcium ions and nitrate ions.

Nonelectrolytes do not dissociate when forming an aqueous solution. An equation can still be written that simply shows the solid going into solution. For example, the process of dissolving sucrose in water can be written as follows:

$$\mathrm{C_{12}H_{22}O_{11}}\,(s) \rightarrow \mathrm{C_{12}H_{22}O_{11}}\,(aq) \tag{11.2.4}$$

Strong and Weak Electrolytes

Some polar molecular compounds are nonelectrolytes when the are in their pure state but become electrolytes when they are dissolved in water. Hydrogen chloride (HCl) is a gas in its pure molecular state and is a nonelectrolyte. However, when HCl is dissolved in water, it conducts a current well because the HCl molecule ionizes into hydrogen and chloride ions.

$$\mathrm{HCl}\,(g) \rightarrow \mathrm{H}^+\,(aq) + \mathrm{Cl}^-\,(aq) \tag{11.2.5}$$

When HCl is dissolved into water, it is called hydrochloric acid. Ionic compounds and some polar compounds are completely broken apart into ions and thus conduct a current very well. A **strong electrolyte** *is a solution in which almost all of the dissolved solute exists as ions*.

Some other polar molecular compounds become electrolytes upon being dissolved into water but do not ionize to a very great extent. For example, nitrous acid $(\mathrm{HNO_2})$ only partially ionizes into hydrogen ions and nitrite ions when dissolved in water. Aqueous nitrous acid is composed of only about 5% ions and 95% intact nitrous acid molecules A **weak electrolyte** *is a solution in which only a small fraction of the dissolved solute exists as ions*. The equation showing the ionization of a weak electrolyte utilizes an equilibrium arrow, indicating an equilibrium between the reactants and products.

$$\mathrm{HNO_2}\,(aq) \rightleftharpoons \mathrm{H}^+\,(aq) + \mathrm{NO_2^-}\,(aq) \tag{11.2.6}$$

Contributors and Attributions

-
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11.2.1: Solute Dissociation Equations

Learning Objectives

- Write ionic equations for chemical reactions between ionic compounds.
- Write net ionic equations for chemical reactions between ionic compounds.

For single-replacement and double-replacement reactions, many of the reactions included ionic compounds—compounds between metals and nonmetals, or compounds that contained recognizable polyatomic ions. Now, we take a closer look at reactions that include ionic compounds.

One important aspect about ionic compounds that differs from molecular compounds has to do with dissolution in a liquid, such as water. When molecular compounds, such as sugar, dissolve in water, the individual molecules drift apart from each other. When ionic compounds dissolve, *the ions physically separate from each other*. We can use a chemical equation to represent this process—for example, with NaCl:

$$\mathrm{NaCl(s)} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

When NaCl dissolves in water, the ions separate and go their own way in solution; the ions are now written with their respective charges, and the (aq) phase label emphasizes that they are dissolved (Figure $11.2.1.1$). This process is called **dissociation;** we say that the ions *dissociate*.

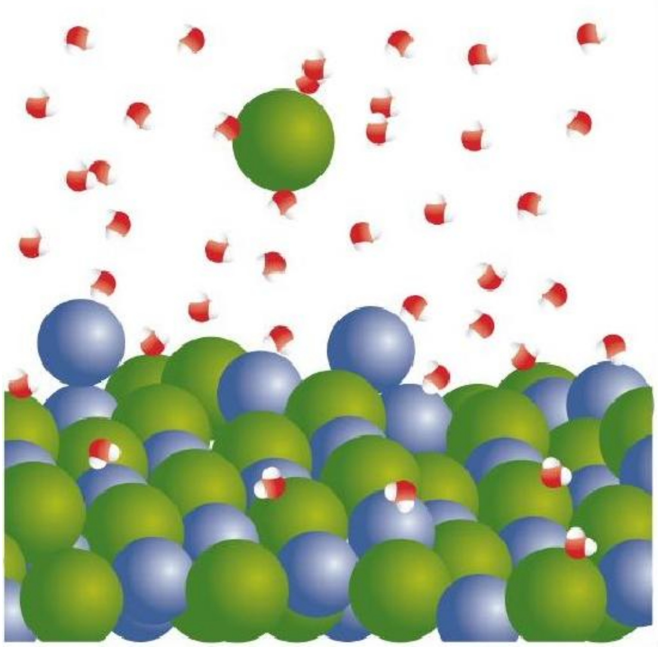


Figure 11.2.1.1 Ionic Solutions. When an ionic compound dissociates in water, water molecules surround each ion and separate it from the rest of the solid. Each ion goes its own way in solution.

All ionic compounds that dissolve behave this way. This behavior was first suggested by the Swedish chemist Svante August Arrhenius [1859–1927] as part of his PhD dissertation in 1884. Interestingly, his PhD examination team had a hard time believing that ionic compounds would behave like this, so they gave Arrhenius a barely passing grade. Later, this work was cited when Arrhenius was awarded the Nobel Prize in Chemistry. Keep in mind that when the ions separate, *all* the ions separate. Thus, when $CaCl_2$ dissolves, the one Ca^{2+} ion and the two Cl^- ions separate from one another:

$$CaCl_2(s) \overset{H_2O}{\rightarrow} Ca^{2+}(aq) + Cl^-(aq) + Cl^-(aq)$$

$$CaCl_2(s) \overset{H_2O}{\rightarrow} Ca^{2+}(aq) + 2Cl^-(aq)$$

That is, the two chloride ions go off on their own. They do not remain as Cl_2 (that would be elemental chlorine; these are chloride ions), and they do not stick together to make Cl_2^- or Cl_2^{2-}. They become dissociated ions in their own right. Polyatomic ions also retain their overall identity when they are dissolved.

Example 11.2.1.1

Write the chemical equation that represents the dissociation of each ionic compound.

1. KBr
2. Na_2SO_4

Solution

1. $KBr(s) \rightarrow K^+(aq) + Br^-(aq)$
2. Not only do the two sodium ions go their own way, but the sulfate ion stays together as the sulfate ion. The dissolving equation is $Na_2SO_4(s) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$

Exercise 11.2.1.1

Write the chemical equation that represents the dissociation of $(NH_4)_2S$.

Answer

$(NH_4)_2S(s) \rightarrow 2NH_4^+(aq) + S^{2-}(aq)$

When chemicals in solution react, the proper way of writing the chemical formulas of the dissolved ionic compounds is in terms of the dissociated ions, not the complete ionic formula. A **complete ionic equation** is a chemical equation in which the dissolved ionic compounds are written as separated ions. Solubility rules are very useful in determining which ionic compounds are dissolved and which are not. For example, when NaCl(aq) reacts with $AgNO_3$(aq) in a double-replacement reaction to precipitate AgCl(s) and form $NaNO_3$(aq), the complete ionic equation includes NaCl, $AgNO_3$, and $NaNO_3$ written as separate ions:

$$\mathrm{Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)}$$

This is more representative of what is occurring in the solution.

Example 11.2.1.1

Write the complete ionic equation for each chemical reaction.

1. $KBr(aq) + AgC_2H_3O_2(aq) \rightarrow KC_2H_3O_2(aq) + AgBr(s)$
2. $MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + BaSO_4(s)$

Solution

For any ionic compound that is aqueous, we will write the compound as separated ions.

1. The complete ionic equation is $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
2. The complete ionic equation is $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Exercise 11.2.1.1

Write the complete ionic equation for

$$\mathrm{CaCl_2(aq) + Pb(NO_3)_2(aq) \rightarrow Ca(NO_3)_2(aq) + PbCl_2(s)}$$

Answer

$Ca^{2+}(aq) + 2Cl^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + PbCl_2(s)$

You may notice that in a complete ionic equation, some ions do not change their chemical form; they stay exactly the same on the reactant and product sides of the equation. For example, in

$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$

the $Ag^+(aq)$ and $Cl^-(aq)$ ions become $AgCl(s)$, but the $Na^+(aq)$ ions and the $NO_3^-(aq)$ ions stay as $Na^+(aq)$ ions and $NO_3^-(aq)$ ions. These two ions are examples of spectator ions—ions that do nothing in the overall course of a chemical reaction. They are present, but they do not participate in the overall chemistry. It is common to cancel spectator ions (something also done with algebraic quantities) on the opposite sides of a chemical equation:

$$Na^+\cancel{(aq)} + Cl^-(aq) + Ag^+(aq) + \cancel{NO_3^-}(aq) \rightarrow AgCl(s) + \cancel{Na}^+(aq) + \cancel{NO}_3^-(aq)$$

What remains when the spectator ions are removed is called the **net ionic equation**, which represents the actual chemical change occurring between the ionic compounds:

$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$

It is important to reiterate that the spectator ions are still present in solution, but they do not experience any net chemical change, so they are not written in a net ionic equation.

✓ Example 11.2.1.1

Write the net ionic equation for each chemical reaction.

1. $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
2. $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Solution

1. In the first equation, the $K^+(aq)$ and $C_2H_3O_2^-(aq)$ ions are spectator ions, so they are canceled:

$$K^+\cancel{(aq)} + Br^-(aq) + Ag^+(aq) + \cancel{C_2H_3O_2^-(aq)} \rightarrow K^+(aq) + \cancel{C_2H_3O_2^-(aq)} + AgBr(s)$$

The net ionic equation is

$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$

2. In the second equation, the $Mg^{2+}(aq)$ and $NO_3^-(aq)$ ions are spectator ions, so they are canceled:

$$Mg^{2+}\cancel{(aq)} + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2\cancel{NO_3^-(aq)} \rightarrow Mg^{2+}(aq) + 2\cancel{NO_3^-(aq)} + BaSo_4(s)$$

The net ionic equation is

$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

? Exercise 11.2.1.1

Write the net ionic equation for

$CaCl_2(aq) + Pb(NO_3)_2(aq) \rightarrow Ca(NO_3)_2(aq) + PbCl_2(s)$

Answer

$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$

✓ Chemistry is Everywhere: Soluble and Insoluble Ionic Compounds

The concept of solubility versus insolubility in ionic compounds is a matter of degree. Some ionic compounds are very soluble, some are only moderately soluble, and some are soluble so little that they are considered insoluble. For most ionic compounds, there is also a limit to the amount of compound that can be dissolved in a sample of water. For example, you can dissolve a maximum of 36.0 g of NaCl in 100 g of water at room temperature, but you can dissolve only 0.00019 g of AgCl in 100 g of water. We consider NaCl soluble but AgCl insoluble.

One place where solubility is important is in the tank-type water heater found in many homes in the United States. Domestic water frequently contains small amounts of dissolved ionic compounds, including calcium carbonate ($CaCO_3$). However,

$CaCO_3$ has the relatively unusual property of being less soluble in hot water than in cold water. So as the water heater operates by heating water, $CaCO_3$ can precipitate if there is enough of it in the water. This precipitate, called *limescale*, can also contain magnesium compounds, hydrogen carbonate compounds, and phosphate compounds. The problem is that too much limescale can impede the function of a water heater, requiring more energy to heat water to a specific temperature or even blocking water pipes into or out of the water heater, causing dysfunction.

Figure 11.2.1.2 Tank water heater © Thinkstock. Most homes in the United States have a tank-type water heater like this one.

Another place where solubility versus insolubility is an issue is the Grand Canyon. We usually think of rock as insoluble. But it is actually ever so slightly soluble. This means that over a period of about two billion years, the Colorado River carved rock from the surface by slowly dissolving it, eventually generating a spectacular series of gorges and canyons. And all because of solubility!

Figure 11.2.1.3: The Grand Canyon was formed by water running through rock for billions of years, very slowly dissolving it. Note the Colorado River is still present in the lower part of the photo. (Sonaal Bangera via unsplash)

Key Takeaways

- Ionic compounds that dissolve separate into individual ions.
- Complete ionic equations show dissolved ionic solids as separated ions.
- Net ionic equations show only the ions and other substances that change in a chemical reaction.

11.2.2: Electrolyte Solutions

Substances whose solutions conduct electricity are called electrolytes. All soluble ionic compounds are strong electrolytes. They conduct very well because they provide a plentiful supply of ions in solution. Some polar covalent compounds are also strong electrolytes. Common examples are HCl, HBr, HI and H_2SO_4, all of which react with H_2O to form large concentrations of ions. A solution of HCl, for example, conducts even better than one of NaCl having the same concentration.

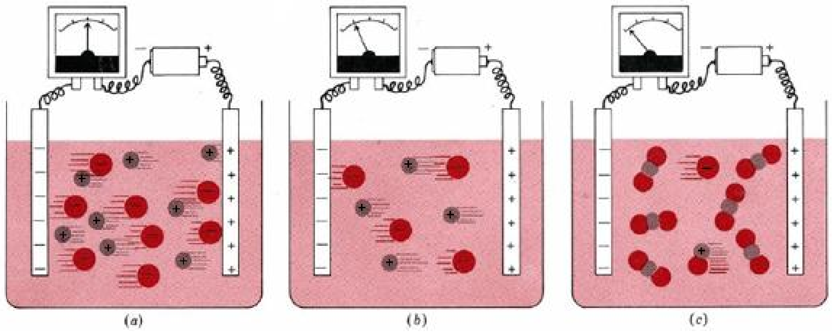


Figure 11.2.2.1: The conductivity of electrolyte solutions: (a) 0.1 M NaCl (b) 0.05 M NaCl (c) 0.1 M $HgCl_2$. An electrolyte solution conducts electricity because of the movement of ions in the solution (see above). The larger the concentration of ions, the better the solutions conducts. Weak electrolytes, such as $HgCl_2$, conduct badly because they produce few ions when dissolved (low concentration of ions) and exist mainly in the form of molecules.

The effect of the concentration of ions on the electrical current flowing through a solution is illustrated in Figure 11.2.2.1. Part *a* of the figure shows what happens when a battery is connected through an electrical meter to two inert metal strips (**electrodes**) dipping in ethanol. Each cubic decimeter of such a solution contains 0.10 mol NaCl (that is, 0.10 mol Na^+ and 0.10 mol $Cl^–$). An electrical current is carried through the solution both by the Na^+ ions moving toward the negative electrode and by the Cl^- ions which are attracted toward the positive electrode. The dial on the meter indicates the quantity of current.

Figure 1*b* shows that if we replace the 0.10-*M* NaCl solution with a 0.05-*M* NaCl solution, the meter reading falls to about one-half its former value. Halving the concentration of NaCl halves the number of ions between the electrodes, and half as many ions can only carry half as much electrical charge. Therefore the current is half as great. Because it responds in such a direct way to the concentration of ions, conductivity of electrical current is a useful tool in the study of solutions.

Conductivity measurements reveal that most covalent compounds, if they dissolve in water at all, retain their original molecular structures. Neutral molecules cannot carry electrical charges through the solution, and so no current flows. A substance whose aqueous solution conducts no better than water itself is called a **nonelectrolyte**. Some examples are oxygen, O_2, ethanol, C_2H_5OH, and sugar, $C_{12}H_{22}O_{11}$.

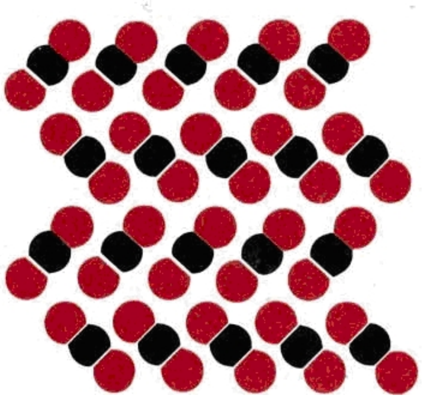


Figure 11.2.2.2: Mercury Bromide Crystals.

Some covalent substances behave as **weak electrolytes**—their solutions allow only a small current flow, but it is greater than that of the pure solvent. An example is mercury(II) chloride (seen in the Figure above). For a 100-*M* $HgCl_2$ solution the meter reading shows only about 0.2 percent as much current as for 0.10 *M* NaCl. A crystal of $HgCl_2$ consists of discrete molecules, like those shown for $HgBr_2$ in Figure 11.2.2.2 When the solid dissolves, most of these molecules remain intact, but a few dissociate into ions according to the equation

$$\underbrace{HgCl_2}_{99.8\%} \rightleftharpoons \underbrace{HgCl^+}_{0.2\%} + Cl^-$$

(The double arrows indicate that the ionization proceeds only to a limited extent and an equilibrium state is attained.) Since only 0.2 percent of the $HgCl_2$ forms ions, the 0.10 *M* solution can conduct only about 0.2 percent as much current as 0.10 *M* NaCl.

Conductivity measurements can tell us more than whether a substance is a strong, a weak, or a nonelectrolyte. Consider, for instance, the data in Table 11.2.2.1which shows the electrical current conducted through various aqueous solutions under identical conditions. At the rather low concentration of 0.001 *M*, the strong electrolyte solutions conduct between 2500 and 10 000 times as much current as pure H_2O and about 10 times as much as the weak electrolytes $HC_2H_3O_2$ (acetic acid) and NH_3 (ammonia).

Closer examination of the data for strong electrolytes reveals that some compounds which contain H or OH groups [such as HCl or $Ba(OH)_2$] conduct unusually well. If these compounds are excluded, we find that 1:1 electrolytes (compounds which consist of equal numbers of +1 ions and –1 ions) usually conduct about half as much current as 2:2 electrolytes (+2 and -2 ions), 1:2 electrolytes (+1 and -2 ions), or 2:1 electrolytes (+2 and -1 ions).

TABLE 11.2.2.1: Electrical Current Conducted Through Various 0.001 M Aqueous Solutions at 18°C.*

Substance	*Current /mA*	Substance	*Current /mA*
Pure Water		**1:2 Electrolytes**	
H_2O	3.69×10^{-4}	Na_2SO_4	2.134
Weak Electrolytes		Na_2CO_3	2.24
$HC_2H_3O_2$	0.41	K_2CO_3	2.660
NH_3	0.28	**2:1 Electrolytes**	
1:1 Electrolytes		$MgCl_2$	2.128
NaCl	1.065	$CaCl_2$	2.239
NaI	1.069	$SrCl_2$	2.290
KCl	1.273	$BaCl_2$	2.312
KI	1,282	$Ba(OH)_2$	4.14
$AgNO_3$	1.131	**2:2 Electrolytes**	
HCl	3.77	$MgSO_4$	2.00
HNO_3	3.75	$CaSO_4$	2.086
NaOH	2.08	$CuSO_4$	1.97
KOH	2.34	$ZnSO_4$	1.97

* All measurements refer to a cell in which the distance between the electrodes is 1.0 mm and the area of each electrode is 1.0 cm^2. A potential difference of 1.0 V is applied to produce the tabulated currents.

There is a simple reason for this behavior. Under similar conditions, most ions move through water at comparable speeds. This means that ions like Mg^{2+} or SO_4^{2-}, which are doubly charged, will carry twice as much current through the solution as will singly charged ions like Na^+ or Cl^-. Consequently, a 0.001 *M* solution of a 2:2 electrolyte like $MgSO_4$ will conduct about twice as well as a 0.001 M solution of a 1:1 electrolyte like NaCl.

A similar argument applies to solutions of 1:2 and 2:1 electrolytes. A solution like 0.001 *M* Na_2SO_4 conducts about twice as well as 0.001 *M* NaCl partly because there are twice as many Na^- ions available to move when a battery is connected, but also because SO_4^{2-} ions carry twice as much charge as Cl^- ions when moving at the same speed. These differences in conductivity between different types of strong electrolytes can sometimes be very useful in deciding what ions are actually present in a given electrolyte solution as the following example makes clear.

A second, slightly more subtle, conclusion can be drawn from the data in Table 11.2.2.1. When an electrolyte dissolves, each type of ion makes an independent contribution to the current the solution conducts. This can be seen by comparing NaCl with KCl, and NaI with KI. In each case the compound containing K^+ conducts about 0.2 mA more than the one containing Na^+. If we apply this observation to Na_2CO_3 and K_2CO_3, each of which produces twice as many Na^+ or K^+ ions in solution, we find that the difference in current is also twice as great—about 0.4 mA.

Thus conductivity measurements confirm our statement that each ion exhibits its own characteristic properties in aqueous solutions, independent of the presence of other ions. One such characteristic property is the quantity of electrical current that a given concentration of a certain type of ion can carry.

✓ Example 11.2.2.1: Ions

At 18°C a 0.001-*M* aqueous solution of potassium hydrogen carbonate, $KHCO_3$, conducts a current of 1.10 mA in a cell of the same design as that used to obtain the data in Table 11.1. What ions are present in solution?

Solution

Referring to Table 6.2 which lists possible polyatomic ions, we can arrive at three possibilities for the ions from which $KHCO_3$ is made:

a. K^+ and H^+ and C^{4+} and three O^{2-}
b. K^+ and H^+ and $CO_3{}^{2-}$
c. K^+ and $HCO_3{}^-$

Since the current conducted by the solution falls in the range of 1.0 to 1.3 mA characteristic of 1:1 electrolytes, possibility *c* is the only reasonable choice.

11.3: Solution Concentration - Molarity

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:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{11.3.1}$$

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

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{11.3.2}$$

or

$$V_{mL} M_{mmol/mL} = \cancel{mL}\left(\frac{mmol}{\cancel{mL}}\right) = mmoles \tag{11.3.3}$$

Figure $11.3.1$ illustrates the use of Equations 11.3.2 and 11.3.3.

(a) An amount of solute is weighed out on an analytical balance and then **(b) A portion of the solvent is added to the volumetric flask.** **(c) The mixture is swirled until *all* of the solute is dissolved.** **(d) Additional solvent is added up to the mark on the volumetric flask.**

Figure 11.3.1: Preparation of a Solution of Known Concentration Using a Solid Solute

Example 11.3.1: 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 11.3.2 or Equation 11.3.3, 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 11.3.2 is more useful:

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

Exercise 11.3.1: 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 11.3.1.

Table 11.3.1: 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
	μg/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 11.3.1 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 11.3.2, for some substances this effect can be significant, especially for concentrated solutions.

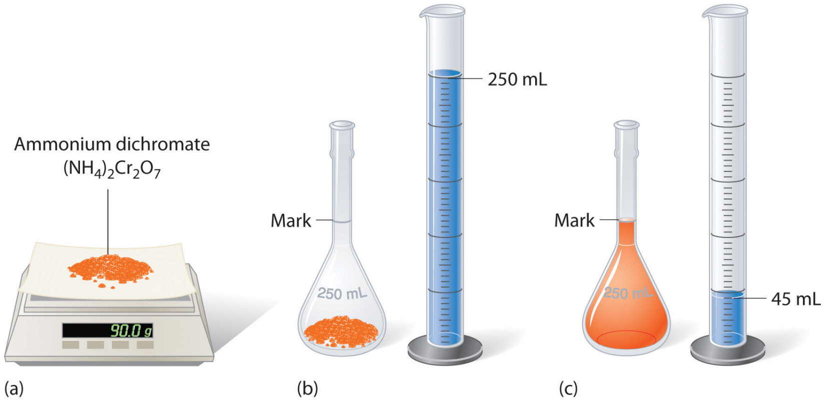


Figure 11.3.2: Preparation of 250 mL of a Solution of $(NH_4)_2Cr_2O_7$ in Water. The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.

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

✓ Example 11.3.2

The solution contains 10.0 g of cobalt(II) chloride dihydrate, $CoCl_2•2H_2O$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $CoCl_2 \bullet 2\,H_2O$?

Given: mass of solute and volume of solution

Asked for: concentration (M)

Strategy:

To find the number of moles of $CoCl_2 \bullet 2\,H_2O$, 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 $CoCl_2•2H_2O$ is 165.87 g/mol. Therefore,

$$moles\ CoCl_2 \cdot 2H_2O = \left(\frac{10.0\ \cancel{g}}{165.87\ \cancel{g}/mol}\right) = 0.0603\ mol$$

The volume of the solution in liters is

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

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

$$molarity = \frac{0.0603\ mol}{0.500\ L} = 0.121\ M = CoCl_2 \cdot H_2O$$

? Exercise 11.3.2

The solution shown in Figure 11.3.2 contains 90.0 g of $(NH_4)_2Cr_2O_7$ in enough water to give a final volume of exactly 250 mL. What is the molar concentration of ammonium dichromate?

Answer

$$(NH_4)_2Cr_2O_7 = 1.43\ M$$

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 11.3.2. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example 11.3.3.

✓ Example 11.3.3: 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:

A. Calculate the number of moles of glucose contained in the specified volume of solution by multiplying the volume of the solution by its molarity.
B. 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:

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

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

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

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

? Exercise 11.3.3

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 $11.3.3$. 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

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d) \tag{11.3.4}$$

where the subscripts *s* and *d* indicate the stock and dilute solutions, respectively. Example $11.3.4$ demonstrates the calculations involved in diluting a concentrated 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)].

Figure 11.3.3: 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 $11.3.4$

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example $11.3.3$?

Given: volume and molarity of dilute solution

Asked for: volume of stock solution

Strategy:

A. 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.
B. 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:

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

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

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

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:

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

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

? Exercise 11.3.4

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 11.3.2, 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 $Cr_2O_7^{2-}$ ion per formula unit. Like other ionic compounds, it is a strong electrolyte that dissociates in aqueous solution to give hydrated NH_4^+ and $Cr_2O_7^{2-}$ ions:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{H_2O(l)} 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \tag{11.3.5}$$

Thus 1 mol of ammonium dichromate formula units dissolves in water to produce 1 mol of $Cr_2O_7^{2-}$ anions and 2 mol of NH_4^+ cations (see Figure 11.3.4).

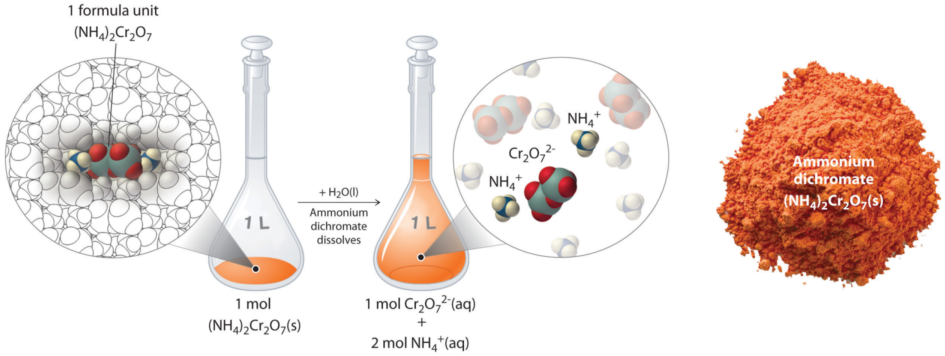


Figure 11.3.4: Dissolution of 1 mol of an Ionic Compound. In this case, dissolving 1 mol of $(NH_4)_2Cr_2O_7$ produces a solution that contains 1 mol of $Cr_2O_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)

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 $(NH_4)_2Cr_2O_7$, then the concentration of $Cr_2O_7^{2-}$ must also be 1.43 M because there is one $Cr_2O_7^{2-}$ ion per formula unit. However, there are two NH_4^+ ions per formula unit, so the concentration of NH_4^+ ions is 2 × 1.43 M = 2.86 M. Because each formula unit of $(NH_4)_2Cr_2O_7$ produces *three* ions when dissolved in water ($2NH_4^+ + 1Cr_2O_7^{2-}$), the *total* concentration of ions in the solution is 3 × 1.43 M = 4.29 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 11.3.5

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

a. 0.21 M NaOH
b. 3.7 M $(CH_3)_2CHOH$
c. 0.032 M $In(NO_3)_3$

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:

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

   $$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$$

   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: $[Na^+]$ = 0.21 M and $[OH^-]$ = 0.21 M.

2. **A** The formula $(CH_3)_2CHOH$ represents 2-propanol (isopropyl alcohol) and contains the –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 $(CH_3)_2CHOH$ molecules, so $[(CH_3)_2CHOH]$ = 3.7 M.

3. **A** 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:

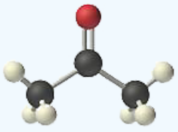
   $$In(NO_3)_3(s) \xrightarrow{H_2O(l)} In^{3+}(aq) + 3NO_3^-(aq)$$

   B One formula unit of $In(NO_3)_3$ produces one In^{3+} ion and three NO_3^- ions, so a 0.032 M $In(NO_3)_3$ solution contains 0.032 M In^{3+} and 3 × 0.032 M = 0.096 M NO_3^-—that is, $[In^{3+}]$ = 0.032 M and $[NO_3^-]$ = 0.096 M.

Exercise 11.3.5

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 Na_2SO_4
c. 0.50 M $(CH_3)_2CO$, commonly known as acetone


Acetone
$(CH_3)_2CO$

Answer a

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

Answer b

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

Answer c

$$[(CH_3)_2CO] = 0.50\ M$$

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:**

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

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

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

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

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

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

- Modified by Joshua Halpern (Howard University)

11.4: Solution Preparation

Preparing a solution of known concentration is perhaps the most common activity in any analytical lab. The method for measuring out the solute and the solvent depend on the desired concentration and how exact the solution's concentration needs to be known. Pipets and volumetric flasks are used when we need to know a solution's exact concentration; graduated cylinders, beakers, and/or reagent bottles suffice when a concentrations need only be approximate. Two methods for preparing solutions are described in this section.

Preparing Stock Solutions

A ***stock solution*** is prepared by weighing out an appropriate portion of a pure solid or by measuring out an appropriate volume of a pure liquid, placing it in a suitable flask, and diluting to a known volume. Exactly how one measure's the reagent depends on the desired concentration unit. For example, to prepare a solution with a known molarity you weigh out an appropriate mass of the reagent, dissolve it in a portion of solvent, and bring it to the desired volume. To prepare a solution where the solute's concentration is a volume percent, you measure out an appropriate volume of solute and add sufficient solvent to obtain the desired total volume.

✓ Example 11.4.1

Describe how to prepare the following three solutions: (a) 500 mL of approximately 0.20 M NaOH using solid NaOH; (b) 1 L of 150.0 ppm Cu^{2+} using Cu metal; and (c) 2 L of 4% v/v acetic acid using concentrated glacial acetic acid (99.8% w/w acetic acid).

Solution

(a) Because the desired concentration is known to two significant figures, we do not need to measure precisely the mass of NaOH or the volume of solution. The desired mass of NaOH is

$$\frac{0.20 \text{ mol NaOH}}{\text{L}} \times \frac{40.0 \text{ g NaOH}}{\text{mol NaOH}} \times 0.50 \text{ L} = 4.0 \text{ g NaOH}$$

To prepare the solution, place 4.0 grams of NaOH, weighed to the nearest tenth of a gram, in a bottle or beaker and add approximately 500 mL of water.

(b) Since the desired concentration of Cu^{2+} is given to four significant figures, we must measure precisely the mass of Cu metal and the final solution volume. The desired mass of Cu metal is

$$\frac{150.0 \text{ mg Cu}}{\text{L}} \times 1.000 \text{ M} \times \frac{1 \text{ g}}{1000 \text{ mg}} = 0.1500 \text{ g Cu}$$

To prepare the solution, measure out exactly 0.1500 g of Cu into a small beaker and dissolve it using a small portion of concentrated HNO_3. To ensure a complete transfer of Cu^{2+} from the beaker to the volumetric flask—what we call a ***quantitative transfer***—rinse the beaker several times with small portions of water, adding each rinse to the volumetric flask. Finally, add additional water to the volumetric flask's calibration mark.

(c) The concentration of this solution is only approximate so it is not necessary to measure exactly the volumes, nor is it necessary to account for the fact that glacial acetic acid is slightly less than 100% w/w acetic acid (it is approximately 99.8% w/w). The necessary volume of glacial acetic acid is

$$\frac{4 \text{ mL CH}_3\text{COOH}}{100 \text{ mL}} \times 2000 \text{ mL} = 80 \text{ mL CH}_3\text{COOH}$$

To prepare the solution, use a graduated cylinder to transfer 80 mL of glacial acetic acid to a container that holds approximately 2 L and add sufficient water to bring the solution to the desired volume.

? Exercise 11.4.1

Provide instructions for preparing 500 mL of 0.1250 M $KBrO_3$.

Answer

Preparing 500 mL of 0.1250 M $KBrO_3$ requires

$$0.5000\text{ L}\times\frac{0.1250\text{ mol KBrO}_3}{\text{L}}\times\frac{167.00\text{ g KBrO}_3}{\text{mol KBrO}_3}=10.44\text{ g KBrO}_3$$

Because the concentration has four significant figures, we must prepare the solution using volumetric glassware. Place a 10.44 g sample of $KBrO_3$ in a 500-mL volumetric flask and fill part way with water. Swirl to dissolve the $KBrO_3$ and then dilute with water to the flask's calibration mark.

Preparing Solutions by Dilution

Solutions are often prepared by diluting a more concentrated stock solution. A known volume of the stock solution is transferred to a new container and brought to a new volume. Since the total amount of solute is the same before and after dilution, we know that

$$C_o\times V_o=C_d\times V_d \tag{11.4.1}$$

where C_o is the stock solution's concentration, V_o is the volume of stock solution being diluted, C_d is the dilute solution's concentration, and V_d is the volume of the dilute solution. Again, the type of glassware used to measure V_o and V_d depends on how precisely we need to know the solution's concentration.

> Note that Equation 11.4.1 applies only to those concentration units that are expressed in terms of the solution's volume, including molarity, formality, normality, volume percent, and weight-to-volume percent. It also applies to weight percent, parts per million, and parts per billion if the solution's density is 1.00 g/mL. We cannot use Equation 11.4.1 if we express concentration in terms of molality as this is based on the mass of solvent, not the volume of solution. See Rodríquez-López, M.; Carrasquillo, A. *J. Chem. Educ.* **2005**, *82*, 1327-1328 for further discussion.

✓ Example 11.4.2

A laboratory procedure calls for 250 mL of an approximately 0.10 M solution of NH_3. Describe how you would prepare this solution using a stock solution of concentrated NH_3 (14.8 M).

Solution

Substituting known volumes into Equation 11.4.1

$$14.8\text{ M}\times V_o=0.10\text{ M}\times 250\text{ mL}$$

and solving for V_o gives 1.7 mL. Since we are making a solution that is approximately 0.10 M NH_3, we can use a graduated cylinder to measure the 1.7 mL of concentrated NH_3, transfer the NH_3 to a beaker, and add sufficient water to give a total volume of approximately 250 mL.

> Although usually we express molarity as mol/L, we can express the volumes in mL if we do so both for both V_o and V_d.

? Exercise 11.4.2

To prepare a standard solution of Zn^{2+} you dissolve a 1.004 g sample of Zn wire in a minimal amount of HCl and dilute to volume in a 500-mL volumetric flask. If you dilute 2.000 mL of this stock solution to 250.0 mL, what is the concentration of Zn^{2+}, in μg/mL, in your standard solution?

Answer

The first solution is a stock solution, which we then dilute to prepare the standard solution. The concentration of Zn^{2+} in the stock solution is

$$\frac{1.004\text{ g Zn}^{2+}}{500.0\text{ mL}}\times\frac{10^6\ \mu\text{g}}{\text{g}}=2008\ \mu\text{g Zn}^{2+}/\text{mL}$$

To find the concentration of the standard solution we use Equation 11.4.1

$$\frac{2008\ \mu\text{g Zn}^{2+}}{\text{mL}}\times 2.000\text{ mL}=C_d\times 250.0\text{ mL}$$

where C_d is the standard solution's concentration. Solving gives a concentration of 16.06 µg Zn^{2+}/mL.

As shown in the following example, we can use Equation 11.4.1 to calculate a solution's original concentration using its known concentration after dilution.

✓ Example 11.4.3

A sample of an ore was analyzed for Cu^{2+} as follows. A 1.25 gram sample of the ore was dissolved in acid and diluted to volume in a 250-mL volumetric flask. A 20 mL portion of the resulting solution was transferred by pipet to a 50-mL volumetric flask and diluted to volume. An analysis of this solution gives the concentration of Cu^{2+} as 4.62 µg/mL. What is the weight percent of Cu in the original ore?

Solution

Substituting known volumes (with significant figures appropriate for pipets and volumetric flasks) into Equation 11.4.1

$$(C_{\mathrm{Cu}})_o \times 20.00 \text{ mL} = 4.62 \; \mu\text{g/mL Cu}^{2+} \times 50.00 \text{ mL}$$

and solving for $(C_{\mathrm{Cu}})_o$ gives the original concentration as 11.55 µg/mL Cu^{2+}. To calculate the grams of Cu^{2+} we multiply this concentration by the total volume

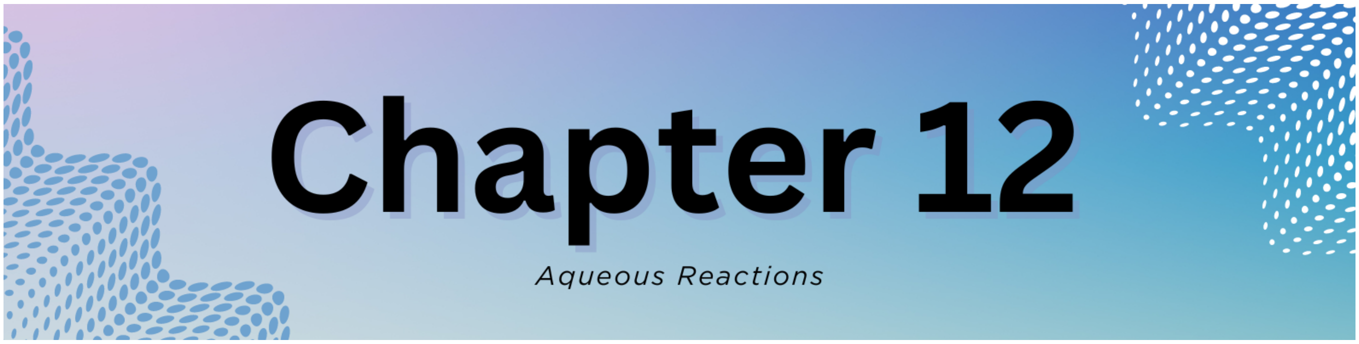
$$\frac{11.55 \mu\text{g Cu}^{2+}}{\text{mL}} \times 250.0 \text{ mL} \times \frac{1 \text{ g}}{10^6 \; \mu\text{g}} = 2.888 \times 10^{-3} \text{ g Cu}^{2+}$$

The weight percent Cu is

$$\frac{2.888 \times 10^{-3} \text{ g Cu}^{2+}}{1.25 \text{ g sample}} \times 100 = 0.231\% \text{ w/w Cu}^{2+}$$

CHAPTER OVERVIEW

12: Aqueous Reactions



Water is by far the most important liquid solvent, partly because it is plentiful and partly because of its unique properties. In your body, in other living systems, and in the outside environment a tremendous number of reactions take place in aqueous solutions. Consequently this chapter, as well as significant portions of many subsequent sections, will be devoted to developing an understanding of reactions which occur in water.

Chapter Sections

Attributions

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12.1: Complete and Net Ionic Equations

Howard University
General Chemistry:
An Atoms First Approach

Unit 1: Atomic Theory   Unit 2: Molecular Structure   Unit 3: Stoichiometry   Unit 4: Thermochem & Gases
Unit 5: States of Matter   Unit 6: Kinetics & Equilibria   Unit 7: Electro & Thermo Chemistry   Unit 8: Materials

The chemical equations discussed in Chapter 7 showed the identities of the reactants and the products and gave the stoichiometries of the reactions, but they told us very little about what was 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. As you learned in Example 9, when aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall chemical equationA chemical equation that shows all the reactants and products as undissociated, electrically neutral compounds. for the reaction shows each reactant and product as undissociated, electrically neutral compounds:

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq) \tag{12.1.1}$$

Although Equation 12.1.1 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 $K_2Cr_2O_7$ are strong electrolytes, they dissociate completely in aqueous solution to form ions. In contrast, because $Ag_2Cr_2O_7$ 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:

$$2Ag^+(aq) + 2NO_3^-(aq) + 2K^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2K^+(aq) + 2NO_3^-(aq) \tag{12.1.2}$$

Note that K^+(aq) and NO_3^-(aq) ions are present on both sides of the equation, 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:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{12.1.3}$$

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 12.1.3, the charge on the left side is 2(+1) + 1(−2) = 0, which is the same as the charge of a neutral $Ag_2Cr_2O_7$ formula unit.

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:

$$2AgF(aq) + (NH_4)_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4F(aq) \tag{12.1.4}$$

The complete ionic equation for this reaction is as follows:

$$2Ag^+(aq) + 2F^-(aq) + 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4^+(aq) + 2F^-(aq) \tag{12.1.5}$$

Because two NH_4^+(aq) and two F^-(aq) ions appear on both sides of Equation 12.1.5, they are spectator ions. They can therefore be canceled to give the net ionic equation (Equation 12.1.6), which is identical to Equation 12.1.3:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{12.1.6}$$

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.

Example 12.1.1

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:

$$Ba(NO_3)_2(aq) + Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + NaNO_3(aq) \tag{12.1.7}$$

Because the product is $Ba_3(PO_4)_2$, which contains three Ba^{2+} ions and two $PO_4{}^{3-}$ ions per formula unit, we can balance the equation by inspection:

$$3Ba(NO_3)_2(aq) + 2Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + 6NaNO_3(aq) \tag{12.1.8}$$

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:

$$3Ba^{2+}(aq) + 6NO_3^-(aq) + 6Na^+(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s) + 6Na^+(aq) + 6NO_3^-(aq) \tag{12.1.9}$$

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:

$$3Ba^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s) \tag{12.1.10}$$

Exercise 12.1.1

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:

$$3AgF(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + 3NaF(aq) \tag{12.1.11}$$

complete ionic equation:

$$3Ag^+(aq) + 3F^-(aq) + 3Na^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s) + 3Na^+(aq) + 3F^-(aq) \tag{12.1.12}$$

net ionic equation:

$$3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s) \tag{12.1.13}$$

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 introduced in Chapter 3 (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.

Summary

The chemical equation for a reaction in solution can be written in three ways. The **overall chemical equation** shows all the substances present in their undissociated forms; the **complete ionic equation** shows all the substances present in the form in which they actually exist in solution; and the **net ionic equation** is derived from the complete ionic equation by omitting all **spectator ions**, ions that occur on both sides of the equation with the same coefficients. Net ionic equations demonstrate that many different combinations of reactants can give the same net chemical reaction.

Key Takeaway

- A complete ionic equation consists of the net ionic equation and spectator ions.

Conceptual Problem

1. What information can be obtained from a complete ionic equation that cannot be obtained from the overall chemical equation?

Contributors

- Modified by Joshua Halpern (Howard University)

12.2: 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:

$$AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + KNO_3(aq) \tag{12.2.1}$$

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

$$\overbrace{AC}^{\text{soluble}} + \overbrace{BD}^{\text{soluble}} \rightarrow \underbrace{AD}_{\text{insoluble}} + \overbrace{BC}^{\text{soluble}} \tag{12.2.2}$$

The solubility and insoluble annotations are specific to the reaction in Equation 12.2.1 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 12.2.1**: Mixing Potassium Chromate and Silver Nitrate together to initiate a precipitation reaction (Equation 12.2.1).*

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:

$$2\,AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2\,KNO_3(aq) \tag{12.2.3}$$

Although Equation 12.2.3 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 $K_2Cr_2O_7$ are *strong electrolytes* (i.e., they dissociate completely in aqueous solution to form ions). In contrast, because $Ag_2Cr_2O_7$ 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:

$$2\,\mathrm{Ag^+(aq)} + 2\,\mathrm{NO_3^-(aq)} + 2\,\mathrm{K^+(aq)} + \mathrm{Cr_2O_7^{2-}(aq)} \rightarrow \mathrm{Ag_2Cr_2O_7(s)} + 2\,\mathrm{K^+(aq)} + 2\,\mathrm{NO_3^-(aq)} \tag{12.2.4}$$

Note that $\mathrm{K^+(aq)}$ and $\mathrm{NO_3^-(aq)}$ ions are present on both sides of Equation 12.2.4 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:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{12.2.5}$$

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 12.2.5, the charge on the left side is 2(+1) + 1(−2) = 0, which is the same as the charge of a neutral $\mathrm{Ag_2Cr_2O_7}$ 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:

$$2AgF(aq) + (NH_4)_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4F(aq) \tag{12.2.6}$$

The complete ionic equation for this reaction is as follows:

$$2\,\mathrm{Ag^+(aq)} + \cancel{2\,\mathrm{F^-(aq)}} + \cancel{2\,\mathrm{NH_4^+(aq)}} + \mathrm{Cr_2O_7^{2-}(aq)} \rightarrow \mathrm{Ag_2Cr_2O_7(s)} + \cancel{2\,\mathrm{NH_4^+(aq)}} + \cancel{2\,\mathrm{F^-(aq)}} \tag{12.2.7}$$

Because two $\mathrm{NH_4^+(aq)}$ and two $\mathrm{F^-(aq)}$ ions appear on both sides of Equation 12.2.7, they are spectator ions. They can therefore be canceled to give the **net ionic equation** (Equation 12.2.8), which is identical to Equation 12.2.5:

$$2\,\mathrm{Ag^+(aq)} + \mathrm{Cr_2O_7^{2-}(aq)} \rightarrow \mathrm{Ag_2Cr_2O_7(s)} \tag{12.2.8}$$

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 12.2.1: 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:

$$\text{Ba(NO}_3)_2\text{(aq)} + \text{Na}_3\text{PO}_4\text{(aq)} \rightarrow \text{Ba}_3(\text{PO}_4)_2\text{(s)} + \text{NaNO}_3\text{(aq)}$$

Because the product is $Ba_3(PO_4)_2$, which contains three Ba^{2+} ions and two $PO_4{}^{3-}$ ions per formula unit, we can balance the equation by inspection:

$$3\,\text{Ba(NO}_3)_2\text{(aq)} + 2\,\text{Na}_3\text{PO}_4\text{(aq)} \rightarrow \text{Ba}_3(\text{PO}_4)_2\text{(s)} + 6\,\text{NaNO}_3\text{(aq)}$$

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:

$$3\,\text{Ba}^{2+}\text{(aq)} + \cancel{6\,\text{NO}_3^-\text{(aq)}} + \cancel{6\,\text{Na}^+\text{(aq)}} + 2\,\text{PO}_4^{3-}\text{(aq)} \rightarrow \text{Ba}_3(\text{PO}_4)_2\text{(s)} + \cancel{6\,\text{Na}^+\text{(aq)}} + \cancel{6\,\text{NO}_3^-\text{(aq)}}$$

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:

$$3\,\text{Ba}^{2+}\text{(aq)} + 2\,\text{PO}_4^{3-}\text{(aq)} \rightarrow \text{Ba}_3(\text{PO}_4)_2\text{(s)}$$

? Exercise 12.2.1: 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:

$$3\,\text{AgF(aq)} + \text{Na}_3\text{PO}_4\text{(aq)} \rightarrow \text{Ag}_3\text{PO}_4\text{(s)} + 3\,\text{NaF(aq)}$$

complete ionic equation:

$$3\,\text{Ag}^+\text{(aq)} + 3\,\text{F}^-\text{(aq)} + 3\,\text{Na}^+\text{(aq)} + \text{PO}_4^{3-}\text{(aq)} \rightarrow \text{Ag}_3\text{PO}_4\text{(s)} + 3\,\text{Na}^+\text{(aq)} + 3\,\text{F}^-\text{(aq)}$$

net ionic equation:

$$3\,\text{Ag}^+\text{(aq)} + \text{PO}_4^{3-}\text{(aq)} \rightarrow \text{Ag}_3\text{PO}_4\text{(s)}$$

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 12.2.1 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 12.2.1 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 12.2.1: 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 dipositive 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 $Na^+(aq)$, 0.50 M $Cl^-(aq)$, 0.50 M $K^+(aq)$, and 0.50 M $Br^-(aq)$. 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 12.2.1).

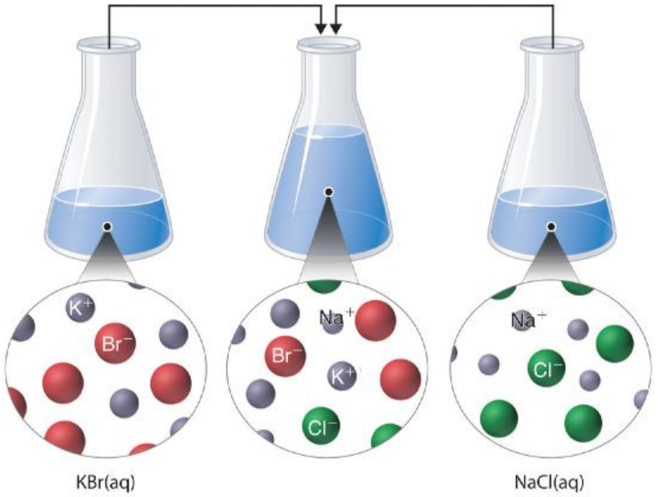


Figure 12.2.1: The Effect of Mixing Aqueous KBr and NaCl Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

Example 12.2.2

Using the information in Table 12.2.1, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

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

Given: reactants

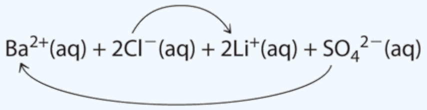
Asked for: reaction and net ionic equation

Strategy:

A. Identify the ions present in solution and write the products of each possible exchange reaction.
B. Refer to Table 12.2.1 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 $BaSO_4$:



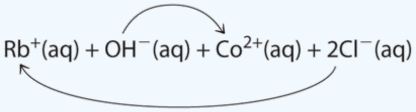
B We now need to decide whether either of these products is insoluble. Table 12.2.1 shows that LiCl is soluble in water (rules 1 and 4), but $BaSO_4$ is not soluble in water (rule 5). Thus $BaSO_4$ will precipitate according to the net ionic equation

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

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.

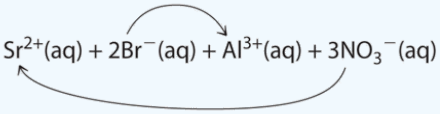
1. **A** Rubidium hydroxide and cobalt(II) chloride are strong electrolytes, so when aqueous solutions of these compounds are mixed, the resulting solution initially contains Rb^+, $OH^−$, Co^{2+}, and $Cl^−$ ions. The possible products of an exchange reaction are rubidium chloride and cobalt(II) hydroxide):



   B According to Table 12.2.1, 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:

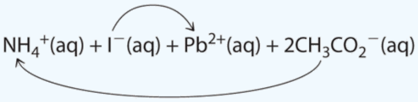
$$Co^{2+}(aq) + 2OH^-(aq) \rightarrow Co(OH)_2(s)$$

2. **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 12.2.1, both $AlBr_3$ (rule 4) and $Sr(NO_3)_2$ (rule 2) are soluble. Thus no net reaction will occur.

1. **A** According to Table 12.2.1, 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 12.2.1, ammonium acetate is soluble (rules 1 and 3), but PbI_2 is insoluble (rule 4). Thus $Pb(C_2H_3O_2)_2$ will dissolve, and PbI_2 will precipitate. The net ionic equation is as follows:

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

? Exercise 12.2.2

Using the information in Table 12.2.1, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

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

Answer a

$$Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_2(s)$$

Answer b

$$2PO_4^{3-}(aq) + 3Hg^{2+}(aq) \rightarrow Hg_3(PO_4)_2(s)$$

Answer c

$NaF(s)$ dissolves; no net reaction

Answer d

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

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

12.3: Acids and Bases

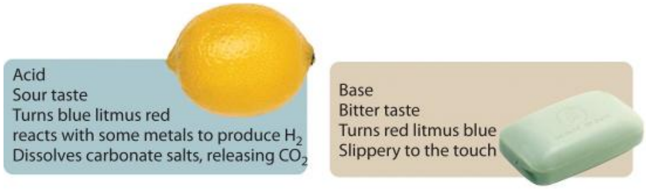
Learning Objectives

- 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 12.3.1), and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide (OH^-) ions (Equation 12.3.2):

$$\underset{\text{an Arrhenius acid}}{HCl_{(g)}} \xrightarrow{H_2O_{(l)}} H^+_{(aq)} + Cl^-_{(aq)} \tag{12.3.1}$$

$$\underset{\text{an Arrhenius base}}{NaOH_{(s)}} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + OH^-_{(aq)} \tag{12.3.2}$$

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

1. First, because acids and bases were defined in terms of ions obtained from water, the Arrhenius concept applied only to substances in aqueous solution.
2. Second, and more important, the Arrhenius definition predicted that *only* substances that dissolve in water to produce H^+ and OH^- ions should exhibit the properties of acids and bases, respectively. For example, according to the Arrhenius definition, the reaction of ammonia (a base) with gaseous HCl (an acid) to give ammonium chloride (Equation 12.3.3) is not an acid–base reaction because it does not involve H^+ and OH^-:

$$NH_{3\ (g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)} \tag{12.3.3}$$

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 12.3.3, 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

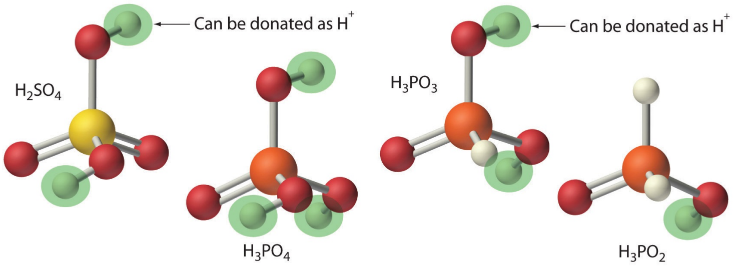
Acids differ in the number of protons they can donate. For example, monoprotic acids (a compound that is capable of donating one proton per molecule) are compounds that are capable of donating a single proton per molecule. Monoprotic acids include HF, HCl, HBr, HI, HNO_3, and HNO_2. All carboxylic acids 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 12.3.4, Equation 12.3.5, and Equation 12.3.6):

$$H_3PO_4(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + H_2PO_4^-(aq) \tag{12.3.4}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \tag{12.3.5}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \tag{12.3.6}$$

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, phosporic 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, HNO_3, $HClO_4$, and H_2SO_4 (H_3PO_4 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, H_2S, HF, oxoacids such as HNO_2 and HClO, and carboxylic acids such as acetic acid. The ionization reaction of acetic acid is as follows:

$$CH_3CO_2H(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + CH_3CO_2^-(aq) \tag{12.3.7}$$

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 12.3.8) but a weak acid when it donates its second proton (Equation 12.3.9) as indicated by the single and double arrows, respectively:

$$\underset{\text{strong acid}}{H_2SO_4(l)} \xrightarrow{H_2O(l)} H^+(aq) + HSO_4^-(aq) \tag{12.3.8}$$

$$\underset{\text{weak acid}}{HSO_4^-(aq)} \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \tag{12.3.9}$$

Consequently, an aqueous solution of sulfuric acid contains $H^+_{(aq)}$ ions and a mixture of $HSO^-_{4\ (aq)}$ and $SO^{2-}_{4\ (aq)}$ ions, but no H_2SO_4 molecules. All other polyprotic acids, such as H_3PO_4, are weak acids.

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

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{12.3.10}$$

Most of the ammonia (>99%) is present in the form of $NH_3(g)$. Amines, which are organic analogues of ammonia, are also weak bases, as are ionic compounds that contain anions derived from weak acids (such as S^{2-}).

> *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 12.3.1 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 12.3.1: Common Strong Acids and Bases

Strong Acids		**Strong Bases**	
Hydrogen Halides	Oxoacids	Group 1 Hydroxides	Hydroxides of Heavy Group 2 Elements
HCl	HNO_3	LiOH	$Ca(OH)_2$

Strong Acids		Strong Bases	
Hydrogen Halides	Oxoacids	Group 1 Hydroxides	Hydroxides of Heavy Group 2 Elements
HBr	H_2SO_4	NaOH	$Sr(OH)_2$
HI	$HClO_4$	KOH	$Ba(OH)_2$
		RbOH	
		CsOH	

✓ Example 12.3.1: Acid Strength

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

a. $CH_3CH_2CO_2H$
b. CH_3OH
c. $Sr(OH)_2$
d. $CH_3CH_2NH_2$
e. $HBrO_4$

Given: compound

Asked for: acid or base strength

Strategy:

A Determine whether the compound is organic or inorganic.

B If inorganic, determine whether the compound is acidic or basic by the presence of dissociable H^+ or OH^- ions, respectively. If organic, identify the compound as a weak base or a weak acid by the presence of an amine or a carboxylic acid group, respectively. Recall that all polyprotic acids except H_2SO_4 are weak acids.

Solution:

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** CH_3OH is methanol, an organic compound that contains the −OH group. **B** As a covalent compound, it does not dissociate to form the OH^- ion. Because it does not contain a carboxylic acid ($-CO_2H$) group, methanol also cannot dissociate to form $H^+(aq)$ ions. Thus we predict that in aqueous solution methanol is neither an acid nor a base.
c. **A** $Sr(OH)_2$ is an inorganic compound that contains one Sr^{2+} and two OH^- ions per formula unit. **B** We therefore expect it to be a strong base, similar to $Ca(OH)_2$.
d. **A** $CH_3CH_2NH_2$ is an amine (ethylamine), an organic compound in which one hydrogen of ammonia has been replaced by an R group. **B** Consequently, we expect it to behave similarly to ammonia (Equation 12.3.7), reacting with water to produce small amounts of the OH^- ion. Ethylamine is therefore a weak base.
e. **A** $HBrO_4$ is perbromic acid, an inorganic compound. **B** It is not listed in Table 12.3.1 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 $HBrO_4$ is chemically similar to $HClO_4$, a strong acid—and, in fact, it is.

? Exercise 12.3.1: 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. HIO_4
c. $CH_3CH_2CH_2CO_2H$
d. $(CH_3)_2NH$
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

12.3.1: Neutralization Reactions

Pouring concrete and working it are messy jobs. In the process, a lot of wastewater with an alkaline pH is generated. Often, regulations require that this wastewater be cleaned up at the site. One practical way to neutralize the basic pH is to bubble CO_2 into the water. The carbon dioxide forms a weak acid (carbonic acid, H_2CO_3) in solution which serves to bring the alkaline pH down to something closer to neutral.

Neutralization Reactions and Net Ionic Equations for Neutralization Reactions

A **neutralization reaction** is a reaction in which an acid and a base react in an aqueous solution to produce a salt and water. The aqueous sodium chloride that is produced in the reaction is called a salt. A **salt** is an ionic compound composed of a cation from a base and an anion from an acid. A salt is essentially any ionic compound that is neither an acid nor a base.

Strong Acid-Strong Base Reactions

When equal amounts of a strong acid such as hydrochloric acid are mixed with a strong base such as sodium hydroxide, the result is a neutral solution. The products of the reaction do not have the characteristics of either an acid or a base. The balanced molecular equation is:

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$$

Chemical reactions occurring in aqueous solution are more accurately represented with a net ionic equation. The full ionic equation for the neutralization of hydrochloric acid by sodium hydroxide is written as follows:

$$\mathrm{H^+}\,(aq) + \mathrm{Cl^-}\,(aq) + \mathrm{Na^+}\,(aq) + \mathrm{OH^-}\,(aq) \rightarrow \mathrm{Na^+}\,(aq) + \mathrm{Cl^-}\,(aq) + \mathrm{H_2O}\,(l)$$

Since the acid and base are both strong, they are fully ionized and so are written as ions, as is the $NaCl$ formed as a product. The sodium and chloride ions are spectator ions in the reaction, leaving the following as the net ionic reaction.

$$\mathrm{H^+}\,(aq) + \mathrm{OH^-}\,(aq) \rightarrow \mathrm{H_2O}\,(l)$$

All neutralization reactions of a strong acid with a strong base simplify to the net ionic reaction of hydrogen ion combining with hydroxide ion to produce water.

What if the acid is a diprotic acid such as sulfuric acid? The balanced molecular equation now involves a 1:2 ratio between acid and base.

$$\mathrm{H_2SO_4}\,(aq) + 2\mathrm{NaOH}\,(aq) \rightarrow \mathrm{Na_2SO_4}\,(aq) + \mathrm{H_2O}\,(l)$$

In order for the reaction to be a full neutralization, twice as many moles of $NaOH$ must react with the H_2SO_4. The sodium sulfate salt is soluble, and so the net ionic reaction is again the same. Different mole ratios occur for other polyprotic acids or bases with multiple hydroxides such as $Ca(OH)_2$.

Reactions Involving a Weak Acid or Weak Base

Reactions where at least one of the components is weak do not generally result in a neutral solution. The reaction between weak nitrous acid and strong potassium hydroxide is shown below.

$$\mathrm{HNO_2}\,(aq) + \mathrm{KOH}\,(aq) \rightarrow \mathrm{KNO_2}\,(aq) + \mathrm{H_2O}\,(l)$$

In order to write the net ionic equation, the weak acid must be written as a molecule since it does not ionize to a great extent in water. The base and the salt are fully dissociated.

$$\mathrm{HNO_2}\,(aq) + \mathrm{K^+}\,(aq) + \mathrm{OH^-}\,(aq) \rightarrow \mathrm{K^+}\,(aq) + \mathrm{NO_2^-}\,(aq) + \mathrm{H_2O}\,(l)$$

The only spectator ion is the potassium ion, resulting in the net ionic equation:

$$\mathrm{HNO_2}\,(aq) + \mathrm{OH^-}\,(aq) \rightarrow \mathrm{NO_2^-}\,(aq) + \mathrm{H_2O}\,(l)$$

The strong hydroxide ion essentially "forces" the weak nitrous acid to become ionized. The hydrogen ion from the acid combines with the hydroxide ion to form water, leaving the nitrite ion as the other product. The resulting solution is not neutral ($\mathrm{pH} = 7$), but instead is slightly basic.

Reactions can also involve a weak base and strong acid, resulting in a solution that is slightly acidic. The molecular and net ionic equations for the reaction of hydrochloric acid and ammonia are shown below.

$$\begin{array}{l} \mathrm{HCl}\,(aq) + \mathrm{NH_3}\,(aq) \rightarrow \mathrm{NH_4Cl}\,(aq) \\ \mathrm{H^+}\,(aq) + \mathrm{NH_3}\,(aq) \rightarrow \mathrm{NH_4^+}\,(aq) \qquad \left(\mathrm{Cl^-} \text{ is a spectator ion}\right) \end{array}$$

Reactions between acids and bases that are both weak may result in solutions that are neutral, acidic, or basic.

Summary

- A neutralization reaction is a reaction in which an acid and a base react in an aqueous solution to produce a salt and water.
- Equations for acid-base neutralizations are given.
- Net ionic equations for neutralization reactions are given.

- **21.16: Neutralization Reaction and Net Ionic Equations for Neutralization Reactions** by CK-12 Foundation is licensed CK-12. Original source: https://flexbooks.ck12.org/cbook/ck-12-chemistry-flexbook-2.0/.

12.4: Oxidation-Reduction 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:

$$\mathrm{Cu_2O(s) + H_2(g) \rightarrow 2\,Cu(s) + H_2O(g)} \tag{12.4.1}$$

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

$$\mathrm{4\,Al(s) + 3\,O_2 \rightarrow 2\,Al_2O_3(s)} \tag{12.4.2}$$

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):

$$4\overset{0}{\mathrm{Al}} + 3\overset{0}{\mathrm{O}}_2 \rightarrow \mathrm{4\,Al^{3+} + 6\,O^{2-}} \tag{12.4.3}$$

Equation 12.4.1 and Equation 12.4.2 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 12.4.3, 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 12.4.1.

> *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 12.4.1), 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.

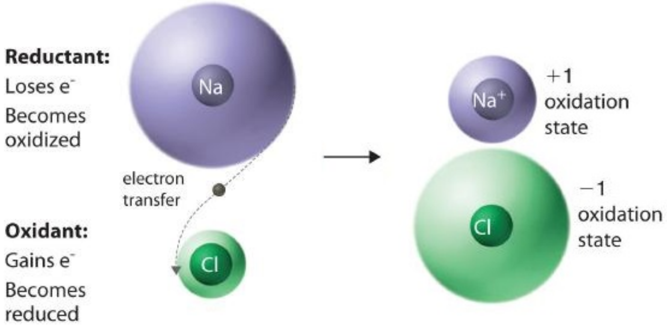


Figure 12.4.1: The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom. The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.

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, $Na^+ = +1$, $Cl^- = -1$.
3. The oxidation state of fluorine in chemical compounds is always −1. Other halogens usually have oxidation states of −1 as well, except when combined with oxygen or other halogens.
4. Hydrogen is assigned an oxidation state of +1 in its compounds with nonmetals and −1 in its compounds with metals.
5. Oxygen is normally assigned an oxidation state of −2 in compounds, with two exceptions: in compounds that contain oxygen–fluorine or oxygen–oxygen bonds, the oxidation state of oxygen is determined by the oxidation states of the other elements present.
6. The sum of the oxidation states of all the atoms in a neutral molecule or ion must equal the charge on the molecule or ion.

> *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 −½ in KO_2. Note that an oxidation state of −½ for O in KO_2 is perfectly acceptable.

The reduction of copper(I) oxide shown in Equation 12.4.4 demonstrates how to apply these rules. Rule 1 states that atoms in their elemental form have an oxidation state of zero, which applies to H_2 and Cu. From rule 4, hydrogen in H_2O has an oxidation state of +1, and from rule 5, oxygen in both Cu_2O and H_2O has an oxidation state of −2. Rule 6 states that the sum of the oxidation states in a molecule or formula unit must equal the net charge on that compound. This means that each Cu atom in Cu_2O must have a charge of +1: 2(+1) + (−2) = 0. So the oxidation states are as follows:

$$\overset{+1}{\mathrm{Cu}_2}\overset{-2}{\mathrm{O}}(s) + \overset{0}{\mathrm{H}_2}(g) \rightarrow 2\overset{0}{\mathrm{Cu}}(s) + \overset{+1}{\mathrm{H}_2}\overset{-2}{\mathrm{O}}(g) \tag{12.4.4}$$

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:

$$\text{electrons lost} = 2\,H\,\text{atoms} \times \frac{1\,e^-\ \text{lost}}{H\,\text{atom}} = 2\,e^-\ \text{lost} \tag{12.4.5}$$

$$\text{electrons gained} = 2\,Cu\,\text{atoms} \times \frac{1\,e^-\ \text{gained}}{Cu\,\text{atom}} = 2\,e^-\ \text{gained} \tag{12.4.6}$$

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 12.4.1: Oxidation States

Assign oxidation states to all atoms in each compound.

a. sulfur hexafluoride (SF_6)
b. methanol (CH_3OH)
c. ammonium sulfate $[(NH_4)2SO_4]$
d. magnetite (Fe_3O_4)
e. ethanoic (acetic) acid (CH_3CO_2H)

Given: molecular or empirical formula

Asked for: oxidation states

Strategy:

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

Solution:

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 SF_6), the oxidation state of sulfur must be +6:

[(6 F atoms)(−1)] + [(1 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 H atoms)(+1)] + [(1 O atom)(−2)] + [(1 C atom)(−2)] = 0

c. Note that $(NH_4)_2SO_4$ is an ionic compound that consists of both a polyatomic cation (NH_4^+) and a polyatomic anion (SO_4^{2-}) (see Table 2.4). We assign oxidation states to the atoms in each polyatomic ion separately. For NH_4^+, hydrogen has an oxidation state of +1 (rule 4), so nitrogen must have an oxidation state of −3:

[(4 H atoms)(+1)] + [(1 N atom)(−3)] = +1, the charge on the NH_4^+ ion

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

[(4 O atoms) (−2)] + [(1 S atom)(+6)] = −2, the charge on the sulfate ion

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 CH_3CO_2H in the same way as any other compound. Hydrogen and oxygen have oxidation states of +1 and −2 (rules 4 and 5, respectively), resulting in a total charge for hydrogen and oxygen of

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

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 ($-CH_3$) is bonded to three hydrogen atoms and one carbon atom. We know from rule 4 that hydrogen has an oxidation state of +1, and we have just said that the carbon–carbon bond can be ignored in calculating the oxidation state of the carbon atom. For the methyl group to be electrically neutral, its carbon atom must have an oxidation state of −3. Similarly, the carbon atom of the carboxylic acid group ($-CO_2H$) is bonded to one carbon atom and two oxygen atoms. Again ignoring the bonded carbon atom, we assign oxidation states of −2 and +1 to the oxygen and hydrogen atoms, respectively, leading to a net charge of

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

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

$$\underset{-3}{C}\overset{+1}{H_3}\overset{+3}{C}\underset{-2}{O_2}\overset{+1}{H}$$

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

? Exercise 12.4.1: Oxidation States

Assign oxidation states to all atoms in each compound.

a. barium fluoride (BaF_2)
b. formaldehyde (CH_2O)
c. potassium dichromate ($K_2Cr_2O_7$)
d. cesium oxide (CsO_2)
e. ethanol (CH_3CH_2OH)

Answer a

Ba, +2; F, −1

Answer b

C, 0; H, +1; O, −2

Answer c

K, +1; Cr, +6; O, −2

Answer d

Cs, +1; O, −½

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:

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

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

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

- **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:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$$

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 $12.4.2$). 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 HCl(aq) to produce iron(II) chloride and hydrogen gas:

$$\mathrm{Fe(s) + 2\,HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)} \tag{12.4.7}$$

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

Figure 12.4.2: 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

$$\mathrm{metal + acid \rightarrow salt + hydrogen} \tag{12.4.8}$$

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:

$$\mathrm{Pb(s) + 2\,H^{+}(aq) \rightarrow Pb^{2\,+}(aq) + H_2(g)} \tag{12.4.9}$$

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 12.4.10) and the reduction of silver salts by copper (Equation 12.4.11and Figure 12.4.3):

$$\mathrm{Zn(s) + Fe^{2\,+}(aq) \rightarrow Zn^{2\,+}(aq) + Fe(s)} \tag{12.4.10}$$

$$\mathrm{Cu(s) + 2\,Ag^{+}(aq) \rightarrow Cu^{2\,+}(aq) + 2\,Ag(s)} \tag{12.4.11}$$

The reaction in Equation 12.4.10is 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.

Figure used with permission (CC BY-SA 3.0; Toby Hudson).

- ## 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 $\mathrm{Zn^{+}_{2}}$. 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:

$$\mathrm{Zn(s) + Mg^{2\,+}(aq) \cancel{\rightarrow} Zn^{2\,+}(aq) + Mg(s)} \tag{12.4.12}$$

$$\mathrm{Mg(s) + Zn^{2\,+}(aq) \rightarrow Mg^{2\,+}(aq) + Zn(s)} \tag{12.4.13}$$

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

Pairwise reactions of this sort are the basis of the activity series (Figure 12.4.4), 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).

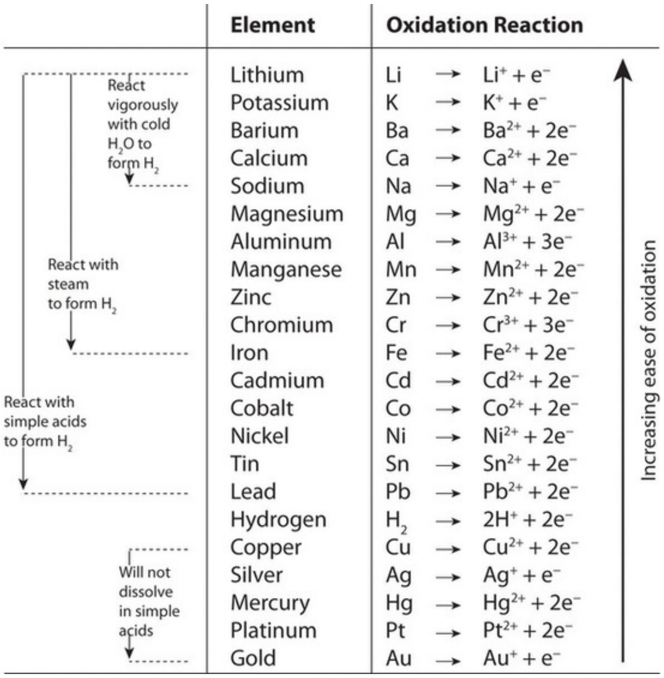


Figure 12.4.4: The Activity Series

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 12.4.4, 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* H_2. Because the precious metals lie below hydrogen, they do not dissolve in dilute acid and therefore do not corrode readily. Example 12.4.2 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions.

✓ Example 12.4.2: Activity

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

a. A strip of aluminum foil is placed in an aqueous solution of silver nitrate.
b. A few drops of liquid mercury are added to an aqueous solution of lead(II) acetate.
c. 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:

A. Locate the reactants in the activity series in Figure 12.4.4 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.
B. Write the net ionic equation for the redox reaction.

Solution:

1. **A** 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:

$$\mathrm{Al(s) + 3\,Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3\,Ag(s)}$$

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 H_2. **B** From our discussion of solubilities, recall that Pb^{2+} and $SO_4{}^{2-}$ form insoluble lead(II) sulfate. In this case, the sulfate ions are *not* spectator ions, and the reaction is as follows:

$$\mathrm{Pb(s) + 2\,H^{+}(aq) + SO_4^{2\,-}(aq) \rightarrow PbSO_4(s) + H_2(g)}$$

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 12.4.2

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

a. A strip of chromium metal is placed in an aqueous solution of aluminum chloride.
b. A strip of zinc is placed in an aqueous solution of chromium(III) nitrate.
c. 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

$$3Zn(s) + 2Cr^{3+}(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr(s)$$

Answer c

\(2Al(s) + 6CH_3CO_2H(aq) \rightarrow 2Al^{3+}(aq) + 6CH_3CO_2^-(aq) + 3H_2(g)\

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 12.4.1), 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 12.4.4), which arranges metals and H_2 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.

12.5: Stoichiometry of Aqueous Reactions

Introduction

At the beginning of this Chapter we covered stoichiometry of reactions where everything was a solid, and we used the mass and formula weight to calculate the moles of reactants or products consumed or produced. For a reaction where two chemicals interact with each other they must come into contact with each other if the reaction is going to proceed. One way of enabling this mobility is to dissolve the reactants into a solvent creating a solution. Unless you have a pure substance, you can not use mass to measure the number of particles, as you are weighting both the solvent and solute(s). So if you have a solution, you need to know the concentration, and the most common way of representing chemical concentrations is the molarity.

Solid phase:

$$n(moles) = \frac{m(g)}{fw(\frac{g}{mol}} \tag{12.5.1}$$

$$n = \frac{m}{fw} \tag{12.5.2}$$

Aqueous phase (solute concentration):

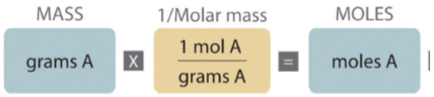
$$n(moles) = M\left(\frac{mol}{L}\right)V(L) \tag{12.5.3}$$

$$n = MV \tag{12.5.4}$$

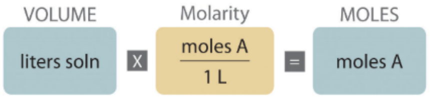
where,
n = moles
m = mass
V = Volume
fw = formula weight (molar mass)

So now we can calculate the moles of a pure substance if we weigh it's mass and know it's molar mass, or if we measure its volume and know it's concentration (Molarity).

If given a solid, you need to know its molar mass



If given a solute, you need to know its concentration (molarity)



Solution Stoichiometry

In sections 4.1 and 4.2 we calculated theoretical yield, limiting reagent and excess reagents for reactions where all chemical species were described as solids where we measured the mass. Now that we have a way to describe solute concentrations (Molarity) we can extend these to include solutions where we measure the volume. Lets look at the reaction of adding a solid soluble salt to an aqueous solution

Dissolving 10.0 g of Copper(II)sulfate into 500.0 mL of 0.100 M sodium phosphate

? Exercise 12.5.1

What are the formulas of the reactants when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate? (see video 12.5.1)

Answer

$CuSO_4$(s) and Na_3PO_4(aq)

? Exercise 12.5.2

What are the formulas and phases of the products when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate?(see video 12.5.1)

Answer

Na_2SO_4(aq) and $Cu_3(PO_4)_2$(s)

Exercise 12.5.3

Write the balanced equation when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate?(see video 12.5.1)

Answer

$3CuSO_4$(aq) + $2Na_3PO_4$(aq) --> $3Na_2SO_4$(aq) and $Cu_3(PO_4)_2$(s)

NOTE: We added copper(II)sulfate as a solid, but it dissolved (see solubility rules, section 3.4.2.1), and so it should be treated as aqueous when writing the equation

Video: 12.5.1: 3'54" YouTube identifying reactants, products, phases and balancing the equation for the dissolution of 10 g of copper(II) sulfate into 500.0 mL of 0.100 M sodium phosphate (https://youtu.be/qdtiFATDMdU).

Calculating the Theoretical Yield for the mass of precipitate formed

Example 12.5.4

Calculate the theoretical yield for the mass of precipitate formed when 10.0 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate.

Solution

See video 12.5.2 for the solution of this problem, and video 12.5.3 for a deeper explanation of the fast technique used in video 2. Note how we set up the equation by writing out the given data under each species, along with the moles that we need to calculate with that data. We calculate for the moles of each reactant (n), divide by its storichiometric coefficient, and the smallest number is the limiting reagent. We then proceed and calculate the mass of copper(II)phosphate formed.

$$\underset{\substack{n= \\ m=10.0g \\ fw=159.61g/mol}}{3CuSO_4(s)} + \underset{\substack{n= \\ M=0.100mol/l \\ V=500.0ml}}{2Na_3PO_4(aq)} \rightarrow \underset{\substack{m=? \\ fw=380.58g/mol}}{Cu_3(PO_4)_2(s)} + 3Na_2SO_4(aq) \tag{12.5.5}$$

at 2'25" into video 12.5.2 we calculated the limiting reagent, which was copper(II)Sulfate and thus based the yield on its consumption. The overall equation is

$$10.0gCuSO_4(s)\left(\frac{molCuSO_4}{159.69g}\right)\left(\frac{1molCu_3(PO_4)_2}{3molCuSO_4}\right)\left(\frac{380.58gCu_3(PO_4)_2(s)}{mol}\right) = 7.95gCu_3(PO_4)_2(s) \tag{12.5.6}$$

Note, the above equation is not used in the fast technique, but is used in video 12.5.3 when we explain the fast technique

Video: 12.5.2: 3'30" YouTube video calculating the mass precipitate formed by complete consumption of the limiting reagent for the dissolution of 10 g of copper(II) sulfate into 500.0 mL of 0.100 M sodium phosphate (https://youtu.be/Vh3Je39bgQc)

Video: 12.5.3: The fast technique in video 12.5.2 explained in more detail (https://youtu.be/5Qlo1bi1uzE).

Calculating excess reagents

Since the copper sulfate is the limiting reagent we can calculate the amount of excess sodium phosphate

Example 12.5.2: Excess Reagent

Calculate the concentration (molarity) of excess phosphate when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate (note: the real reaction is expressed by the net ionic equation:

$$3Cu^{+2}(aq) + 2PO_4^{-3}(aq) \rightarrow Cu_3(PO_4)_2(s) \tag{12.5.7}$$

Solution

see Video 12.5.4

First calculate moles excess phosphate

$$\text{Initial moles} - \text{amount consumed by reaction with limiting reagent} \tag{12.5.8}$$

$$0.050 mol PO_4^{-3} - 0.06265 mol Cu^{+2}\left(\frac{2\ mol\ PO_4^{-3}}{3\ mol\ Cu^{+2}}\right) = 0.0082 mol PO_4^{-3}$$

then divide into total volume

$$\frac{0.0082 mol PO_4^{-3}}{0.500 l} = 0.016 M PO_4^{-3}(aq)$$

Video 12.5.4: Determining the excess phosphate when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate https://youtu.be/xsp1_BADnqA).

Calculating Concentration of Spectator Ions

For the reaction that occurs when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate we have calculated the theoretical yield

✓ Example 12.5.3 Spectator Ion Concentrations

Calculate spectator ion concentrations when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate

Solution

See video $12.5.5$ for the solution to this problem. There are several ways you can set this up. In calculating the limiting reagent we determined the moles of each reactant and so that would be a logical place to start

$$\underset{\substack{n=\frac{m(g)}{fw(g/mol)}=\frac{10.0g}{159.61g/m0l} \\ n=0.06265mol}}{3CuSO_4(s)} + \underset{\substack{n=MV=(0.100mol/l)(0.5000l \\ n=0.0500mol}}{Na_3PO_4(aq)} \rightarrow Cu_3(PO_4))2(s)+3Na_2SO_4(aq) \tag{12.5.9}$$

$$\frac{molSO_4^{-2}}{V_{total}}=\frac{0.06265molCuSO_4\left(\frac{1molSO_4^{-2}}{molCuSO_4}\right)}{0.500l}=0.125M \tag{12.5.10}$$

$$\frac{molNa^+}{V_{total}}=\frac{0.0500molNa_3PO_4\left(\frac{3molNa^+}{molNa_3PO_4}\right)}{0.500l}=0.300M \tag{12.5.11}$$

Video 12.5.5: 2'44" YouTube calculating the spectator ion concentration when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate.

Test Yourself

Homework: Section 8.3

Graded Assignment: Section 8.3

Exercise 12.5.4

Consider the reaction of sodium phosphate and barium chloride, where 25.00 ml of 0.8000M Na_3PO_4 is mixed with 25.00ml of 0.1000M $BaCl_2$ (and the final volume is 50.00 ml, that is there is no change in volume upon mixing).

a. What is the limiting reagent?
b. What is the identity and mass of precipitate formed?
c. What is the concentration of the sodium spectator ion?
d. What is the concentration of the excess phosphate?

Answer a

$BaCl_2$

4-12q1h.gif

Answer b

$0.5016 g Ba_3(PO_4)_2$

$0.002500 mol BaCl_2 \left(\frac{1 mol Ba_3(PO_4)_3)}{3 mol BaCl_2}\right)\left(\frac{601.93 g Ba_3(PO_4)_2)}{mol}\right) = 0.5016 g Ba_3(PO_4)_2$

Answer c

0.1200M

$M_f V_f = M_i V_i$

$M_F = \frac{M_i V_i}{V_f}$

$\frac{0.8000 mol/L\ Na_3PO_4\left(\frac{3 mol Na^+}{mol Na_3PO_4}\right)0.02500L\ Na_3PO_4}{0.02500L+0.02500L} = 1.200 M Na^+$

Answer d

$$mol_{excess}\, PO_4^{-3} = mole_{initial} - mol_{consumed}$$

$$0.8000 mol Na_3PO_4/L\left(\frac{1 mol PO_4^{-3}}{mol Na_3PO_4}\right)0.02500L - \left(0.100 mol/L\ BaCl_2\left(\frac{1 mol Ba^{+2}}{mol BaCl_2}\right)0.02500L\left(\frac{2 mol PO_4^{-3}}{3 mol Ba^{+2}}\right)\right) = 0.01833 mol PO_4^{-3}$$

$$Concentration = \frac{mol_{excess}\, PO_4^{-3}}{V_T} = \frac{0.01833 mol PO_4^{-3}}{0.02500L + 0.02500L} = 0.3667 M\ PO_4^{-3}$$

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

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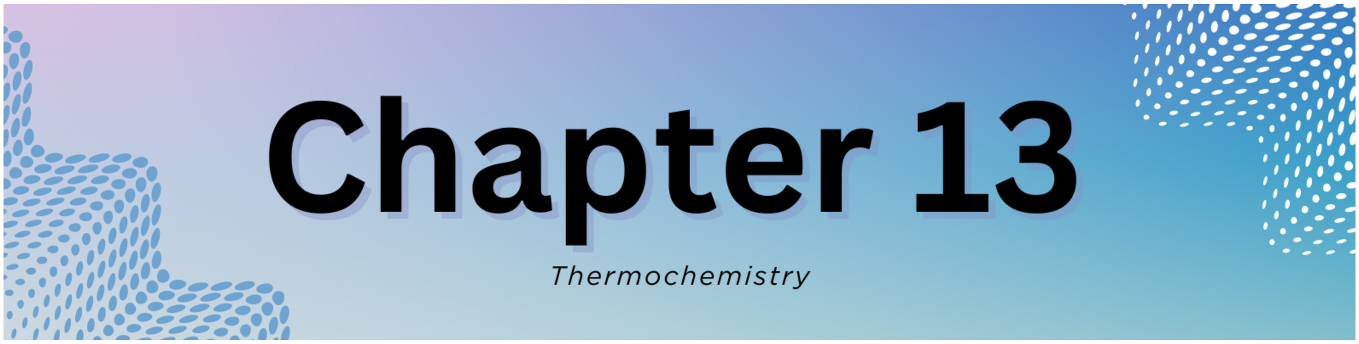
- anonymous

CHAPTER OVERVIEW

13: Thermochemistry



Our contemporary society requires the constant expenditure of huge amounts of energy to heat our homes, provide telephone and cable service, transport us from one location to another, provide light when it is dark outside, and run the machinery that manufactures material goods. The United States alone consumes almost 10^6 kJ per person per day, which is about 100 times the normal required energy content of the human diet. This figure is about 30% of the world's total energy usage, although only about 5% of the total population of the world lives in the United States.

In contrast, the average energy consumption elsewhere in the world is about 10^5 kJ per person per day, although actual values vary widely depending on a country's level of industrialization. In this chapter, we will discuss the nature of energy and how chemical reactions consume and release energy from/to their surroundings.

Chapter Sections

References and Attributions

1. Joshua Halpern, Chemistry: The Cetral Science by Brown, LeMay, Burston, Murphy and Woodward (https://chem.libretexts.org/Bookshel...hermochemistry)

13.1: The Nature of Energy

6.02: The Nature of Energy

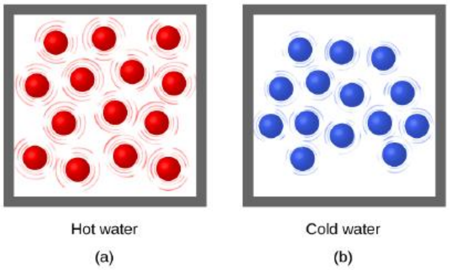
13.2: The First Law of Thermodynamics

13.2.1: Heat and Work

Learning Objectives

- To calculate changes in internal energy
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

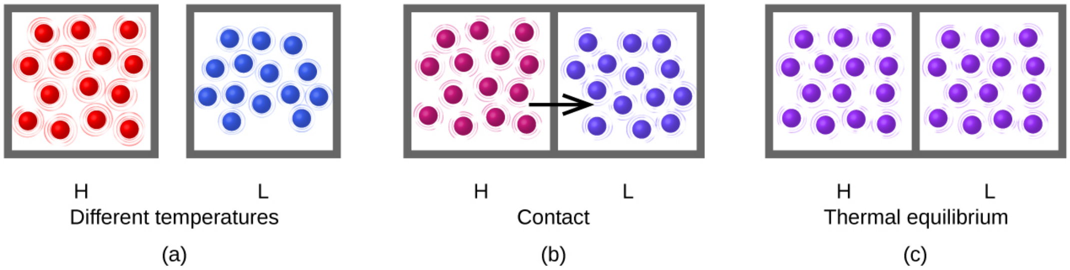
Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" (Figure $13.2.1.1$). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.



Drawing a is a box containing red spheres that are surrounded by lines indicating that the particles are moving rapidly. Drawing b depicts another box which also contains spheres, but these are blue. They are all surrounded by smaller lines that depict a slower motion compared to drawing a.

Figure $13.2.1.1$: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Heat (*q*) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure $13.2.1.2$).



Drawing a shows two separated boxes with red and blue spheres respectively. The radial lines along each sphere are more concentrated for the box containing hotter molecules. Drawing b shows the two boxes in contact as well as the direction of heat transfer from the hotter to colder region. The colors of the two molecules are turning into two different shades of maroon. The final drawing depicts two boxes where molecules in each box are exactly identical in terms of color and motion.

Figure $13.2.1.2$: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an exothermic process. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure $13.2.1.3a$). A reaction or change that absorbs heat is an endothermic process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.

Two pictures are shown and labeled a and b. Picture a shows a metal railroad tie being cut with the flame of an acetylene torch. Picture b shows a chemical cold pack containing ammonium nitrate.

Figure $13.2.1.3$ (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons).

Historically, energy was measured in units of *calories* (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

$$1\,cal \equiv 4.184\,J \tag{13.2.1.1}$$

Application: Heat can do more than increase temperature

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure $13.2.1.4$ The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

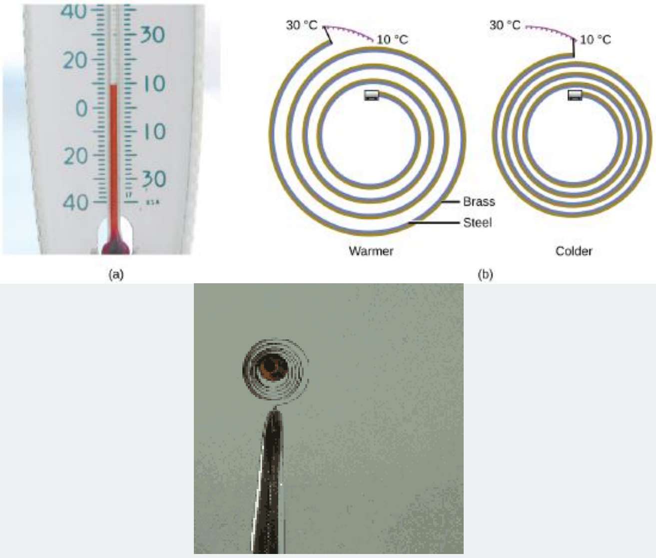


Figure 13.2.1.4: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by “dwstucke”/Flickr). (c) The demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.A bimetallic coil from a thermometer reacts to the heat from a lighter, by uncoiling and then coiling back up when the lighter is removed. Animation used with permission from Hustvedt (via Wikipedia)

Picture a shows the lower portion of an alcohol thermometer. The two images labeled b both depict a metal strip coiled into a spiral and composed of brass and steel. The left coil, which is loosely coiled, is labeled along its upper edge with the 30 degrees C and 10 degrees C. The end of the coil is near the 30 degrees C label. The right hand coil is much more tightly wound and the end is near the 10 degree C label.

Direction of Heat Flow: Endothermic vs. Exothermic Processes

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel. The balanced chemical equation for the reaction is as follows:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} \tag{13.2.1.2}$$

We can also write this chemical equation as

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} + \mathrm{heat} \tag{13.2.1.3}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$\text{heat} + H_2O_{(s)} \rightarrow H_2O_{(l)} \tag{13.2.1.4}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

> *By convention, $q < 0$ for an exothermic reaction and $q > 0$ for an endothermic reaction.*

Exercise 13.2.1.1

Decide whether the following are endothermic or exothermic processes

a. water evaporates off a shower door
b. an acid tablet being added to a pool and the surrounding water heats up
c. NH_4Cl is dissolved in water and the solution cools
d. the burning of a log in a campfire

Hint

During an endothermic process heat is absorbed from surroundings, causing them to cool, so in every case where there is cooling there is most likely an endothermic process taking place. For exothermic reactions energy is being released to the surroundings and so the surroundings feel like they have been heated by the process.

Answer a

endothermic

Answer b

exothermic

Answer c

endothermic

Answer d

exothermic

Heat is technically not a component in Chemical Reactions

Technically, it is poor form to have a $heat$ term in the chemical reaction like in Equations 13.2.1.3 and 13.2.1.4 since is it not a true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

Contributors and Attributions

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Learning Objectives

- To know the relationship between energy, work, and heat.

One definition of energy is the capacity to do work. There are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will consider only mechanical work and focus on the work done during changes in the pressure or the volume of a gas.

Mechanical Work

The easiest form of work to visualize is mechanical work (Figure $13.2.1.5$), which is the energy required to move an object a distance d when *opposed* by a force F, such as gravity:

$$w = F\,d \tag{13.2.1.5}$$

with w is work, F is opposing force, and d is distance.

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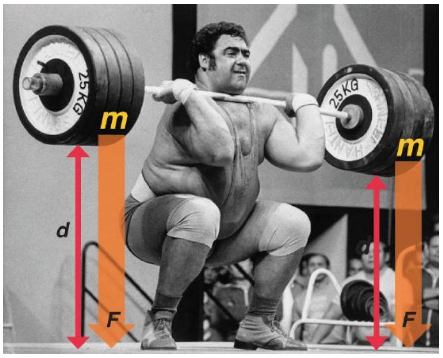


Figure $13.2.1.5$: One form of energy is mechanical work, the energy required to move an object of mass m through distance d when opposed by a force F, i.e., as gravity.

A powerlifter in the middle of lifting a barbell bar with multiple weights attached on each side. The weights are labeled m and an arrow labeled F is shown pointing downwards. The height of the weights from the ground is labeled d.

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), Equation $13.2.1.5$ can be rewritten to:

$$w = m\,a\,d \tag{13.2.1.6}$$

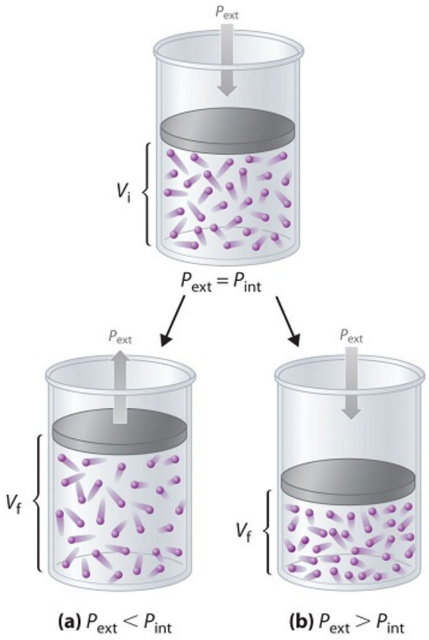
with w is work, m is mass, a is acceleration, and d is distance.

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth. Hence for works against gravity (on Earth), a can be set to $g = 9.8\ m/s^2$. Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the opposing force of gravity. The amount of work done (w) and thus the energy required depends on three things:

1. the height of the second floor (the distance d);
2. your mass, which must be raised that distance against the downward acceleration due to gravity; and
3. your path.

Pressure-Volume (PV) Work

To describe this pressure–volume work (PV work), we will use such imaginary oddities as frictionless pistons, which involve no component of resistance, and ideal gases, which have no attractive or repulsive interactions. Imagine, for example, an ideal gas, confined by a frictionless piston, with internal pressure P_{int} and initial volume V_i (Figure 13.2.1.6). If $P_{ext} = P_{int}$, the system is at equilibrium; the piston does not move, and no work is done. If the external pressure on the piston (P_{ext}) is less than P_{int}, however, then the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings; that is, the final volume (V_f) will be greater than V_i. If $P_{ext} > P_{int}$, then the gas will be compressed, and the surroundings will perform work on the system.



The three diagrams which represents the different cases show gaseos molecules shown as spheres in motion in an enclosed cylinder with piston acting from above. The top diagram shows the equilibrium case while the two diagram below it shows cases where external pressure is not equal to internal pressure.

Figure 13.2.1.6: PV Work demonstrated with a frictionless piston. (a) if the external pressure is less than P_{int}, the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume (V_f) will be greater than V_i. (b) Alternatively, if the external pressure is greater than P_{int}, the gas will be compressed, and the surroundings will perform work on the system.

If the piston has cross-sectional area A, the external pressure exerted by the piston is, by definition, the force per unit area:

$$P_{ext} = \frac{F}{A} \tag{13.2.1.7}$$

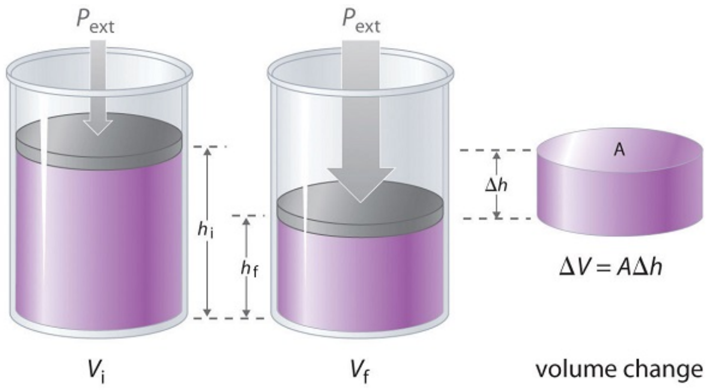
The volume of any three-dimensional object with parallel sides (such as a cylinder) is the cross-sectional area times the height ($V = Ah$). Rearranging Equation 13.2.1.7 to give

$$F = P_{ext} A \tag{13.2.1.8}$$

and defining the distance the piston moves (d) as Δh, we can calculate the magnitude of the work performed by the piston by substituting into Equation 13.2.1.5:

$$w = Fd = P_{ext} A \Delta h \tag{13.2.1.9}$$

The change in the volume of the cylinder (ΔV) as the piston moves a distance d is $\Delta V = A\Delta h$, as shown in Figure 13.2.1.7.



A cylinder containing an initial volume of fluid has a height labeled h subscript i and volume V subscript i. The following diagram shows a compressed volume labeled V subscript f and height of fluid h subscript f. The diagram on the right shows the cylindrical portion of fluid which represents the change in volume as a result of the piston pushing down. It has height of delta h and area A.

Figure 13.2.1.7: Work Performed with a change in volume. The change in the volume (ΔV) of the cylinder housing a piston is $\Delta V = A\Delta h$ as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by Equation 13.2.1.10

The PV work performed is thus

$$w = P_{ext}\Delta V \tag{13.2.1.10}$$

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m^2) and volume has units of cubic meters, so

$$w = \left(\frac{F}{A}\right)_{\text{ext}}(\Delta V) = \frac{\text{newton}}{\text{m}^2} \times \text{m}^3 = \text{newton} \cdot \text{m} = \text{joule} \tag{13.2.1.11}$$

If we use atmospheres for P and liters for V, we obtain units of L·atm for work. These units correspond to units of energy, as shown in the different values of the ideal gas constant R:

$$R = \frac{0.08206\ \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = \frac{8.314\ \text{J}}{\text{mol} \cdot \text{K}} \tag{13.2.1.12}$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J.

Exercise: Expansion (PV) work

a. How much work is done by a gas that expands from 2 liters to 5 liters against an external pressure of 750 mmHg?
b. How much work is done by 0.54 moles of a gas that has an initial volume of 8 liters and expands under the following conditions: 30 ^{o}C and 1.3 atm?
c. How much work is done by a gas (P=1.7 atm, V=1.56 L) that expands against an external pressure of 1.8 atm?

Solution a

$$w = -P\Delta V \tag{13.2.1.13}$$

$$\Delta V = V_{final} - V_{Initial} = 5\,L - 2\,L = 3L \tag{13.2.1.14}$$

Convert 750 mmHg to atm:

$$750 mmHg * 1/760 (atm/mmHg) = 0.9868 atm. \tag{13.2.1.15}$$

$$W = -p\Delta V = -(.9868\,atm)(3\,L) = -2.96\,L\,atm. \tag{13.2.1.16}$$

Solution b

First we must find the final volume using the ideal gas law:

$$pV = nRT \tag{13.2.1.17}$$

or

$$V = \frac{nRT}{P} = \frac{[(0.54\,moles)(0.082057(L\,atm)/(mol\,K))(303\,K)]}{1.3\,atm} = 10.33\,L \tag{13.2.1.18}$$

$$\Delta V = V_{final} - V_{initial} = 10.3\,L - 8\,L = 2.3\,L \tag{13.2.1.19}$$

$$w = -p\Delta V = -(1.3\,atm)(2.3\,L) = -3\,L\,atm. \tag{13.2.1.20}$$

Solution c

$$w = -p * \Delta V\backslash) = -(1.8\,atm)\,\Delta V. \tag{13.2.1.21}$$

Given p_1, V_1, and p_2, find V_2: $p_1V_1 = p_2V_2$ (at constant T and n)

$V_2 = (V_1 * P_1)/P_2$ = (1.56 L * 1.7 atm) / 1.8 atm = 1.47 L

Now,

$$\Delta V = V_2 - V_1 = 1.47\,L - 1.56\,L = -0.09 \tag{13.2.1.22}$$

$$w = -(1.8atm) * (-0.09L) = 0.162Latm. \tag{13.2.1.23}$$

Whether work is defined as having a positive sign or a negative sign is a matter of convention. Heat flow is defined from a system to its surroundings as negative; using that same sign convention, we define work done by a system on its surroundings as having a negative sign because it results in a transfer of energy from a system to its surroundings. This is an arbitrary convention and one that is not universally used. Some engineering disciplines are more interested in the work done on the surroundings than in the work done by the system and therefore use the opposite convention. Because ΔV > 0 for an expansion, Equation 13.2.1.10must be written with a negative sign to describe PV work done by the system as negative:

$$w = -P_{ext}\Delta V \tag{13.2.1.24}$$

The work done by a gas expanding against an external pressure is therefore negative, corresponding to work done by a system on its surroundings. Conversely, when a gas is compressed by an external pressure, ΔV < 0 and the work is positive because work is being done on a system by its surroundings.

A Matter of Convention

- Heat flow is defined from the system to its surroundings as **negative**
- Work is defined as by the system on its surroundings as **negative**

Suppose, for example, that the system under study is a mass of steam heated by the combustion of several hundred pounds of coal and enclosed within a cylinder housing a piston attached to the crankshaft of a large steam engine. The gas is not ideal, and the cylinder is not frictionless. Nonetheless, as steam enters the engine chamber and the expanding gas pushes against the piston, the piston moves, so useful work is performed. In fact, PV work launched the Industrial Revolution of the 19th century and powers the internal combustion engine on which most of us still rely for transportation.

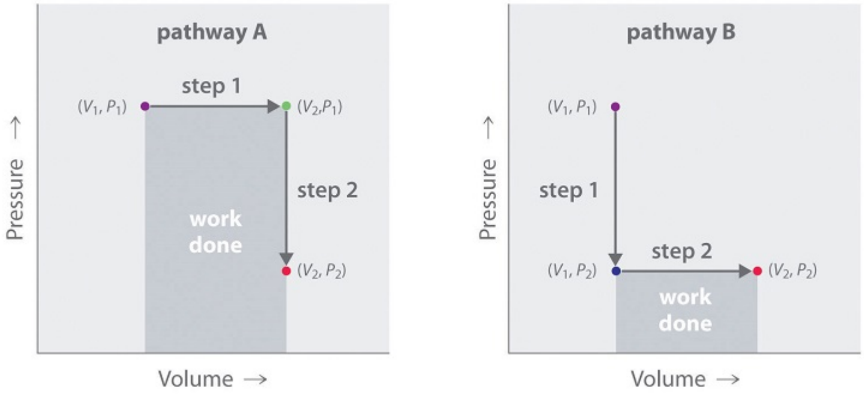


Figure 13.2.1.8: Work Is Not a State Function. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1). Its pressure is then decreased while the volume remains constant (step 2). Pathway B reverses these steps. Although (V_1, P_1) and (V_2, P_2) are identical in both cases, the amount of work done (shaded area) depends on the pathway taken.

Two graphs are shown with pressure on the vertical axis and volume on the horizontal axis. Pathway A with arrow pointing right then step 2 has arrow which points from the first arrow straight down. Pathway B has step 1 with arrow pointing straight down then step 2 with an arrow pointing from step 1 straight to the right. The area in pathway A is encompassed by the two arrows. The area in pathway B is found under the step 2 arrow.

In contrast to internal energy, work is not a state function. We can see this by examining Figure 13.2.1.8, in which two different, two-step pathways take a gaseous system from an initial state to a final state with corresponding changes in temperature. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1); then its pressure is decreased while the volume remains constant (step 2). In pathway B, the order of the steps is reversed. The temperatures, pressures, and volumes of the initial and final states are identical in both cases, but the amount of work done, indicated by the shaded areas in the figure, is substantially different. As we can see, the amount of work done depends on the pathway taken from (V_1, P_1) to (V_2, P_2), which means that work is **not** a state function.

> *Internal energy is a state function, whereas work is not.*

Example 13.2.1.1: Internal Combustion Engine

A small high-performance internal combustion engine has six cylinders with a total nominal displacement (volume) of 2.40 L and a 10:1 compression ratio (meaning that the volume of each cylinder decreases by a factor of 10 when the piston compresses the air–gas mixture inside the cylinder prior to ignition). How much work in joules is done when a gas in one cylinder of the engine expands at constant temperature against an opposing pressure of 40.0 atm during the engine cycle? Assume that the gas is ideal, the piston is frictionless, and no energy is lost as heat.

Given: final volume, compression ratio, and external pressure

Asked for: work done

Strategy:

Calculate the final volume of gas in a single cylinder. Then compute the initial volume of gas in a single cylinder from the compression ratio. Use Equation 13.2.1.24 to calculate the work done in liter-atmospheres. Convert from liter-atmospheres to joules.

Solution:

A To calculate the work done, we need to know the initial and final volumes. The final volume is the volume of one of the six cylinders with the piston all the way down: V_f = 2.40 L/6 = 0.400 L. With a 10:1 compression ratio, the volume of the same cylinder with the piston all the way up is V_i = 0.400 L/10 = 0.0400 L. Work is done by the system on its surroundings, so work is negative.

$$\begin{aligned} w &= -P_{ext}\Delta V \\ &= -(40.0\,atm)(0.400\,L - 0.0400\,L) \\ &= -14.4\,L \cdot atm \end{aligned}$$

Converting from liter-atmospheres to joules,

$$\begin{aligned} w &= -(14.4\ \mathrm{L \cdot atm})[101.3\ \mathrm{J/(L \cdot atm)}] \\ &= -1.46 \times 10^3\ \mathrm{J} \end{aligned}$$

In the following exercise, you will see that the concept of work is not confined to engines and pistons. It is found in other applications as well.

Exercise 13.2.1.1: Work to Breath

Breathing requires work, even if you are unaware of it. The lung volume of a 70 kg man at rest changed from 2200 mL to 2700 mL when he inhaled, while his lungs maintained a pressure of approximately 1.0 atm. How much work in liter-atmospheres and joules was required to take a single breath? During exercise, his lung volume changed from 2200 mL to 5200 mL on each in-breath. How much additional work in joules did he require to take a breath while exercising?

Answer

−0.500 L·atm, or −50.7 J; −304 J; if he takes a breath every three seconds, this corresponds to 1.4 Calories per minute (1.4 kcal).

Work and Chemical Reactions

We have stated that the change in energy (ΔU) is equal to the sum of the heat produced and the work performed. Work done by an expanding gas is called *pressure-volume work*, (or just *PV work)*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)} \tag{13.2.1.25}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 13.2.1.9). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of *PV* work done by multiplying the external pressure *P* by the change in volume caused by movement of the piston (Δ*V*). At a constant external pressure (here, atmospheric pressure)

$$w = -P\Delta V \tag{13.2.1.26}$$

The negative sign associated with PV work done indicates that the system loses energy. If the volume increases at constant pressure (Δ*V* > 0), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases (Δ*V* < 0), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

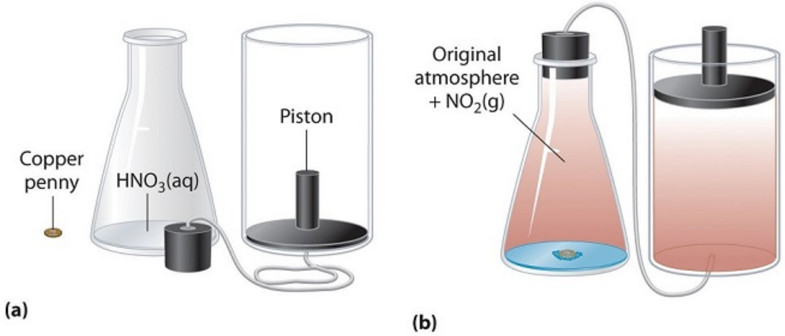


Figure 13.2.1.9: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.

Diagram a shows an Erlenmeyer flask with nitric acid in it and a copper penny beside the flask. A cylidrical container with a piston is shown connected by a tube to a flask stopper. The second diagram shows the copper penny inside the flask and the stopper placed on the neck of the flask. The flask and the cylindrical container is filled with a brownish vapor. The piston is at an elevated position compared to the first diagram since it's pushed upwards by the vapor.

The symbol U represents the internal energy of a system, which is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called enthalpy (H) (from the Greek *enthalpein*, meaning “to warm”). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

$$H = U + PV \tag{13.2.1.27}$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (i.e., for a given P, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta PV = \Delta U + P\Delta V \tag{13.2.1.28}$$

Substituting $q + w$ for ΔU (Equation 13.2.1.28) and $-w$ for $P\Delta V$ (Equation 13.2.1.26), we obtain

$$\Delta H = \Delta U + P\Delta V = q_p + w - w = q_p \tag{13.2.1.29}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 13.2.1.29 we see that at constant pressure the change in enthalpy, ΔH of the system, defined as $H_{final} - H_{initial}$, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} = q_p \tag{13.2.1.30}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

> *To find ΔH for a reaction, measure q_p under constant pressure.*

Summary

All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work.

Outside Links

- Gasparro, Frances P. "Remembering the sign conventions for q and w in deltaU = q - w." J. Chem. Educ. 1976: 53, 389.
- Koubek, E. "PV work demonstration (TD)." J. Chem. Educ. 1980: 57, 374. '

13.3: Enthalpy, ΔH, and Heat of Reaction

Learning Objectives

- To understand how enthalpy pertains to chemical reactions

We have stated that the change in energy (ΔU) is equal to the sum of the heat produced and the work performed. Work done by an expanding gas is called *pressure-volume work*, (or just *PV work)*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)} \tag{13.3.1}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure (\PageIndex{1}\)). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of *PV* work done by multiplying the external pressure P by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure)

$$w = -P\Delta V \tag{13.3.2}$$

The negative sign associated with *PV* work done indicates that the system loses energy when the volume increases. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

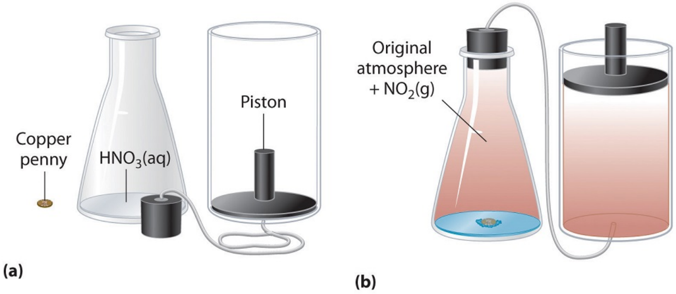


Figure 13.3.1: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.

The internal energy U of a system is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called enthalpy (H) (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

$$H = U + PV \tag{13.3.3}$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (i.e., for a given P, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta PV = \Delta U + P\Delta V \tag{13.3.4}$$

Substituting $q + w$ for ΔU (Equation 13.3.4) and $-w$ for $P\Delta V$ (Equation 13.3.2), we obtain

$$\Delta H = \Delta U + P\Delta V = q_p + w - w = q_p \tag{13.3.5}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 13.3.5 we see that at constant pressure the change in enthalpy, ΔH of the system, defined as $H_{\text{final}} - H_{\text{initial}}$, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} = q_p \tag{13.3.6}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

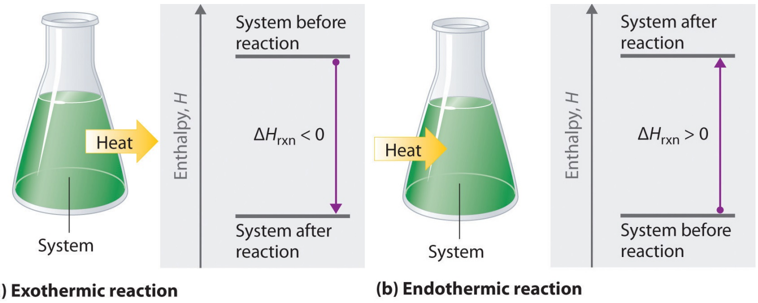
> *To find ΔH for a reaction, measure q_p.*

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus $\Delta H_{rxn} < 0$ *for an exothermic reaction*, and $\Delta H_{rxn} > 0$ *for an endothermic reaction*. In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (part (a) in Figure 5.4.2). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (part (b) in Figure 13.3.2). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

> *Bond breaking **ALWAYS** requires an input of energy; bond making **ALWAYS** releases energy.y.*



(a) Exothermic reaction **(b) Endothermic reaction**

Figure 13.3.2: The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill.

- **Reversing a reaction or a process changes the sign of ΔH.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$heat + H_2O(s) \rightarrow H_2O(l) \qquad \Delta H > 0$$
$$H_2O(l) \rightarrow H_2O(s) + heat \qquad \Delta H < 0$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 13.3.7, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

$$2Al\,(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s) + 815.5\;kJ \tag{13.3.7}$$

Thus Δ*H* = −851.5 kJ/mol of Fe_2O_3. We can also describe Δ*H* for the reaction as −425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide −851.5 kJ by 2. When a value for Δ*H*, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 13.3.8, it is the value of Δ*H* corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

$$2Al\,(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s) \qquad \Delta H_{rxn} = -851.5\ kJ \tag{13.3.8}$$

If 4 mol of Al and 2 mol of Fe_2O_3 react, the change in enthalpy is 2 × (−851.5 kJ) = −1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{13.3.9}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 13.3.1.

✓ Example 13.3.1: Melting Icebergs

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If Δ*H* is 6.01 kJ/mol for the reaction at 0°C and constant pressure:

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \tag{13.3.10}$$

How much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00 × 10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A. Calculate the number of moles of ice contained in 1 million metric tons (1.00 × 10^6 metric tons) of ice.
B. Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given Δ*H* for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by Δ*H* (+6.01 kJ/mol):

$$\begin{aligned} moles\ H_2O &= 1.00 \times 10^6\ metric\ tons H_2O \left(\frac{1000\ \ \cancel{kg}}{1\ \ \cancel{metric\ ton}}\right)\left(\frac{1000\ \ \cancel{g}}{1\ \ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \ \cancel{g\ H_2O}}\right) \\ &= 5.55 \times 10^{10}\ mol H_2O \end{aligned} \tag{13.3.11}$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{mol\ \cancel{H_2O}}\right)\left(5.55 \times 10^{10}\ \ mol\ \cancel{H_2O}\right) = 3.34 \times 10^{11}\ kJ \tag{13.3.12}$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown in the table below.

Possible sources of the approximately 3.34 × 10^{11} kJ needed to melt a 1.00 × 10^6 metric ton iceberg

- Combustion of 3.8 × 10^3 ft^3 of natural gas
- Combustion of 68,000 barrels of oil
- Combustion of 15,000 tons of coal
- 1.1 × 10^8 kilowatt-hours of electricity

Exercise 13.3.1: Thermite Reaction

If 17.3 g of powdered aluminum are allowed to react with excess Fe_2O_3, how much heat is produced?

Answer:

273 kJ

Enthalpies of Reaction

One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- Enthalpy of combustion (ΔH_{comb}) The change in enthalpy that occurs during a combustion reaction. Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of fusion (ΔH_{fus}) The enthalpy change that acompanies the melting (fusion) of 1 mol of a substance. The enthalpy change that accompanies the melting, or fusion, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.
- Enthalpy of vaporization (ΔH_{vap}) The enthalpy change that accompanies the vaporization of 1 mol of a substance. The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- Enthalpy of solution (ΔH_{soln}) The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent. The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.

Table 13.3.1: Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points

Substance	**ΔH_{vap} (kJ/mol)**	**ΔH_{fus} (kJ/mol)**
argon (Ar)	6.3	1.3
methane (CH_4)	9.2	0.84
ethanol (CH_3CH_2OH)	39.3	7.6
benzene (C_6H_6)	31.0	10.9
water (H_2O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Summary

For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

13.3.1: Calorimetry

Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure 13.3.1.1). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

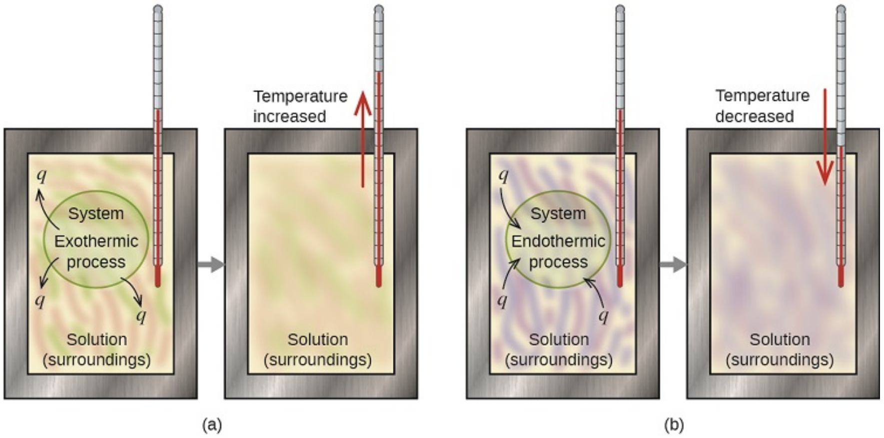


Figure 13.3.1.1: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

Two diagrams labeled a and b are shown. Each is made up of two rectangular containers with a thermometer inserted into the top right and extending inside. There is a right facing arrow connecting each box in each diagram. The left container in diagram a depicts a pink and green swirling solution with the terms “Exothermic process” and “System” written in the center with arrows facing away from the terms pointing to “q.” The labels “Solution” and “Surroundings” are written at the bottom of the container. The right container in diagram a has the term “Solution” written at the bottom of the container and a red arrow facing up near the thermometer with the phrase “Temperature increased” next to it. The pink and green swirls are more blended in this container. The left container in diagram b depicts a purple and blue swirling solution with the terms “Endothermic process” and “System” written in the center with arrows facing away from the terms and “Solution” and “Surroundings” written at the bottom. The arrows point away from the letter “q.” The right container in diagram b has the term “Solution” written at the bottom and a red arrow facing down near the thermometer with the phrase “Temperature decreased” next to it. The blue and purple swirls are more blended in this container.

> By convention, q is given a negative (-) sign when the system releases heat to the surroundings (exothermic); q is given a positive (+) sign when the system absorbs heat from the surroundings (endothermic).

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment. This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure 13.3.1.2). These easy-to-use “coffee cup” calorimeters allow more heat exchange with their surroundings, and therefore produce less accurate energy values.

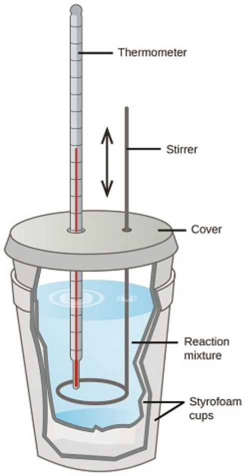


Figure 13.3.1.2: A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Two Styrofoam cups are shown nested in one another with a cover over the top. A thermometer and stirring rod are inserted through the cover and into the solution inside the cup, which is shown as a cut-away. The stirring rod has a double headed arrow next to it facing up and down. The liquid mixture inside the cup is labeled "Reaction mixture."

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor (Figure 13.3.1.3).

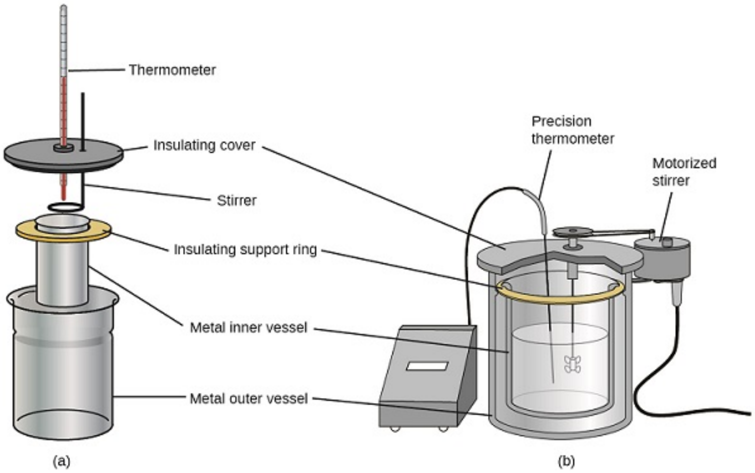


Figure 13.3.1.3: Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Two diagrams are shown and labeled a and b. Diagram a depicts a thermometer which passes through a disk-like insulating cover and into a metal cylinder which is labeled "metal inner vessel," which is in turn nested in a metal cylinder labeled "metal outer vessel." The inner cylinder rests on an insulating support ring. A stirrer passes through the insulating cover and into the inner cylinder as well. Diagram b shows an inner metal vessel half full of liquid resting on an insulating support ring and nested in a metal outer vessel. A precision temperature probe and motorized stirring rod are placed into the solution in the inner vessel and connected by wires to equipment exterior to the set-up.

Before we practice calorimetry problems involving chemical reactions, consider a simple example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure 13.3.1.4). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0 \tag{13.3.1.1}$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}} \tag{13.3.1.2}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{substance\ M}$ and $q_{substance\ W}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{substance\ M}$ is a negative value and $q_{substance\ W}$ is positive, since heat is transferred from M to W.

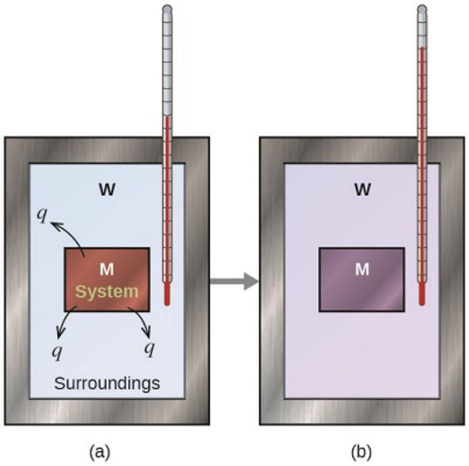


Figure 13.3.1.4: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Two diagrams are shown and labeled a and b. Each diagram is composed of a rectangular container with a thermometer inserted inside from the top right corner. Both containers are connected by a right-facing arrow. Both containers are full of water, which is depicted by the letter “W,” and each container has a square in the middle which represents a metal which is labeled with a letter “M.” In diagram a, the metal is drawn in brown and has three arrows facing away from it. Each arrow has the letter “q” at its end. The metal is labeled “system” and the water is labeled “surroundings.” The thermometer in this diagram has a relatively low reading. In diagram b, the metal is depicted in purple and the thermometer has a relatively high reading.

✓ Example 13.3.1.1: Heat Transfer between Substances at Different Temperatures

A hot 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water is measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat “lost” to the surroundings, then heat given off by rebar = − heat taken in by water, or:

$$q_{\text{rebar}} = -q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449\ \text{J/g}\ ^\circ\text{C})(360\text{g})(42.7^\circ\text{C} - T_{\text{i,rebar}}) = -(4.184\ \text{J/g}\ ^\circ\text{C})(425\ \text{g})(42.7^\circ\text{C} - 24.0^\circ\text{C})$$

$$T_{\text{i,rebar}} = \frac{(4.184\ \text{J/g}\ ^\circ\text{C})(425\ \text{g})(42.7^\circ\text{C} - 24.0^\circ\text{C})}{(0.449\ \text{J/g}\ ^\circ\text{C})(360\ \text{g})} + 42.7^\circ\text{C}$$

Solving this gives Ti,rebar= 248 °C, so the initial temperature of the rebar was 248 °C.

? Exercise 13.3.1.1A

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer

The initial temperature of the copper was 335.6 °C.

? Exercise 13.3.1.1B

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer

The final temperature (reached by both copper and water) is 38.7 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

✓ Example 13.3.1.2: Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, heat given off by metal = −heat taken in by water, or:

$$q_{\text{metal}} = -q_{\text{water}}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7\text{ g})(28.5^\circ\text{C} - 100.0^\circ\text{C}) = -(4.18\text{ J/g }^\circ\text{C})(60.0\text{ g})(28.5^\circ\text{C} - 22.0^\circ\text{C})$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184\text{ J/g }^\circ\text{C})(60.0\text{ g})(6.5^\circ\text{C})}{(59.7\text{ g})(-71.5^\circ\text{C})} = 0.38\text{ J/g }^\circ\text{C}$$

Comparing this with values in Table T4, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

? Exercise 13.3.1.2

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer

$c_{metal} = 0.13\ J/g\ ^\circ C$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the "system"), q_{reaction}, plus the heat absorbed or lost by the solution (the "surroundings"), $q_{solution}$, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0 \tag{13.3.1.3}$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -q_{\text{solution}} \tag{13.3.1.4}$$

This concept lies at the heart of all calorimetry problems and calculations.

✓ Example 13.3.1.3: Heat Produced by an Exothermic Reaction

When 50.0 mL of 0.10 M HCl(*aq*) and 50.0 mL of 1.00 M NaOH(*aq*), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and its surroundings.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{\text{solution}} = (c \times m \times \Delta T)_{\text{solution}}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.18 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{\text{solution}} = (4.184\ \mathrm{J/g\ ^\circ C})(1.0 \times 10^2\ \mathrm{g})(28.9\,^\circ\mathrm{C} - 22.0\,^\circ\mathrm{C}) = 2.89 \times 10^3\ \mathrm{J}$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.89 \times 10^3\ J$$

The negative sign indicates that the reaction is exothermic. It produces 2.89 kJ of heat.

? Exercise 13.3.1.3

When 100 mL of 0.200 M NaCl(*aq*) and 100 mL of 0.200 M $\mathrm{AgNO_3}$(*aq*), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

Answer

$1.34 \times 10^3\ J$; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water

Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 13.3.1.5). A common reusable hand warmer contains a supersaturated solution of $\mathrm{NaC_2H_3O_2}$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $\mathrm{NaC_2H_3O_2}$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process $\mathrm{NaC_2H_3O_2}(aq) \longrightarrow \mathrm{NaC_2H_3O_2}(s)$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $\mathrm{NaC_2H_3O_2}$ redissolves and can be reused.

Figure 13.3.1.5: Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

A series of three photos is shown. There are two right-facing arrows connecting one photo to the next. The first photo shows a chemical hand warmer. It is a bag that contains a clear, colorless liquid. There is a white disk located to the right inside the bag. The second photo shows the same thing, except the white disc has become a white, cloudy substance. The third photo shows the entire bag filled with this white substance.

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is

$$2\,\mathrm{Fe(s)} + \tfrac{3}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{Fe_2O_3(s)}.\ n$$

Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

✓ Example 13.3.1.4: Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an "instant ice pack" (Figure 13.3.1.5). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

Calculate the value of q for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.

Figure 13.3.1.5: An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.

Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{\text{rxn}} = -q_{\text{soln}}$$

with "rxn" and "soln" used as shorthand for "reaction" and "solution," respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

$$\begin{aligned} q_{\text{rxn}} &= -q_{\text{soln}} = -(c \times m \times \Delta T)_{\text{soln}} \\ &= -[(4.184\,\mathrm{J/g\ ^\circ C}) \times (53.2\ \mathrm{g}) \times (20.3\,^\circ\mathrm{C} - 24.9\,^\circ\mathrm{C})] \\ &= -[(4.184\,\mathrm{J/g\ ^\circ C}) \times (53.2\ \mathrm{g}) \times (-4.6\,^\circ\mathrm{C})] \\ & +1.0 \times 10^3\ \mathrm{J} = +1.0\ \mathrm{kJ} \end{aligned}$$

The positive sign for q indicates that the dissolution is an endothermic process.

? Exercise 13.3.1.4

When a 3.00-g sample of KCl was added to 3.00×10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05 °C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

Answer

1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water.

If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

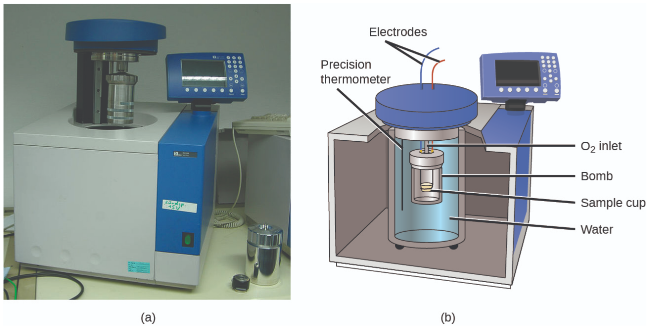
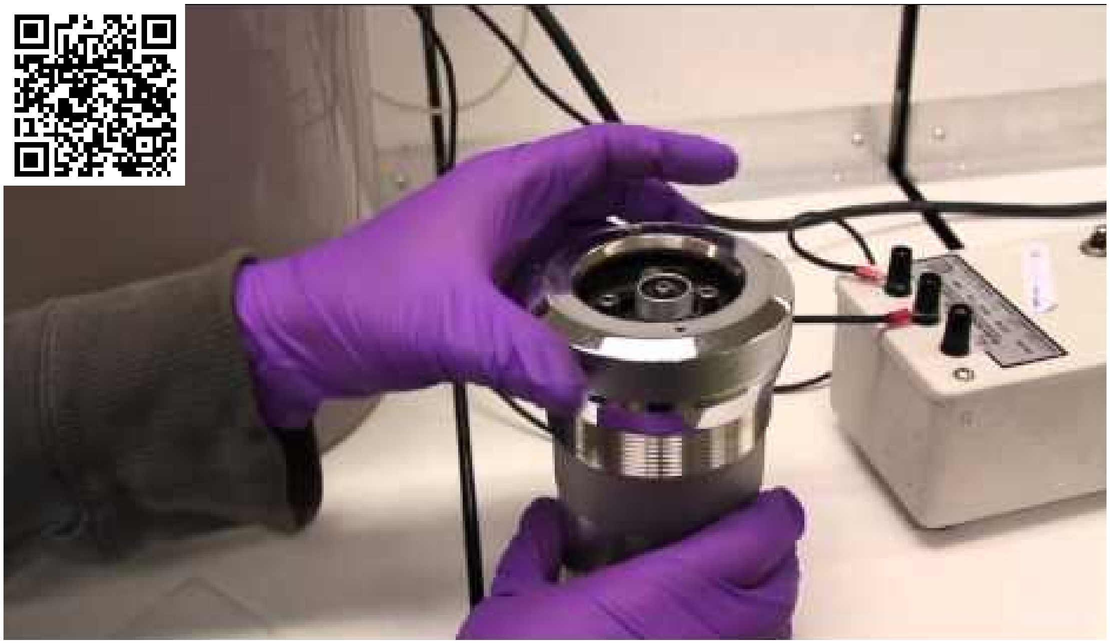


Figure 13.3.1.6: (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight “bomb,” which is submerged in water and surrounded by insulating materials. (credit a: modification of work by “Harbor1”/Wikimedia commons)

A picture and a diagram are shown, labeled a and b, respectively. Picture a depicts a bomb calorimeter. It is a cube-shaped machine with a cavity in the top, a metal cylinder that is above the cavity, and a read-out panel attached to the top-right side. Diagram b depicts a cut away figure of a cube with a cylindrical container full of water in the middle of it. Another container, labeled “bomb,” sits inside of a smaller cylinder which holds a sample cup and is nested in the cylindrical container surrounded by the water. A black line extends into the water and is labeled “Precision thermometer.” Two wires labeled “Electrodes” extend away from a cover that sits on top of the interior container. A read-out panel is located at the top right of the cube.

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a bomb calorimeter, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term “bomb” comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the “bomb”) that contains the reactants and is itself submerged in water (Figure 13.3.1.6). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is trapped in the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known *q*, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.



Video 13.3.1.1: Video of view how a bomb calorimeter is prepared for action.

✓ Example 13.3.1.5: Bomb Calorimetry

When 3.12 g of glucose, $C_6H_{12}O_6$, is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8 °C to 35.6 °C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C. How much heat was produced by the combustion of the glucose sample?

Solution

The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.)

The heat produced by the reaction is absorbed by the water and the bomb:

$$\begin{aligned} q_{\text{rxn}} &= -(q_{\text{water}} + q_{\text{bomb}}) \\ &= -[(4.184\ \text{J/g}\ ^\circ\text{C}) \times (775\ \text{g}) \times (35.6^\circ\text{C} - 23.8^\circ\text{C}) + 893\ \text{J}/^\circ\text{C} \times (35.6^\circ\text{C} - 23.8^\circ\text{C})] \\ &= -(38,300\ \text{J} + 10,500\ \text{J}) \\ &= -48,800\ \text{J} = -48.8\ \text{kJ} \end{aligned}$$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

? Exercise 13.3.1.5

When 0.963 g of benzene, C_6H_6, is burned in a bomb calorimeter, the temperature of the calorimeter increases by 8.39 °C. The bomb has a heat capacity of 784 J/°C and is submerged in 925 mL of water. How much heat was produced by the combustion of the glucose sample?

Answer

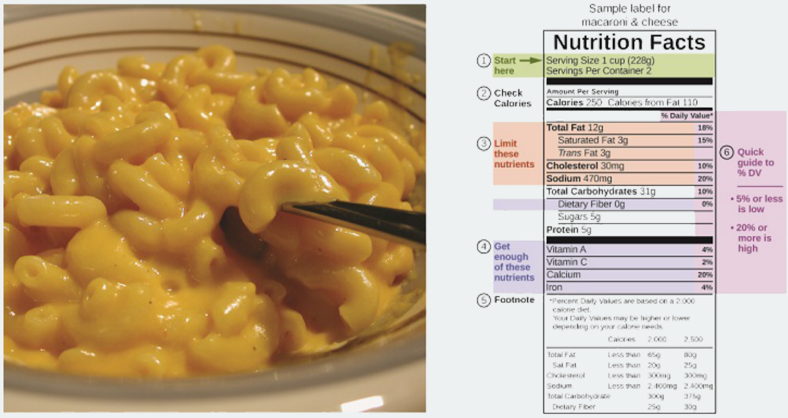
39.0 kJ

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.[1] These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, different dietary regimes, and with different health conditions, such as diabetes. In humans, metabolism is typically measured in Calories per day. A nutritional calorie (Calorie) is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by 1 °C.

Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by 1 °C.)

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients (Figure $13.3.1.7$).



(a) (b)

Figure 13.3.1.7: (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), the total energy per 228-g portion is calculated by:

$$(5\text{ g protein} \times 4\text{ Calories/g}) + (31\text{ g carb} \times 4\text{ Calories/g}) + (12\text{ g fat} \times 9\text{ Calories/g}) = 252\text{ Calories} \tag{13.3.1.5}$$

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Summary

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations. Calorimeters are designed to minimize energy exchange between the system being studied and its surroundings. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

Footnotes

1. 1 Francis D. Reardon et al. "The Snellen human calorimeter revisited, re-engineered and upgraded: Design and performance characteristics." *Medical and Biological Engineering and Computing* 8 (2006)721–28, The Snellen human calorimeter revisited, re-engineered and upgraded: design and performance characteristics [link.springer.com].

Glossary

bomb calorimeter

device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

calorimeter

device used to measure the amount of heat absorbed or released in a chemical or physical process

calorimetry

process of measuring the amount of heat involved in a chemical or physical process

nutritional calorie (Calorie)

unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

surroundings

all matter other than the system being studied

system

portion of matter undergoing a chemical or physical change being studied

---

13.3.2: Hess' Law

Learning Objectives

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Because enthalpy is a state function, the enthalpy change for a reaction depends on only two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does not depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

> *Hess's Law argues that ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This is nothing more than arguing that ΔH is a state function.*

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 5.6.1 can be viewed as occurring in three distinct steps with known ΔH values. As shown in Figure 5.6.1, the first reaction produces 1 mol of solid aluminum oxide (Al_2O_3) and 2 mol of liquid iron at its melting point of 1758°C (part (a) in Equation 5.6.1); the enthalpy change for this reaction is −732.5 kJ/mol of Fe_2O_3. The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (part (b) in Equation 5.6.1); the enthalpy change for this reaction is −13.8 kJ/mol of Fe (−27.6 kJ per 2 mol Fe). In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (part (c) in Equation 5.6.1); the enthalpy change for this reaction is −45.5 kJ/mol of Fe (−91.0 kJ per 2 mol Fe). As you can see in Figure 5.6.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding parts (a), (b), and (c) in Equation 5.6.1 gives the overall reaction, shown in part (d):

$$\begin{array}{rcllc}
2\,\mathrm{Al(s,25\,^\circ C)} + \mathrm{Fe_2O_3(s,25\,^\circ C)} & \longrightarrow & 2\,\mathrm{Fe(l,1758\,^\circ C)} + \mathrm{Al_2O_3(s,1758\,^\circ C)} & \Delta H = -732.5\,\mathrm{kJ} & \text{(a)} \\
2\,\mathrm{Fe(l,1758\,^\circ C)} & \longrightarrow & 2\,\mathrm{Fe(s,1758\,^\circ C)} & \Delta H = -\ \ 27.6\,\mathrm{kJ} & \text{(b)} \\
2\,\mathrm{Fe(s,1758\,^\circ C)} + \mathrm{Al_2O_3(s,1758\,^\circ C)} & \longrightarrow & 2\,\mathrm{Fe(s,25\,^\circ C)} + \mathrm{Al_2O_3(s,25\,^\circ C)} & \Delta H = -\ \ 91.0\,\mathrm{kJ} & \text{(c)} \\
\hline
2\,\mathrm{Al(s,25\,^\circ C)} + \mathrm{Fe_2O_3(s,25\,^\circ C)} & \longrightarrow & \mathrm{Al_2O_3(s,25\,^\circ C)} + 2\,\mathrm{Fe(s,25\,^\circ C)} & \Delta H = -851.1\,\mathrm{kJ} & \text{(d)}
\end{array} \tag{5.6.1}$$

The net reaction in part (d) in Equation 5.6.1 is identical to the equation for the thermite reaction that we saw in a previous section. By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 13.3.2.1

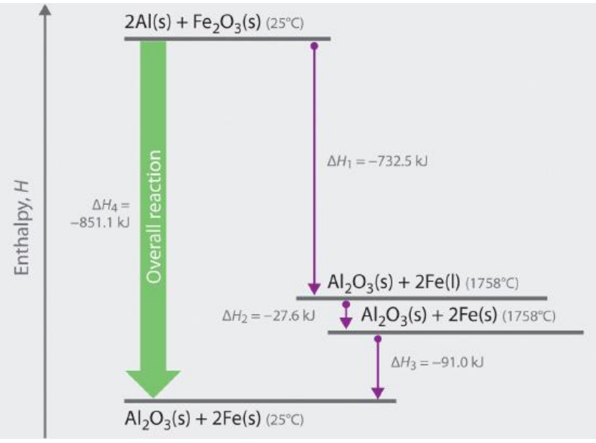


Figure 13.3.2.1: Energy Changes accompanying the thermite reaction. Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid Al_2O_3 and liquid iron (ΔH_1), solid iron at 1758°C (ΔH_2), and solid iron at 25°C (ΔH_3). Thus $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, as stated by Hess's law.

Comparing parts (a) and (d) in Equation 5.6.1 also illustrates an important point: The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution). When the product is liquid iron at its melting point (part (a) in Equation 5.6.1), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is solid iron at 25°C (part (d) in Equation 5.6.1). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and write individual reactions with known ΔH values that, when added together, will give the desired equation. We illustrate how to use this procedure in Example 13.3.2.1.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

✓ Example 13.3.2.1

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

$$(1)\ \ 2\,\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO(g)} \quad \Delta H = -221.0\ \mathrm{kJ}$$

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

$$(2)\ \ \mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H = -393.5\ \mathrm{kJ}$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2.

Given: two balanced chemical equations and their ΔH values

Asked for: enthalpy change for a third reaction

Strategy:

A. After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH.)
B. Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:

$$(3)\ \ \mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H_{rxn} = ?$$

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in Equation 3, is a product in Equation 1, we can reverse Equation (1) to give

$$2\,\mathrm{CO(g)} \longrightarrow 2\,\mathrm{C(s)} + \mathrm{O_2(g)} \quad \Delta H = +221.0\ \mathrm{kJ}$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use Equation 2 as written because its product, CO_2, is the product we want in Equation 3:

$$\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(s)} \quad \Delta H = -393.5\ \mathrm{kJ}$$

B Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(s)} \quad \Delta H = -787.0\ \mathrm{kJ}$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{array}{rcll}
2\,\mathrm{CO(g)} & \longrightarrow & 2\,\cancel{\mathrm{C(s)}} + \cancel{\mathrm{O_2(g)}} & \Delta H = -\Delta H_1 = +221.0\ \mathrm{kJ} \\
2\,\cancel{\mathrm{C(s)}} + \cancel{2}\mathrm{O_2(g)} & \longrightarrow & 2\,\mathrm{CO_2(g)} & \Delta H = -2\Delta H_2 = -787.0\ \mathrm{kJ} \\
\hline
2\,\mathrm{CO(g)} + \mathrm{O_2(g)} & \longrightarrow & 2\,\mathrm{CO_2(g)} & \Delta H = -566.0\ \mathrm{kJ}
\end{array}$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with O_2, and the problem asks for the amount per mole of CO. Consequently, we must divide both sides of the final equation and the magnitude of ΔH by 2:

$$\mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H = -283.0\ \mathrm{kJ}$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$\begin{array}{clll}
(\mathrm{A}) & 2\,\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow 2\,\cancel{\mathrm{CO(g)}} & \Delta H_A = \Delta H_1 & = +221.0\ \mathrm{kJ} \\
(\mathrm{B}) & 2\,\cancel{\mathrm{CO(g)}} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(g)} & \Delta H_B & = ? \\
(\mathrm{C}) & 2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(g)} & \Delta H = 2\Delta H_2 = 2 \times (-393.5\ \mathrm{kJ}) & = -787.0\ \mathrm{kJ}
\end{array}$$

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give CO_2. From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given ΔH for reactions A and C. Substituting the appropriate values gives

$$-221.0\ kJ + \Delta H_B = -787.0\ kJ$$
$$\Delta H_B = -566.0$$

This is again the enthalpy change for the conversion of 2 mol of CO to CO_2. The enthalpy change for the conversion of 1 mol of CO to CO_2 is therefore −566.0 ÷ 2 = −283.0 kJ/mol of CO, which is the same result we obtained earlier. As you can see, there may be more than one correct way to solve a problem.

? Exercise 13.3.2.1

The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$C_2H_2\ (g) + H_2\ (g) \rightarrow C_2H_4\ (g) \qquad \Delta H = -175.7\ kJ/mol\ C_2H_2$$
$$C_2H_2\ (g) + 2H_2\ (g) \rightarrow C_2H_6\ (g) \qquad \Delta H = -312.0\ kJ/mol\ C_2H_2$$

What is ΔH for the reaction of C_2H_4 with H_2 to form C_2H_6?

Answer

-136.3 kJ/mol of C_2H_4

Hess’s Law: Hess's Law, YouTube(opens in new window) [youtu.be]

Summary

Hess's law is arguing the overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions. For a chemical reaction, the **enthalpy of reaction (ΔH_{rxn})** is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}. The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion (ΔH_{fus})** and the **enthalpy of vaporization (ΔH_{vap})**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess’s law**. The **enthalpy of combustion (ΔH_{comb})** is the enthalpy change that occurs when a substance is burned in excess oxygen.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

13.3.3: Standard Enthalpy of Formation

Learning Objectives

- To understand Enthalpies of Formation and be able to use them to calculate Enthalpies of Reaction

One way to report the heat absorbed or released by chemical reactions would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, starting from the elemental forms of each atom at 25 ^{o}C and 1 atm pressure.

Enthalpy of formation (ΔH_f) is the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The formation of any chemical can be as a reaction from the corresponding elements:

$$\text{elements} \rightarrow \text{compound}$$

which in terms of the the Enthalpy of formation becomes

$$\Delta H_{rxn} = \Delta H_f \tag{13.3.3.1}$$

For example, consider the combustion of carbon:

$$\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)}$$

then

$$\Delta H_{rxn} = \Delta H_f\,[CO_2\,(g)]$$

The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed.

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Standard Enthalpies of Formation

The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The standard conditions for which most thermochemical data are tabulated are a *pressure* of 1 atmosphere (atm) for all gases and a *concentration* of 1 M for all species in solution (1 mol/L). In addition, each pure substance must be in its standard state, which is usually its most stable form at a pressure of 1 atm at a specified temperature. We assume a temperature of 25°C (298 K) for all enthalpy changes given in this text, unless otherwise indicated. Enthalpies of formation measured under these conditions are called **standard enthalpies of formation** (ΔH^o_f) The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition.

> *The standard enthalpy of formation of any element in its standard state is zero by definition.*

For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), O_2 is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H_2(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure 13.3.3.1). Therefore, $\mathrm{O_2(g)}$, $\mathrm{H_2(g)}$, and graphite have ΔH^o_f values of zero.

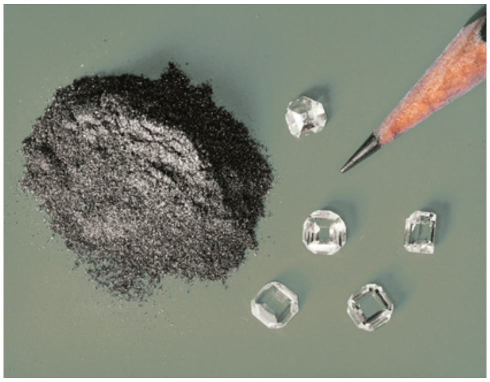


Figure 13.3.3.1: Elemental Carbon. Although graphite and diamond are both forms of elemental carbon, graphite is slightly more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H^o_f = -1273.3\ kJ \tag{13.3.3.2}$$

It is not possible to measure the value of $\Delta H^o{}_f$ for glucose, −1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, O_2, and H_2 and measuring the heat evolved as glucose is formed since the reaction shown in Equation 13.3.3.2 does not occur at a measurable rate under any known conditions. Glucose is not unique; most compounds cannot be prepared by the chemical equations that define their standard enthalpies of formation. Instead, values of $\Delta H^o{}_f$ are obtained using **Hess's law** and standard enthalpy changes that have been measured for other reactions, such as combustion reactions. Values of ΔH^o_f for an extensive list of compounds are given in Table T1. Note that ΔH^o_f values are always reported in kilojoules per mole of the substance of interest. Also notice in Table T1 that the standard enthalpy of formation of O_2(g) is zero because it is the most stable form of oxygen in its standard state.

✓ Example 13.3.3.1: Enthalpy of Formation

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $HCl(g)$
b. $MgCO_3(s)$
c. $CH_3(CH_2)_{14}CO_2H(s)$ (*palmitic acid*)

Given:

compound formula and phase.

Asked for:

balanced chemical equation for its formation from elements in standard states

Strategy:

Use Table T1 to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

Solution:

To calculate the standard enthalpy of formation of a compound, we must start with the elements in their standard states. The standard state of an element can be identified in Table T1: by a ΔH^o_f value of 0 kJ/mol.

Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $H_2(g)$ and $Cl_2(g)$, respectively, the unbalanced chemical equation is

$$H_2(g) + Cl_2(g) \rightarrow HCl(g)$$

Fractional coefficients are required in this case because $\Delta H^o{}_f$ values are reported for *1 mol* of the product, HCl. Multiplying both $H_2(g)$ and $Cl_2(g)$ by 1/2 balances the equation:

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(g)$$

The standard states of the elements in this compound are $\mathrm{Mg(s)}$, $\mathrm{C(s, graphite)}$, and $\mathrm{O_2(g)}$. The unbalanced chemical equation is thus

$$\mathrm{Mg(s) + C(s, graphite) + O_2(g) \rightarrow MgCO_3(s)}$$

This equation can be balanced by inspection to give

$$\mathrm{Mg(s) + C(s, graphite) + \tfrac{3}{2} O_2(g) \rightarrow MgCO_3(s)}$$

Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows:

$$\mathrm{C(s, graphite) + H_2(g) + O_2(g) \rightarrow CH_3(CH_2)_{14}CO_2H(s)}$$

There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is

$$\mathrm{16\,C(s, graphite) + 16\,H_2(g) + O_2(g) \longrightarrow CH_3(CH_2)_{14}CO_2H(s)}$$

? Exercise 13.3.3.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathrm{NaCl(s)}$
b. $\mathrm{H_2SO_4(l)}$
c. $\mathrm{CH_3CO_2H(l)}$ (*acetic acid*)

Answer a

$$\mathrm{Na(s) + \tfrac{1}{2} Cl_2(g) \rightarrow NaCl(s)}$$

Answer b

$$\mathrm{H_2(g) + \tfrac{1}{8} S_8(s) + 2\,O_2(g) \rightarrow H_2SO_4(l)}$$

Answer c

$$\mathrm{2\,C(s) + O_2(g) + 2\,H_2(g) \longrightarrow CH_3CO_2H(l)}$$

Definition of Heat of Formation Reactions: https://youtu.be/A20k0CK4doI

Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose ΔH^o_f values are known. The standard enthalpy of reaction ΔH^o_{rxn} is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

$$aA + bB \rightarrow cC + dD \tag{13.3.3.3}$$

where A, B, C, and D are chemical substances and a, b, c, and d are their stoichiometric coefficients. The magnitude of ΔH^o is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

$$\Delta H^o_{rxn} = \underbrace{\left[c\Delta H^o_f(C) + d\Delta H^o_f(D)\right]}_{\text{products}} - \underbrace{\left[a\Delta H^o_f(A) + b\Delta H^o_f(B)\right]}_{\text{reactants}} \tag{13.3.3.4}$$

More generally, we can write

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f(products) - \sum n\Delta H^o_f(reactants) \tag{13.3.3.5}$$

where the symbol $\sum$ means “sum of” and m and n are the stoichiometric coefficients of each of the products and the reactants, respectively. “Products minus reactants” summations such as Equation 13.3.3.5 arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, “products minus reactants” summations are very common in chemistry; we will encounter many others in subsequent chapters.

> "Products minus reactants" summations are typical of state functions.

To demonstrate the use of tabulated ΔH^o values, we will use them to calculate ΔH_{rxn} for the combustion of glucose, the reaction that provides energy for your brain:

$$\mathrm{C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)} \tag{13.3.3.6}$$

Using Equation 13.3.3.5, we write

$$\Delta H^o_f = \left\{6\Delta H^o_f[CO_2(g)] + 6\Delta H^o_f[H_2O(g)]\right\} - \left\{\Delta H^o_f[C_6H_{12}O_6(s)] + 6\Delta H^o_f[O_2(g)]\right\} \tag{13.3.3.7}$$

From Table T1, the relevant ΔH^o_f values are ΔH^o_f [CO_2(g)] = -393.5 kJ/mol, ΔH^o_f [H_2O(l)] = -285.8 kJ/mol, and ΔH^o_f [$C_6H_{12}O_6$(s)] = -1273.3 kJ/mol. Because O_2(g) is a pure element in its standard state, ΔH^o_f [O_2(g)] = 0 kJ/mol. Inserting these values into Equation 13.3.3.7and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\begin{aligned}\Delta H^o_{comb} &= [6(-393.5\ kJ/mol) + 6(-285.8\ kJ/mol)] - [-1273.3 + 6(0\ kJ\ mol)] && (13.3.3.8)\\ &= -2802.5\ kJ/mol && (13.3.3.9)\end{aligned}$$

As illustrated in Figure 13.3.3.2, we can use Equation 13.3.3.8to calculate ΔH^o_f for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH^o_{comb}. The alternative hypothetical pathway consists of **four separate reactions** that convert the reactants to the elements in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH^o_f values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned}\Delta H^o_1 &= \Delta H^o_f[glucose(s)]\\ &= -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right)\\ &= +1273.3\ kJ\\ \Delta H^o_2 &= 6\Delta H^o_f[O_2(g)]\\ &= 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right)\\ &= 0\ kJ && (13.3.3.10)\end{aligned}$$

> *Recall that when we reverse a reaction, we must also reverse the **sign** of the accompanying enthalpy change (Equation 13.3.3.4 since the products are now reactants and vice versa.*

The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

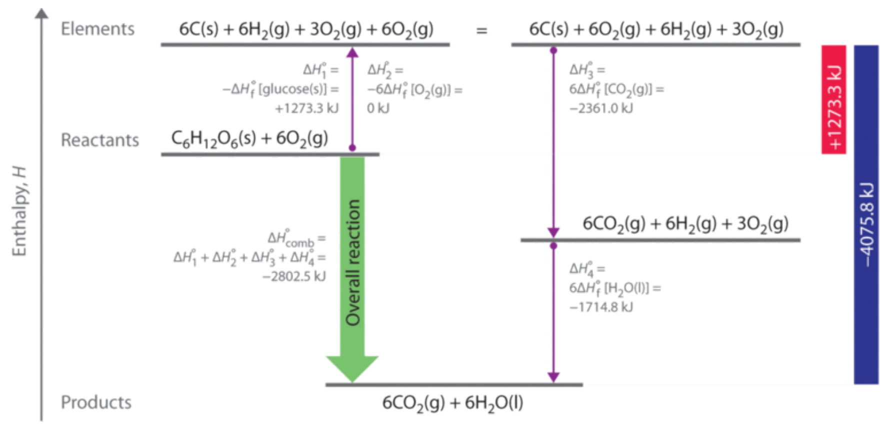


Figure 13.3.3.1: A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled ΔH^o_1 and ΔH^o_2). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled ΔH^o_3 and ΔH^o_4). Because enthalpy is a state function, ΔH^o_{comb} is equal to the sum of the enthalpy changes $\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$.

The reactions that convert the elements to final products (downward purple arrows in Figure 13.3.3.2) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes (from Table T1) are

$$\Delta H_3^o = \Delta H_f^o\left[CO_2\left(g\right)\right] = 6\ \ mol\ \cancel{CO_2}\left(\frac{393.5\ kJ}{1\ \ mol\ \cancel{CO_2}}\right) = -2361.0\ kJ$$
$$\Delta H_4^o = 6\Delta H_f^o\left[H_2O\left(l\right)\right] = 6\ \ mol\ \cancel{H_2O}\left(\frac{-285.8\ kJ}{1\ \ mol\ \cancel{H_2O}}\right) = -1714.8\ kJ \tag{13.3.3.11}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore −4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (−4075.8 kJ):

$$\Delta H_{comb}^o = +1273.3\ kJ + \left(-4075.8\ kJ\right) = -2802.5\ kJ \tag{13.3.3.12}$$

This is the same result we obtained using the "products minus reactants" rule (Equation 13.3.3.5) and ΔH^o_f values. The two results must be the same because Equation 13.3.3.12is just a more compact way of describing the thermochemical cycle shown in Figure 13.3.3.1.

✓ Example 13.3.3.2: Heat of Combustion

Long-chain fatty acids such as palmitic acid ($CH_3(CH_2)_{14}CO_2H$) are one of the two major sources of energy in our diet (ΔH_f^o =−891.5 kJ/mol). Use the data in Table T1 to calculate ΔH^o_{comb} for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel — glucose or palmitic acid?

Given: compound and ΔH_f^o values

Asked for: ΔH_{comb}^o per mole and per gram

Strategy:

A. After writing the balanced chemical equation for the reaction, use Equation 13.3.3.5and the values from Table T1 to calculate ΔH_{comb}^o the energy released by the combustion of 1 mol of palmitic acid.
B. Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated in Equation 13.3.3.8for the combustion of glucose to determine which is the better fuel.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH_f^o. As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_{2(s)} + 23O_{2(g)} \rightarrow 16CO_{2(g)} + 16H_2O_{(l)}$$

Using Equation 13.3.3.5 ("products minus reactants") with ΔH^o_f values from Table T1 (and omitting the physical states of the reactants and products to save space) gives

$$\begin{aligned} \Delta H^o_{comb} &= \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants) \\ &= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\ )] \\ &- [-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\ )] \\ &= -9977.3\ kJ/mol \end{aligned}$$

This is the energy released by the combustion of 1 mol of palmitic acid.

B The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{9977.3\ kJ}{1\ \cancel{mol}}\right)\left(\frac{1\ \cancel{mol}}{256.42\ g}\right) = -38.910\ kJ/g$$

As calculated in Equation 13.3.3.8, \(ΔH^o_f\) of glucose is −2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{-2802.5\ kJ}{1\ \cancel{mol}}\right)\left(\frac{1\ \cancel{mol}}{180.16\ g}\right) = -15.556\ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

? Exercise 13.3.3.2: Water–gas shift reaction

Use Table T1 to calculate ΔH^o_{rxn} for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain $H_2(g)$:

$$\mathrm{CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)}$$

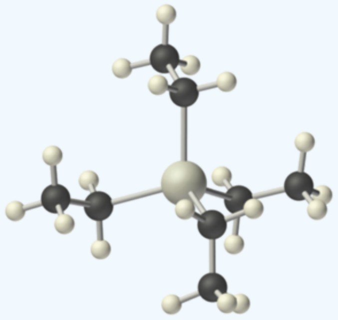
Answer

−41.2 kJ/mol

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's ΔH^o_f which we cannot obtain otherwise. This procedure is illustrated in Example 13.3.3.3

✓ Example 13.3.3.3: Tetraethyllead

Beginning in 1923, tetraethyllead $[(C_2H_5)_4Pb]$ was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are $CO_2(g)$, $H_2O(l)$, and red $PbO(s)$. What is the standard enthalpy of formation of tetraethyllead, given that ΔH^o_f is −19.29 kJ/g for the combustion of tetraethyllead and ΔH^o_f of red PbO(s) is −219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH^o_{comb} values

Asked for: ΔH_f^o of the reactants

Strategy:

A. Write the balanced chemical equation for the combustion of tetraethyl lead. Then insert the appropriate quantities into Equation 13.3.3.5to get the equation for ΔH^o_f of tetraethyl lead.
B. Convert ΔH^o_{comb} per gram given in the problem to ΔH^o_{comb} per mole by multiplying ΔH^o_{comb} per gram by the molar mass of tetraethyllead.
C. Use Table T1 to obtain values of ΔH_f^o for the other reactants and products. Insert these values into the equation for ΔH_f^o of tetraethyl lead and solve the equation.

Solution:

A The balanced chemical equation for the combustion reaction is as follows:

$$2\,(C_2H_5)_4Pb(l) + 27\,O_2(g) \rightarrow 2\,PbO(s) + 16\,CO_2(g) + 20\,H_2O(l)$$

Using Equation 13.3.3.5gives

$$\Delta H^o_{comb} = \left[2\Delta H_f^o\,(PbO) + 16\Delta H_f^o\,(CO_2) + 20\Delta H_f^o\,(H_2O)\right] - \left[2\Delta H_f^o\,((C_2H_5)_4Pb) + 27\Delta H_f^o\,(O_2)\right]$$

Solving for $\Delta H_f^o[(C_2H_5)_4Pb]$ gives

$$\Delta H_f^o\,((C_2H_5)_4Pb) = \Delta H_f^o\,(PbO) + 8\Delta H_f^o\,(CO_2) + 10\Delta H_f^o\,(H_2O) - \frac{27}{2}\Delta H_f^o\,(O_2) - \frac{\Delta H^o_{comb}}{2}$$

The values of all terms other than $\Delta H_f^o[(C_2H_5)_4Pb]$ are given in Table T1.

B The magnitude of ΔH^o_{comb} is given in the problem in kilojoules per *gram* of tetraethyl lead. We must therefore multiply this value by the molar mass of tetraethyl lead (323.44 g/mol) to get ΔH^o_{comb} for 1 mol of tetraethyl lead:

$$\begin{aligned}\Delta H^o_{comb} &= \left(\frac{-19.29\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right) \\ &= -6329\ kJ/mol\end{aligned}$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, ΔH^o_{rxn} is

$$\begin{aligned}\Delta H^o_{rxn} &= 2\ \ mol\ \cancel{(C_2H5)_4Pb}\left(\frac{-6329\ kJ}{1\ \ mol\ \cancel{(C_2H5)_4Pb}}\right) \\ &= -12,480\ kJ\end{aligned}$$

C Inserting the appropriate values into the equation for $\Delta H_f^o[(C_2H_5)_4Pb]$ gives

$$\begin{aligned}\Delta H_f^o\,[(C_2H_4)_4Pb] &= [1\ mol\ PbO\ \times 219.0\ kJ/mol] + [8\ mol\ CO_2 \times (-393.5\ kJ/mol)] + [10\ mol\ H_2O \times (-285.8\ kJ/mol)] \\ &\quad + [-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2]\,[12,480.2\ kJ/mol\ (C_2H_5)_4Pb] \\ &= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol\end{aligned}$$

? Exercise 13.3.3.3

Ammonium sulfate, $(NH_4)_2SO_4$, is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$$2\,NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(s)$$

The value of ΔH^o_{rxn} is -179.4 kJ/mole H_2SO_4. Use the data in Table T1 to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer

−1181 kJ/mol

Calculating DH° using DHf°: https://youtu.be/Y3aJJno9W2c

Summary

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 ^{o}C and 1 atm.
- The elemental form of each atom is that with the lowest enthalpy in the standard state.
- The standard state heat of formation for the elemental form of each atom is zero.

The **enthalpy of formation** (ΔH_f) is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH_f^o) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH_{rxn}^o) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the “products minus reactants” rule. The **enthalpy of solution** (ΔH_{soln}) is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

13.4: Heat Transfer Involving Phase Changes

Learning Objectives

- Apply an equation to quantify the heat transfer that is associated with changing the state of matter of a substance.

The primary objective of this chapter is to quantify the amount of heat that is transferred during physical and chemical changes. As stated previously, heat must be applied in order to overcome the attractive forces between a substance's constituent particles, in order to transform that substance from a solid to a liquid, and then, subsequently, from a liquid to a gas. Heat must also be transferred to a substance in order to raise its temperature. Because these transformations cannot occur simultaneously with one another, the heat transfers that are associated with these physical changes must be calculated separately.

This section will present and apply the equation that can be used to quantify the heat transfer that is associated with changing the state of matter of a substance.

Equation and Variables

In order to quantify the heat transfer, q, that is associated with changing the state of matter of a substance, the mass, m, of that substance must be multiplied by a phase change constant, ΔH, that corresponds to the phase change that is occurring, as shown in the equation below. Each of these quantities can be measured using multiple units. However, in order to be incorporated into this equation, the heat transfer must be recorded in calories (cal) or joules (J) and the mass must be reported in grams (g).

$$q = m(\Delta H)$$

A **phase change constant**, **ΔH**, for a substance is a physical property that quantifies the amount of heat that is required required to change the state of matter of 1 gram that substance. The value of a phase change constant, ΔH, is dependent on the strength of the attractive forces that exist between that substance's constituent particles. By definition, complementary phase changes relate the same states of matter. As a result, the relative attractive forces that are involved in melting and freezing, vaporization and condensation, and sublimation and deposition are *identical*. Therefore, the phase changes *within* each of these complementary pairs share a *common* phase change constant. Finally, the value of a phase change constant *varies between* each pair of complementary phase changes, as each combination involves a transformation between *different* states of matter. Therefore, three unique phase change constants, ΔH_{fusion}, ΔHvaporization, and $\Delta H_{sublimation}$, can be incorporated into the "$q = m(\Delta H)$" equation for a particular substance. Finally, because the variables in this equation are related multiplicatively, the unit for these phase change constants must incorporate the heat and mass units that are indicated in the previous paragraph, in order to achieve unit cancelation. As a result, phase change constants, which consist of both a numerator and a denominator, are reported in either cal/g or J/g. The phase change constants for several compounds and elements are shown below in Table 13.4.1. Because sublimation and its complement, deposition, are rarely studied, the corresponding $\Delta H_{sublimation}$ values for many chemicals have not been determined and, therefore, are not reported in this table.

Table 13.4.1: Selected Phase Change Constant Values

Substance	**ΔH_{fusion} (cal/g)**	**ΔH_{fusion} (J/g)**	**$\Delta H_{vaporization}$ (cal/g)**	**$\Delta H_{vaporization}$ (J/g)**
Water	79.9	540.	334	2,260
Benzene	30.4	94.1	127	394
Ethanol	25.6	200.3	107	838.1
Sodium Chloride	123.5	691	516.7	2,890
Aluminum	94.0	2,602	393	10,890
Gold	15.3	409	64.0	1,710
Iron	63.2	1,504	264	6,293

Indicator Phrases

Because the equation that is shown above is used to quantify the heat transfer that is associated with changing the state of matter of a substance, the phrases "to freeze," "to melt," "to boil," and "to condense" indicate that this equation should be applied to solve a problem. Additionally, since freezing and melting are complementary phase changes, the presence of the phrases "to freeze" and "to melt" within a given problem both indicate that a ΔH_{fusion} phase change constant should be incorporated into the "q = m(ΔH)" equation. Furthermore, because vaporization and condensation are complementary phase changes, any reference to boiling or condensation denotes that a ΔHvaporization phase change constant should be utilized to solve the given problem. Finally, if heat is *added to* a substance, its state of matter will change from a solid to a liquid or from a liquid to a gas, and the corresponding heat transfer, q, will have a *positive* value. In contrast, the *removal of heat from* a substance will cause its state of matter to change from a gas to a liquid or from a liquid to a solid, and the associated heat transfer, q, will be *negative*.

Calculations

For example, calculate how many calories of heat are required to melt a 6,387 milligram block of iron. The phase change constants for iron are given in Table 13.4.1.

The phrase "to melt" indicates that a ΔH_{fusion} phase change constant should be incorporated into the "q = m(ΔH)" equation to solve this problem. Before this equation can be applied, each numerical quantity that is given in the problem must be assigned to a variable. Finally, in order to be incorporated into this equation, the validity of the units that are associated with the given numerical values must be confirmed. As stated above, the heat transfer must be recorded in calories (cal) or joules (J), the mass must be provided in grams (g), and the phase change constant must be expressed in either cal/g or J/g.

The numerical values that are given in the problem, the variables to which these quantities are assigned, and an indication of the validity of their corresponding units are shown in the following table.

Numerical Quantity	Variable	Unit Validity
q	q	
6,387 mg	m	✗
63.2 cal/g	ΔH_{fusion}	✓

Because q is the only variable that cannot be assigned to a numerical value in the given problem, heat transfer is the unknown quantity that will be calculated upon solving the "q = m(ΔH)" equation. The problem specifies that the final answer must be expressed in calories. Therefore, while Table 13.4.1 lists two values for the ΔH_{fusion} of iron, 63.2 cal/g and 1,504 J/g, the first value must be incorporated into the equation that is indicated above, because its associated unit, cal/g, is consistent with the unit that is specified for the unknown quantity, q. Of the remaining variables, only mass, m, is not reported in an acceptable unit. Therefore, as shown below, this quantity must be converted to grams before it can be incorporated into the "q = m(ΔH)" equation.

$$6{,}387\ \cancel{\text{mg}} \times \frac{\text{g}}{1{,}000\ \ \cancel{\text{mg}}} = 6.387\ \text{g}$$

The updated numerical values that are summarized in the following table are all expressed in the appropriate units and, therefore, can be utilized to solve the given problem.

Numerical Quantity	Variable	Unit Validity
q	q	
6.387 g	m	✓
63.2 cal/g	ΔH_{fusion}	✓

The quantities that are shown in the table above can now be incorporated into the "q = m(ΔH)" equation. When solving for q, the mass and phase change constant are multiplied, resulting in the cancelation of the mass unit, "g," which is present in a numerator and a denominator in the second equation that is shown below. The unit that remains after these cancelations is "cal," which, per the information in the given problem, is the unit in which the unknown quantity, heat transfer, q, must be expressed. Applying the correct number of significant figures to the calculated quantity results in the final answer that is shown below.

$$q = m\left(\Delta H_{fusion}\right)$$

$$q = (6.387\ \cancel{g})\left(63.2\ \frac{cal}{\cancel{g}}\right)$$

$$q = 403.6584\ cal \approx 404\ cal$$

✓ Example 13.4.1

8,432 joules of heat are required to boil 21.4 grams of an unknown substance. Calculate the phase change constant for this chemical and compare its value the entries in Table 13.4.1 to identify the substance.

Solution

The phrase "to boil" indicates that a $\Delta H_{vaporization}$ phase change constant should be incorporated into the "$q = m(\Delta H)$" equation to solve this problem. Before this equation can be applied, each numerical quantity that is given in the problem must be assigned to a variable. Finally, in order to be incorporated into this equation, the validity of the units that are associated with the given numerical values must be confirmed. As stated above, the heat transfer must be recorded in calories (cal) or joules (J), the mass must be provided in grams (g), and the phase change constant must be expressed in either cal/g or J/g.

The numerical values that are given in the problem, the variables to which these quantities are assigned, and an indication of the validity of their corresponding units are shown in the following table.

Numerical Quantity	Variable	Unit Validity
8,432 J	q	✓
21.4 g	m	✓
$\Delta H_{vaporization}$	$\Delta H_{vaporization}$	

Because $\Delta H_{vaporization}$ is the only variable that cannot be assigned to a numerical value in the given problem, the phase change constant, $\Delta H_{vaporization}$, is the unknown quantity that will be calculated upon solving the "$q = m(\Delta H)$" equation. Since the problem does not specify whether the final answer should be expressed in cal/g or J/g, the given unit for heat, "joules," is acceptable for this problem. Finally, the numerical values that are summarized in the table that is shown above are all expressed in the appropriate units and, therefore, can be utilized to solve the given problem.

The quantities that are shown in the table above can be incorporated into the "$q = m(\Delta H)$" equation. To solve for $\Delta H_{vaporization}$, the heat transfer value on the left side of the equal sign must be divided by the mass of the substance. No unit cancelation occurs, because the unit in the numerator, "J" does not match the unit that is shown in the denominator, "g," in the resultant fraction. Therefore, unit that results from this division is "J/g," which is a valid unit for expressing the unknown quantity, $\Delta H_{vaporization}$. Applying the correct number of significant figures to the calculated quantity results in the final answer that is shown below.

$$q = m\left(\Delta H_{vaporization}\right)$$

$$8,432\ J = (21.4\ g)(\Delta H_{vaporization})$$

$$\Delta H_{vaporization} = 394.01869\ldots\ \frac{J}{g} \approx 394\ \frac{J}{g}$$

This value corresponds to the ΔHvaporization phase change constant that is shown for **benzene** in Table 13.4.1.

? Exercise 13.4.1

739 calories of heat are required to melt an unknown amount of mercury. Calculate the mass of the mercury, which has a ΔHfusion of 11.8 J/g and a ΔHvaporization of 272 J/g.

Answer

The phrase "to melt" indicates that a ΔH_{fusion} phase change constant should be incorporated into the "$q = m(\Delta H)$" equation to solve this problem. Before this equation can be applied, each numerical quantity that is given in the problem must be assigned to a variable. Finally, in order to be incorporated into this equation, the validity of the units that are associated with the given numerical values must be confirmed. As stated above, the heat transfer must be recorded in calories (cal) or joules (J), the mass must be provided in grams (g), and the phase change constant must be expressed in either cal/g or J/g.

The numerical values that are given in the problem, the variables to which these quantities are assigned, and an indication of the validity of their corresponding units are shown in the following table.

Numerical Quantity	Variable	Unit Validity
739 cal	q	×
m	m	
11.8 J/g	ΔH_{fusion}	✓

Because m is the only variable that cannot be assigned to a numerical value in the given problem, the mass of the substance is the unknown quantity that will be calculated upon solving the "$q = m(\Delta H)$" equation. While the problem does not specify a unit for the final answer, masses that are determined using this equation must be expressed in grams, as stated above. All of the remaining variables are reported in acceptable units. However, the units that are associated with the given values for heat transfer, q, and the phase change constant, ΔH_{fusion}, are not consistent with one another and, therefore, will not cancel when incorporated into the "$q = m(\Delta H)$" equation. In order to remedy this discrepancy, one of these units must be converted to match the other. While altering either unit is acceptable, modifying the unit for heat transfer, q, is more straight-forward and, therefore, is shown below.

$$739\ \cancel{\text{cal}} \times \frac{4.184\ \text{J}}{1\ \cancel{\text{cal}}} = 3{,}091.976\ \text{J} \approx 3{,}090\ \text{J}$$

The updated numerical values that are summarized in the following table are all expressed in the appropriate units and, therefore, can be utilized to solve the given problem.

Numerical Quantity	Variable	Unit Validity
3,090 J	q	✓
m	m	
11.8 J/g	ΔH_{fusion}	✓

The quantities that are shown in the table above can now be incorporated into the "$q = m(\Delta H)$" equation. When solving for m, the heat transfer value on the left side of the equal sign must be divided by the phase change constant, ΔH_{fusion}. This division causes the cancelation of the heat unit, "J," which appears in both the numerator and the denominator of the resultant fraction. Applying the correct number of significant figures to the calculated quantity results in the final answer that is shown below.

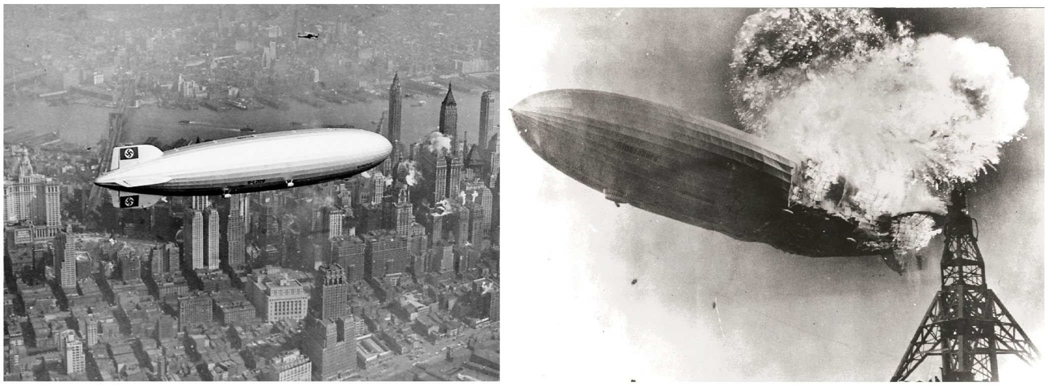
$$q = m\left(\Delta H_{\text{vaporization}}\right)$$

$$3{,}090\ \cancel{\text{J}} = m\left(11.8\ \frac{\cancel{\text{J}}}{\text{g}}\right)$$

$$m = 261.8644\ldots\ \text{g} \approx 262\ \text{g}$$

14: Gases

Perhaps one of the most spectacular chemical reactions involving a gas occurred on May 6, 1937, when the German airship *Hindenburg* exploded on approach to the Naval Air Station in Lakehurst, New Jersey. The actual cause of the explosion is still unknown, but the entire volume of hydrogen gas used to float the airship, about 200,000 m^3, burned in less than one minute. Thirty-six people, including one on the ground, were killed. Hydrogen is the lightest known gas. Any balloon filled with hydrogen gas will float in air if its mass is not too great. This makes hydrogen an obvious choice for flying machines based on balloons—airships, dirigibles, and blimps.



The German airship Hindenburg (left) was one of the largest airships ever built. However, it was filled with hydrogen gas and exploded in Lakehurst, New Jersey, at the end of a transatlantic voyage in May 1937 (right).

However, hydrogen also has one obvious drawback—it burns in air according to the well-known chemical equation:

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

So although hydrogen is an obvious choice, it is also a dangerous choice. Helium gas is also lighter than air and has 92% of the lifting power of hydrogen. Why, then, was helium not used in the *Hindenburg*? In the 1930s, helium was much more expensive. In addition, the best source of helium at the time was the United States, which banned helium exports to pre–World War II Germany. Today all airships use helium, a legacy of the *Hindenburg* disaster.

14.1: Kinetic Molecular Theory and Gas Pressure

Learning Outcomes

- Define pressure and describe how gases exert pressure.
- Convert between units of gas pressure (atm, mmHg, torr, and Pa).
- Relate temperature to average kinetic energy.
- Relate mass to molecular speed.
- Describe the behavior of an ideal gas.

The **kinetic-molecular theory** *is a theory that explains the states of matter and is based on the idea that matter is composed of tiny particles that are always in motion*. The theory helps explain observable properties and behaviors of solids, liquids, and gases. However, the theory is most easily understood as it applies to gases. The theory applies specifically to a model of a gas called an ideal gas. An **ideal gas** *is an imaginary gas whose behavior perfectly fits all the assumptions of the kinetic-molecular theory*. In reality, gases are not ideal, but they are very close to being so under most everyday conditions.

The kinetic-molecular theory, as it applies to gases, has five basic assumptions.

1. **Gases consist of very large numbers of tiny spherical particles that are far apart from one another compared to their size**. The particles of a gas may be either atoms or molecules. The distance between the particles of a gas is much, much greater than the distances between the particles of a liquid or a solid. Most of the volume of a gas, therefore, is composed of the empty space between the particles. In fact, the volume of the particles themselves is considered to be insignificant compared to the volume of the empty space.
2. **Gas particles are in constant rapid motion in random directions**. The fast motion of gas particles gives them a relatively large amount of kinetic energy. Recall that kinetic energy is the energy that an object possesses because of its motion. The particles of a gas move in a straight line until they collide with another particle or with one of the walls of their container (see figure below).
3. **Collisions between gas particles and between particles and the container walls are elastic collisions**. An elastic collision is one in which there is no overall loss of kinetic energy. Kinetic energy may be transferred from one particle to another during an elastic collision, but there is no change in the total energy of the colliding particles.
4. **There are no forces of attraction or repulsion between gas particles**. Attractive forces are responsible for particles of a real gas condensing together to form a liquid. It is assumed that the particles of an ideal gas have no such attractive forces. The motion of each particle is completely independent of the motion of all other particles.
5. **The average kinetic energy of gas particles is dependent upon the temperature of the gas**. As the temperature of a gas is increased, its component particles begin to move faster, resulting in an increase in their kinetic energies. Not all particles in a given sample have the same speed, so the sample will contain particles with a range of different kinetic energies. However, the average kinetic energy of the particles in a sample is proportional to its temperature.

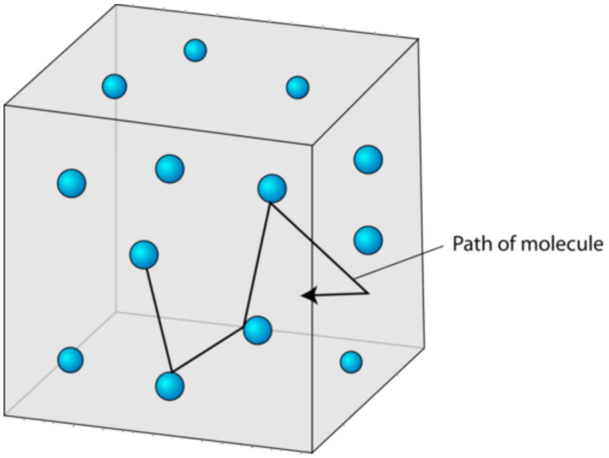


Figure 14.1.1: Gas particles move in a random, linear fashion according to the kinetic-molecular theory. The space between particles is very large compared to the size of the particles.

Gas Pressure

Pressure *is defined as the force per unit area on a surface.*

$$\text{Pressure} = \frac{\text{force}}{\text{area}} \tag{14.1.1}$$

When a person stands on the floor, his feet exert pressure on the surface. That pressure is related to both the mass of the person and the surface area of his feet. If the person were holding a heavy object, the pressure would increase because of a greater force. Alternatively, if the person stands on his toes, the pressure also increases because of a decrease in the surface area.

Gas molecules also exert pressure. Earth's atmosphere exerts pressure because gravity acts on the huge number of gas particles contained in the atmosphere, holding it in place. Pressure is also exerted by small samples of gas, such as the outward pressure exerted by the gas inside a balloon. **Gas pressure** *is the pressure that results from collisions of gas particles with an object*. Inside the balloon, the gas particles collide with the balloon's inner walls. It is those collisions that keep the balloon inflated. If the gas particles were to suddenly stop moving, the balloon would instantly deflate. The figure below is an illustration of gas particles exerting pressure inside a container.

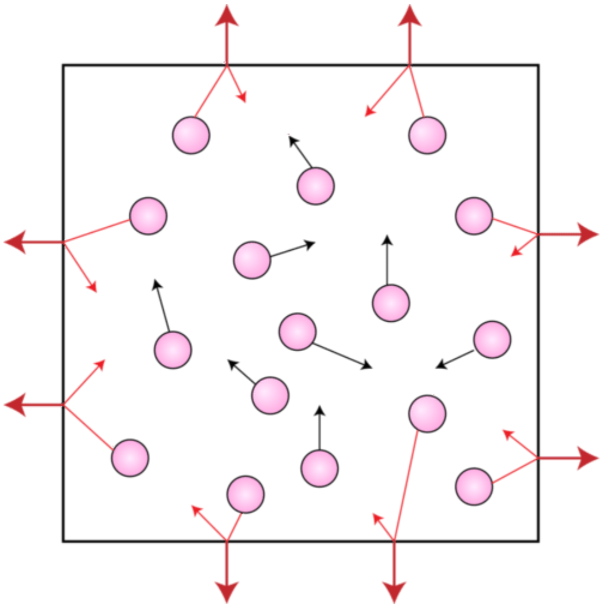


Figure 14.1.2: Gas pressure results from collisions with the surface of its container.

Measuring Pressure

Atmospheric pressure *is the pressure exerted by the gas particles in Earth's atmosphere as those particles collide with objects*. A **barometer** *is an instrument used to measure atmospheric pressure*. A traditional mercury barometer consists of an evacuated tube immersed in a container of mercury. Air molecules from the atmosphere push down on the outer surface of the mercury, but, because the inside of the tube is a vacuum, there is no corresponding downward push on the mercury in the tube. As a result, the mercury rises inside the tube. The height to which the mercury rises is dependent on the external air pressure.

At sea level, a mercury column will rise a distance of 760 mm. This atmospheric pressure is reported as 760 mm Hg (millimeters of mercury). At higher altitudes, the atmospheric pressure is lower, so the column of mercury will not rise as high. For example, on the summit of Mt. Everest (at an elevation of 8848 m), the air pressure is 253 mm Hg. Atmospheric pressure is also slightly dependent on weather conditions.

A more convenient barometer, called an aneroid barometer, measures pressure by the expansion and contraction of a small spring within an evacuated metal capsule.

Units of Gas Pressure

A barometers measures gas pressure by the height of the column of mercury. One unit of gas pressure is the millimeter of mercury (mm Hg). An equivalent unit to the mm Hg is called the torr, in honor of the inventor of the barometer, Evangelista Torricelli. The **pascal** (Pa) *is the standard unit of pressure*. A pascal is a very small amount of pressure, so a more useful unit for everyday gas pressures is the kilopascal (kPa). A kilopascal is equal to 1000 pascals. Another commonly used unit of pressure is the atmosphere (atm). Standard atmospheric pressure is called $1 \mathrm{~atm}$ of pressure and is equal to $760 \mathrm{~mm} \mathrm{Hg}$ and $101.3 \mathrm{kPa}$ The relationships between the most common units of pressure are shown below.

$$1 \mathrm{~atm}=760 \mathrm{~mm} \mathrm{Hg}=760 \text { torr }=101.3 \mathrm{kPa} \tag{14.1.2}$$

✓ Example 14.1.1

The atmospheric pressure in a mountainous location is measured to be $613 \mathrm{~mm} \mathrm{Hg}$. What is this pressure in atm and in kPa?

Solution

Step 1: List the known quantities and plan the problem.

Known

- Given: $613 \mathrm{~mm} \mathrm{Hg}$
- $1 \mathrm{~atm}=760 \mathrm{~mm} \mathrm{Hg}$
- $101.3 \mathrm{kPa}=760 \mathrm{~mm} \mathrm{Hg}$

Unknown

- Pressure $=? \mathrm{~atm}$
- Pressure $=? \mathrm{kPa}$

Use conversion factors from the equivalent pressure units to convert from $\mathrm{mm} \mathrm{Hg}$ to atm and from $\mathrm{mm} \mathrm{Hg}$ to kPa.

Step 2: Solve.

$$613 \mathrm{~mm} \mathrm{Hg} \times \frac{1 \mathrm{~atm}}{760 \mathrm{~mm} \mathrm{Hg}}=0.807 \mathrm{~atm}$$

$$613 \mathrm{~mm} \mathrm{Hg} \times \frac{101.3 \mathrm{kPa}}{760 \mathrm{~mm} \mathrm{Hg}}=81.7 \mathrm{kPa}$$

Step 3: Think about your result.

The air pressure is about 80% of the standard atmospheric pressure at sea level. The standard pressure of $760 \mathrm{~mm} \mathrm{Hg}$ can be considered to have three significant figures.

Kinetic Energy and Temperature

As stated in the kinetic-molecular theory, the temperature of a substance is related to the average kinetic energy of the particles of that substance. When a substance is heated, some of the absorbed energy is stored within the particles, while some of the energy increases the speeds at which the particles are moving. This is observed as an increase in the temperature of the substance.

Average Kinetic Energy

At any given temperature, not all of the particles in a sample of matter have the same kinetic energy. Instead, the particles display a wide range of kinetic energies. Most of the particles have a kinetic energy near the middle of the range. However, some of the particles have kinetic energies a great deal lower or a great deal higher than the average (see figure below).

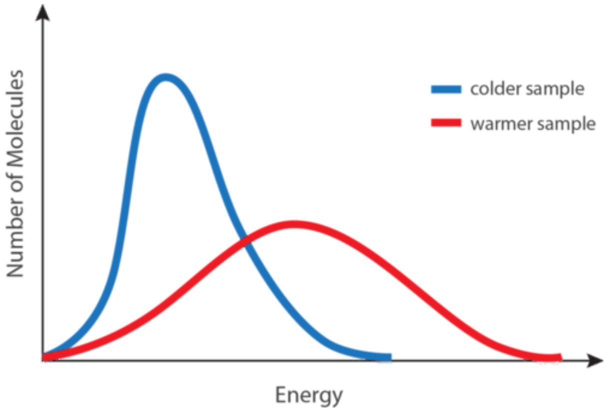


Figure 14.1.3: A distribution of molecular kinetic energies as a function of temperature. The blue curve is for a low temperature, while the red curve is for a high temperature.

The blue curve shown (see figure above) is for a sample of matter at a relatively low temperature, while the red curve is for a sample at a relatively high temperature. In both cases, most of the particles have intermediate kinetic energies, close to the average. Notice that as temperature increases, the range of kinetic energies increases and the distribution curve "flattens out".

At a given temperature, the particles of any substance have the same average kinetic energy. At room temperature, the molecules in a sample of liquid water have the same average kinetic energy as the molecules in a sample of oxygen gas or the ions in a sample of sodium chloride.

Absolute Zero

As a sample of matter is continually cooled, the average kinetic energy of its particles decreases. Eventually, one would expect the particles to stop moving completely. **Absolute zero** *is the temperature at which the motion of particles theoretically ceases.* Absolute zero has never been attained in the laboratory, but temperatures on the order of $1 \times 10^{-10}\ \mathrm{K}$ have been achieved. The Kelvin temperature scale is based on this theoretical limit, so absolute zero is equal to $0\ \mathrm{K}$. The Kelvin temperature of a substance is directly proportional to the average kinetic energy of the particles of the substance. For example, the particles in a sample of hydrogen gas at $200\ \mathrm{K}$ have twice the average kinetic energy as the particles in a hydrogen sample at $100\ \mathrm{K}$.

Contributors and Attributions

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14.2: The Gas Laws

Learning Objectives

- Learn what is meant by the term *gas laws*.
- Learn and apply Boyle's law.
- Learn and apply Charles's law.

When seventeenth-century scientists began studying the physical properties of gases, they noticed some simple relationships between some of the measurable properties of the gas. Take pressure (P) and volume (V), for example. Scientists noted that for a given amount of a gas (usually expressed in units of moles [n]), if the temperature (T) of the gas was kept constant, pressure and volume were related: As one increases, the other decreases. As one decreases, the other increases. We say that pressure and volume are *inversely related*.

There is more to it, however: pressure and volume of a given amount of gas at constant temperature are *numerically* related. If you take the pressure value and multiply it by the volume value, the product is a constant for a given amount of gas at a constant temperature:

$$P \times V = \text{constant at constant } n \text{ and } T$$

If either volume or pressure changes while amount and temperature stay the same, then the other property must change so that the product of the two properties still equals that same constant. That is, if the original conditions are labeled P_1 and V_1 and the new conditions are labeled P_2 and V_2, we have

$$P_1V_1 = \text{constant} = P_2V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1V_1 = P_2V_2 \text{ at constant } n \text{ and } T$$

This equation is an example of a gas law. A **gas law** is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. This particular gas law is called **Boyle's law**, after the English scientist Robert Boyle, who first announced it in 1662. Figure 14.2.1 shows two representations of how Boyle's law works.

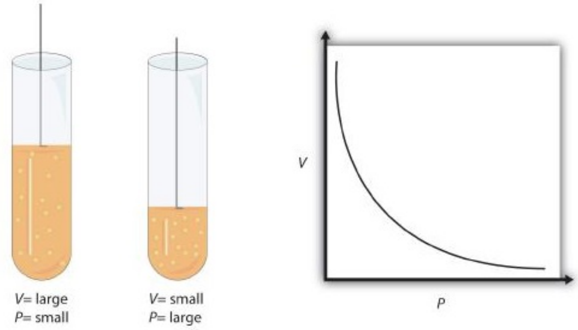

Figure 14.2.1: Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

Boyle's law is an example of a second type of mathematical problem we see in chemistry—one based on a mathematical formula. Tactics for working with mathematical formulas are different from tactics for working with conversion factors. First, most of the questions you will have to answer using formulas are word-type questions, so the first step is to identify what quantities are known and assign them to variables. Second, in most formulas, some mathematical rearrangements (i.e., algebra) must be performed to solve for an unknown variable. The rule is that to find the value of the unknown variable, you must mathematically isolate the unknown variable *by itself and in the numerator* of one side of the equation. Finally, units must be consistent. For example, in Boyle's law there are two pressure variables; they must have the same unit. There are also two volume variables; they also must have the same unit. In most cases, it won't matter *what* the unit is, but the unit must be the *same* on both sides of the equation.

✓ Example 14.2.1

A sample of gas has an initial pressure of 2.44 atm and an initial volume of 4.01 L. Its pressure changes to 1.93 atm. What is the new volume if temperature and amount are kept constant?

Solution

First, determine what quantities we are given. We are given an initial pressure and an initial volume, so let these values be P_1 and V_1:

$$P_1 = 2.44 \text{ atm and } V_1 = 4.01 \text{ L}$$

We are given another quantity, final pressure of 1.93 atm, but not a final volume. This final volume is the variable we will solve for.

$$P_2 = 1.93 \text{ atm and } V_2 = ? \text{ L}$$

Substituting these values into Boyle's law, we get

$$(2.44 \text{ atm})(4.01 \text{ L}) = (1.93 \text{ atm})V_2$$

To solve for the unknown variable, we isolate it by dividing both sides of the equation by 1.93 atm—both the number *and* the unit:

$$\frac{(2.44\,atm)(4.01\,L)}{1.93\,atm} = \frac{(1.93\,atm)\,V_2}{1.93\,atm}$$

Note that, on the left side of the equation, the unit *atm* is in the numerator and the denominator of the fraction. They cancel algebraically, just as a number would. On the right side, the unit *atm* and the number 1.93 are in the numerator and the denominator, so the entire quantity cancels:

$$\frac{(2.44\ \cancel{atm})(4.01\,L)}{1.93\ \cancel{atm}} = \frac{(1.93\ \cancel{atm})\,V_2}{1.93\ \cancel{atm}}$$

What we have left is

$$\frac{(2.44)(4.01\,L)}{1.93} = V_2$$

Now we simply multiply and divide the numbers together and combine the answer with the L unit, which is a unit of volume. Doing so, we get $V_2 = 5.07\,L$

Does this answer make sense? We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's law.

? Exercise 14.2.1

If P_1 = 334 torr, V_1 = 37.8 mL, and P_2 = 102 torr, what is V_2?

Answer

124 mL

As mentioned, you can use any units for pressure or volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

✓ Example 14.2.2

A sample of gas has an initial pressure of 722 torr and an initial volume of 88.8 mL. Its volume changes to 0.663 L. What is the new pressure?

Solution

We can still use Boyle's law to answer this, but now the two volume quantities have different units. It does not matter which unit we change, as long as we perform the conversion correctly. Let us change the 0.663 L to milliliters:

$$0.663\,L \times \frac{1000\,ml}{1\,L} = 663\,ml$$

Now that both volume quantities have the same units, we can substitute into Boyle's law:

$$(722\,torr)(88.8\,ml) = P_2(663\,ml)$$

$$\frac{(722\,torr)(88.8)\,ml}{(663\,ml)} = P_2$$

The mL units cancel, and we multiply and divide the numbers to get P_2 = 96.7 torr

The volume is increasing, and the pressure is decreasing, which is as expected for Boyle's law.

? Exercise 14.2.2

If V_1 = 456 mL, P_1 = 308 torr, and P_2 = 1.55 atm, what is V_2?

Answer

119 mL

There are other measurable characteristics of a gas. One of them is temperature (T). Perhaps one can vary the temperature of a gas sample and note what effect it has on the other properties of the gas. Early scientists did just this, discovering that if the amount of a gas and its pressure are kept constant, then changing the temperature changes the volume (V). As temperature increases, volume increases; as temperature decreases, volume decreases. We say that these two characteristics are *directly related*.

A mathematical relationship between V and T should be possible except for one thought: what temperature scale should we use? We know from Chapter 2 that science uses several possible temperature scales. Experiments show that the volume of a gas is related to its absolute temperature in Kelvin, *not its temperature in degrees Celsius*. If the temperature of a gas is expressed in kelvins, then experiments show that the *ratio* of volume to temperature is a constant:

$$\frac{V}{T} = constant$$

We can modify this equation as we modified Boyle's law: the initial conditions V_1 and T_1 have a certain value, and the value must be the same when the conditions of the gas are changed to some new conditions V_2 and T_2, as long as pressure and the amount of the gas remain constant. Thus, we have another gas law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}\ at\ constant\ P\ and\ n$$

This gas law is commonly referred to as **Charles's law**, after the French scientist Jacques Charles, who performed experiments on gases in the 1780s. The tactics for using this mathematical formula are similar to those for Boyle's law. To determine an unknown quantity, use algebra to isolate the unknown variable by itself and in the numerator; the units of similar variables must be the same. But we add one more tactic: all temperatures must be expressed in the absolute temperature scale (Kelvin). As a reminder, we review the conversion between the absolute temperature scale and the Celsius temperature scale:

K = °C + 273

where K represents the temperature in kelvins, and °C represents the temperature in degrees Celsius.

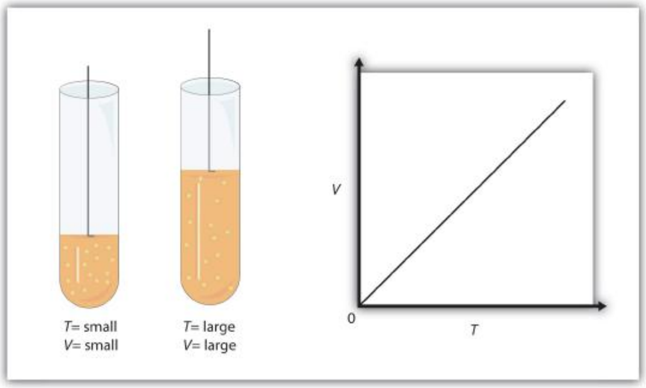

Figure 14.2.2: Charles's Law. A piston having a certain volume and temperature (left piston) will have twice the volume when its temperature is twice as much (right piston). One can also plot V versus T for a given amount of gas at a certain pressure; such a plot will look like the graph on the right.

✓ Example 14.2.3

A sample of gas has an initial volume of 34.8 mL and an initial temperature of 315 K. What is the new volume if the temperature is increased to 559 K? Assume constant pressure and amount for the gas.

Solution

First, we assign the given values to their variables. The initial volume is V_1, so V_1 = 34.8 mL, and the initial temperature is T_1, so T_1 = 315 K. The temperature is increased to 559 K, so the final temperature T_2 = 559 K. We note that the temperatures are already given in kelvins, so we do not need to convert the temperatures. Substituting into the expression for Charles's law yields

$$\frac{34.8\,ml}{315\;K}=\frac{V_2}{559\;K}$$

We solve for V_2 by algebraically isolating the V_2 variable on one side of the equation. We do this by multiplying both sides of the equation by 559 K (number and unit). When we do this, the temperature unit cancels on the left side, while the entire 559 K cancels on the right side:

$$\frac{(559\;\cancel{K})(34.8\,ml)}{315\;\cancel{K}}=\frac{V_2(\cancel{559\;K})}{\cancel{559\;K}}$$

The expression simplifies to

$$\frac{(559)(34.8\,ml)}{315}=V_2$$

By multiplying and dividing the numbers, we see that the only remaining unit is mL, so our final answer is

V_2 = 61.8 mL

Does this answer make sense? We know that as temperature increases, volume increases. Here, the temperature is increasing from 315 K to 559 K, so the volume should also increase, which it does.

? Exercise 14.2.3

If V_1 = 3.77 L and T_1 = 255 K, what is V_2 if T_2 = 123 K?

Answer

1.82 L

It is more mathematically complicated if a final temperature must be calculated because the *T* variable is in the denominator of Charles's law. There are several mathematical ways to work this, but perhaps the simplest way is to take the reciprocal of Charles's law. That is, rather than write it as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

write the equation as

$$\frac{T_1}{V_1} = \frac{T_2}{V_2}$$

It is still an equality and a correct form of Charles's law, but now the temperature variable is in the numerator, and the algebra required to predict a final temperature is simpler.

✓ Example 14.2.4

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must the temperature of the gas be for its volume to be 25.0 L?

Solution

Here, we are looking for a final temperature, so we will use the reciprocal form of Charles's law. However, the initial temperature is given in degrees Celsius, not kelvins. We must convert the initial temperature to kelvins:

−67°C + 273 = 206 K

In using the gas law, we must use T_1 = 206 K as the temperature. Substituting into the reciprocal form of Charles's law, we get

$$\frac{206\ K}{34.8\ L} = \frac{T_2}{25.0\ L}$$

Bringing the 25.0 L quantity over to the other side of the equation, we get

$$\frac{(25.0\ \cancel{L})(206\ K)}{34.8\ \cancel{L}} = T_2$$

The L units cancel, so our final answer is T_2 = 148 K

This is also equal to −125°C. As temperature decreases, volume decreases, which it does in this example.

? Exercise 14.2.4

If V_1 = 623 mL, T_1 = 255°C, and V_2 = 277 mL, what is T_2?

Answer

235 K, or −38°C

Summary

- The behavior of gases can be modeled with gas laws.
- Boyle's law relates a gas's pressure and volume at constant temperature and amount.
- Charles's law relates a gas's volume and temperature at constant pressure and amount.
- In gas laws, temperatures must always be expressed in kelvins.

14.2.1: Other Gas Relationships

Learning Objectives

- Review other simple gas laws.
- Learn and apply the combined gas law.

You may notice in Boyle's law and Charles's law that we actually refer to four physical properties of a gas: pressure (*P*), volume (*V*), temperature (*T*), and amount (in moles—*n*). We do this because these are the only four independent physical properties of a gas. There are other physical properties, but they are all related to one (or more) of these four properties.

Boyle's law is written in terms of two of these properties, with the other two being held constant. Charles's law is written in terms of two different properties, with the other two being held constant. It may not be surprising to learn that there are other gas laws that relate other pairs of properties—as long as the other two are held constant. In this section, we will mention a few.

Gay-Lussac's law relates pressure with absolute temperature. In terms of two sets of data, Gay-Lussac's law is

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

at constant V and n.

Note that it has a structure very similar to that of Charles's law, only with different variables—pressure instead of volume. **Avogadro's law** introduces the last variable for amount. The original statement of Avogadro's law states that equal volumes of different gases at the same temperature and pressure contain the same number of particles of gas. Because the number of particles is related to the number of moles (1 mol = 6.022×10^{23} particles), Avogadro's law essentially states that equal volumes of different gases, at the same temperature and pressure, contain the same *amount* (moles, particles) of gas. Put mathematically into a gas law, Avogadro's law is

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

at constant V and T.

(First announced in 1811, it was Avogadro's proposal that volume is related to the number of particles that eventually led to naming the number of things in a mole as Avogadro's number.) Avogadro's law is useful because for the first time we are seeing amount, in terms of the number of moles, as a variable in a gas law.

Example 14.2.1.1

A 2.45 L volume of gas contains 4.5×10^{21} gas particles. How many gas particles are there in 3.87 L if the gas is at constant pressure and temperature?

Solution

We can set up Avogadro's law as follows:

$$\frac{2.45\ L}{4.5 \times 10^{21}\ \text{particles}} = \frac{3.87\ L}{n_2}$$

We algebraically rearrange to solve for n_2:

$$n_2 = \frac{(3.87\ \cancel{L})(4.5 \times 10^{21}\ \text{particles})}{2.45\ \cancel{L}}$$

The L units cancel, so we solve for n_2:

$$n_2 = 7.1 \times 10^{21}\ \text{particles}$$

? Exercise 14.2.1.1

A 12.8 L volume of gas contains 3.00 × 10^{20} gas particles. At constant temperature and pressure, what volume does 8.22 × 10^{18} gas particles fill?

Answer

0.351 L

The variable *n* in Avogadro's law can also stand for the number of moles of gas, in addition to number of particles.

One thing we notice about all gas laws, collectively, is that volume and pressure are always in the numerator, and temperature is always in the denominator. This suggests that we can propose a gas law that combines pressure, volume, and temperature. This gas law is known as the **combined gas law**, and its mathematical form is

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}\ at\ constant\ n$$

This allows us to follow changes in all three major properties of a gas. Again, the usual warnings apply about how to solve for an unknown algebraically (isolate it on one side of the equation in the numerator), units (they must be the same for the two similar variables of each type), and units of temperature must be in kelvins.

✓ Example 14.2.1.2

A sample of gas at an initial volume of 8.33 L, an initial pressure of 1.82 atm, and an initial temperature of 286 K simultaneously changes its temperature to 355 K and its volume to 5.72 L. What is the final pressure of the gas?

Solution

We can use the combined gas law directly; all the units are consistent with each other, and the temperatures are given in Kelvin. Substituting,

$$\frac{(1.82\,atm)(8.33\,L)}{286\,K}=\frac{P_2(5.72\,L)}{355\,K}$$

We rearrange this to isolate the P_2 variable all by itself. When we do so, certain units cancel:

$$\frac{(1.82\,atm)(8.33\,\cancel{L})(355\,\cancel{K})}{(286\,\cancel{K})(5.72\,\cancel{L})}=P_2$$

Multiplying and dividing all the numbers, we get

$$P_2=3.29\,atm$$

Ultimately, the pressure increased, which would have been difficult to predict because two properties of the gas were changing.

? Exercise 14.2.1.2

If P_1 = 662 torr, V_1 = 46.7 mL, T_1 = 266 K, P_2 = 409 torr, and T_2 = 371 K, what is V_2?

Answer

105 mL

As with other gas laws, if you need to determine the value of a variable in the denominator of the combined gas law, you can either cross-multiply all the terms, or just take the reciprocal of the combined gas law. Remember, the variable you are solving for must be in the numerator and all by itself on one side of the equation.

Summary

- There are gas laws that relate any two physical properties of a gas.
- The combined gas law relates pressure, volume, and temperature of a gas.

14.3: The Ideal Gas Law

Learning Objective

- To use the ideal gas law to describe the behavior of a gas.

Motivating the Ideal Gas Law

In a gas, molecules freely move, filling any volume that they occupy. The kinetic energy of the molecules greatly exceeds any potential energy of attraction or repulsion between molecules and the size of the molecules are miniscule compared to the average space between them. Contrast this with solids, where the molecules are held in place by the attractive forces and the comparatively small kinetic energy only results in the molecules jiggling in place when thermally excited. Again, in a solid, the molecules are packed so closely together that the volume of the solid is essentially that of the sum of the molecular volumes of all of the molecules in it. Liquids represent a situation where molecular attraction and kinetic energy are balanced and the spacing between molecules is higher than in solids but much less than in gases.

At high temperatures and low pressures, where the kinetic energy and the spacing between molecules are both large, one may neglect both the miniscule attractive forces and molecular volume. Under such conditions the properties of the gas, the pressure, P, volume, V, number of moles, n, and the temperature, T are independent of the mixture of molecules in the gas. In that limit the behavior of the gas is called ideal, and governed by the ideal gas law

No gases are truly ideal, but while no model is perfect, some are useful, and under most commonly encountered conditions, the ideal gas law is very useful indeed to describe the behavior of gases. It is also easy to predict that the conditions where the ideal gas law would have trouble describing the behavior of a gas would be low temperature (small molecular kinetic energy) and high pressure (little space between molecules). The behavior of gases under such conditions becomes increasingly like that of liquids and will be discussed in the next chapter.

The Ideal Gas Law

The ideal gas law

$$PV = nRT \tag{6.3.1}$$

relates the pressure, volume, temperature and number of moles in a gas to each other. R is a constant called the gas constant. The ideal gas law is what is called an equation of state because it is a complete description of the gas's thermodynamic state. No other information is needed to calculate any other thermodynamic variable, and, since the equation relates four variables, a knowledge of any three of them is sufficient.

Pressure, volume and number of moles, the latter sometime called extent, share an important property, they can never be negative. What would a negative volume be, or an absolute negative pressure or extent? The concepts do not even exist. This means that temperature in the ideal gas law is similarly limited. **It can never be negative.**

We can determine what zero temperature on the ideal gas scale is by holding the number of moles and the pressure constant and extrapolate the temperature measured in Celcius to what its value would be at zero volume

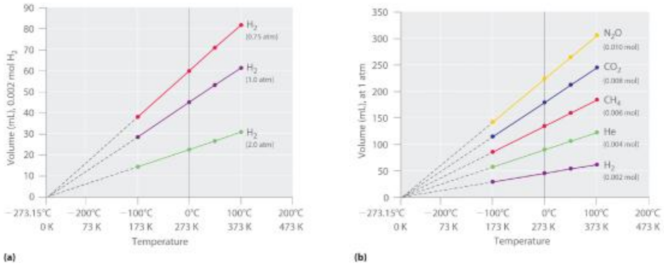

Figure 6.3.1 *The Relationship between Volume and Temperature (a) In these plots of volume versus temperature for equal-sized samples of* H_2 *at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data to V = 0. The temperature scale is given in both degrees Celsius and Kelvin. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at V = 0 (−273.15°C = 0*

K). (b) In these plots of volume versus temperature for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of V = 0 at −273.15°C, regardless of the identity or the amount of the gas.

The extrapolated temperature corresponding to zero volume at constant pressure and amount is -273.15 °C, which is called absolute zero because no lower temperature is possible (unless, of course you can come up with a negative volumes, but you cannot). For convenience we set the degrees on the Kelvin scale to the size of the degree on the Celcius scale. In other words

$$1\ K = 1^{o}C \tag{6.3.2}$$

Note the Pattern

Before we can use the ideal gas law, however, we need to know the value of the gas constant *R*. Its form depends on the units used for the other quantities in the expression. If *V* is expressed in liters (L), *P* in atmospheres (atm), *T* in kelvins (K), and *n* in moles (mol), then

$$R = 0.08206\ L \cdot atm/\left(K \cdot \cdot mol\right) \tag{6.3.3}$$

Because the product *PV* has the units of energy, *R* can also have units of J/(K·mol) or cal/(K·mol):

$$R = 8.3145\ J/\left(K \cdot mol\right) = 1.9872 cal/\left(K \cdot mol\right) \tag{6.3.4}$$

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and 1 atm pressure, referred to as standard temperature and pressure (STP) The conditions 0°C (273.15 K) and 1 atm pressure for a gas.

We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the ideal gas law given in Equation 6.3.1:

$$V = \frac{nRT}{P} = \frac{\left(1.000\ \cancel{mol}\left(0.082057\ L \cdot\ \cancel{atm}/\ \cancel{K} \cdot\ \cancel{mol}\right)\right)\left(273.15\ \ \cancel{K}\right)}{1.000\ \ \cancel{atm}} = 22.31\ L \tag{6.3.5}$$

Thus the volume of 1 mol of an ideal gas at 0°C and 1 atm pressure is 22.41 L, approximately equivalent to the volume of three basketballs. The quantity 22.41 L is called the standard molar volumeThe volume of 1 mol of an ideal gas at STP (0°C and 1 atm pressure), which is 22.41 L. of an ideal gas. The molar volumes of several real gases at STP are given in Table 6.3.1, which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at STP.

Table 6.3.1 *Molar Volumes of Selected Gases at Standard Temperature (0°C) and Pressure (1 atm)*

Gas	Molar Volume (L)
He	22.434
Ar	22.397
H_2	22.433
N_2	22.402
O_2	22.397
CO_2	22.260
NH_3	22.079

Applying the Ideal Gas Law

The ideal gas law allows us to calculate the value of the fourth variable for a gaseous sample if we know the values of any three of the four variables (*P*, *V*, *T*, and *n*). It also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (*P*, *V*, *T*, and *n*) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same equation—the ideal gas law—and then determine which quantities are given and which need to be calculated. Let’s begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

Example 6.3.1

The balloon that Charles used for his flight in 1783 was destroyed, but we can estimate that its volume was 31,150 L (1100 ft^3), given the dimensions recorded at the time. If the temperature at ground level was 86°F (30°C) and the atmospheric pressure was 745 mmHg, how many moles of hydrogen gas were needed to fill the balloon?

Given: volume, temperature, and pressure

Asked for: amount of gas

Strategy:

A Solve the ideal gas law for the unknown quantity, in this case *n*.

B Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

Solution:

A We are given values for *P*, *T*, and *V* and asked to calculate *n*. If we solve the ideal gas law (Equation 6.3.1) for *n*, we obtain

$$n = \frac{PV}{RT}$$

B *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.082057 (L·atm)/(K·mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$745\ \ \text{T}\cancel{\text{orr}} \times \frac{1\ \text{atm}}{760\ \ \text{T}\cancel{\text{orr}}} = 0.980\ \text{atm} \tag{14.3.1}$$

$$T = 273 + 30 = 303\text{K} \tag{14.3.2}$$

Substituting these values into the expression we derived for *n*, we obtain

$$n = \frac{PV}{RT} = \frac{0.980\ \ \text{at}\cancel{\text{m}} \times 31150\ \ \cancel{\text{L}}}{0.08206 \dfrac{\text{at}\cancel{\text{m}} \cdot\ \cancel{\text{L}}}{\text{mol} \cdot\ \cancel{\text{K}}} \times 303\ \ \cancel{\text{K}}} = 1.23 \times 10^3\ \text{mol} \tag{14.3.3}$$

Exercise

Suppose that an “empty” aerosol spray-paint can has a volume of 0.406 L and contains 0.025 mol of a propellant gas such as CO_2. What is the pressure of the gas at 25°C?

Answer: 1.5 atm

In Example 5, we were given three of the four parameters needed to describe a gas under a particular set of conditions, and we were asked to calculate the fourth. We can also use the ideal gas law to calculate the effect of *changes* in any of the specified conditions on any of the other parameters, as shown in Example 6.

Using the Ideal Gas Law to Calculate Gas Densities and Molar Masses

The ideal gas law can also be used to calculate molar masses of gases from experimentally measured gas densities. To see how this is possible, we first rearrange the ideal gas law to obtain

$$\frac{n}{V} = \frac{P}{RT} \tag{6.3.6}$$

The left side has the units of moles per unit volume (mol/L). The number of moles of a substance equals its mass (*m*, in grams) divided by its molar mass (*M*, in grams per mole):

$$n = \frac{m}{M} \tag{6.3.7}$$

Substituting this expression for *n* into Equation 6.3.6 gives

$$\frac{m}{MV}=\frac{P}{RT} \tag{6.3.8}$$

Because *m*/*V* is the density *d* of a substance, we can replace *m*/*V* by *d* and rearrange to give

$$d=\frac{m}{V}=\frac{MP}{RT} \tag{6.3.9}$$

The distance between particles in gases is large compared to the size of the particles, so their densities are much lower than the densities of liquids and solids. Consequently, gas density is usually measured in grams per liter (g/L) rather than grams per milliliter (g/mL).

Example 6.3.2

Calculate the density of butane at 25°C and a pressure of 750 mmHg.

Given: compound, temperature, and pressure

Asked for: density

Strategy:

A Calculate the molar mass of butane and convert all quantities to appropriate units for the value of the gas constant.

B Substitute these values into Equation 6.3.9 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$(4)(12.011)+(10)(1.0079)=58.123\ g/mol$$

Using 0.082057 (L·atm)/(K·mol) for *R* means that we need to convert the temperature from degrees Celsius to kelvins (*T* = 25 + 273 = 298 K) and the pressure from millimeters of mercury to atmospheres:

$$P=750\text{ mmHg}\times\frac{1\text{ atm}}{760\text{ Torr}}=0.987\text{ atm} \tag{14.3.4}$$

B Substituting these values into Equation 6.3.9 gives

$$d=\frac{58.123\text{ g/mol}\times 0.987\text{ atm}}{0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\times 298\text{ K}}=2.35\text{ g/L} \tag{14.3.5}$$

Exercise

Radon (Rn) is a radioactive gas formed by the decay of naturally occurring uranium in rocks such as granite. It tends to collect in the basements of houses and poses a significant health risk if present in indoor air. Many states now require that houses be tested for radon before they are sold. Calculate the density of radon at 1.00 atm pressure and 20°C and compare it with the density of nitrogen gas, which constitutes 80% of the atmosphere, under the same conditions to see why radon is found in basements rather than in attics.

Answer: radon, 9.23 g/L; N_2, 1.17 g/L

A common use of Equation 6.3.9 is to determine the molar mass of an unknown gas by measuring its density at a known temperature and pressure. This method is particularly useful in identifying a gas that has been produced in a reaction, and it is not difficult to carry out. A flask or glass bulb of known volume is carefully dried, evacuated, sealed, and weighed empty. It is then filled with a sample of a gas at a known temperature and pressure and re-weighed. The difference in mass between the two readings is the mass of the gas. The volume of the flask is usually determined by weighing the flask when empty and when filled with a liquid of known density such as water. The use of density measurements to calculate molar masses is illustrated in Example 10.

Example 6.3.3

The reaction of a copper penny with nitric acid results in the formation of a red-brown gaseous compound containing nitrogen and oxygen. A sample of the gas at a pressure of 727 mmHg and a temperature of 18°C weighs 0.289 g in a flask with a volume of 157.0 mL. Calculate the molar mass of the gas and suggest a reasonable chemical formula for the compound.

Given: pressure, temperature, mass, and volume

Asked for: molar mass and chemical formula

Strategy:

A Solve Equation 6.3.9 for the molar mass of the gas and then calculate the density of the gas from the information given.

B Convert all known quantities to the appropriate units for the gas constant being used. Substitute the known values into your equation and solve for the molar mass.

C Propose a reasonable empirical formula using the atomic masses of nitrogen and oxygen and the calculated molar mass of the gas.

Solution:

A Solving Equation 6.3.9 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P} \tag{14.3.6}$$

Density is the mass of the gas divided by its volume:

$$d = \frac{m}{V} = \frac{0.289\mathrm{g}}{0.17\mathrm{L}} = 1.84\mathrm{g/L} \tag{14.3.7}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K \tag{14.3.8}$$

$$P = 727\mathrm{Torr} \times \frac{1\mathrm{atm}}{760\mathrm{Torr}} = 0.957\mathrm{atm} \tag{14.3.9}$$

The molar mass of the unknown gas is thus

$$d = \frac{1.84\ \mathrm{g/L} \times 0.08206 \dfrac{\mathrm{L \cdot atm}}{\mathrm{K \cdot mol}} \times 291\ \mathrm{K}}{0.957\ \mathrm{atm}} = 45.9\mathrm{g/mol} \tag{14.3.10}$$

C The atomic masses of N and O are approximately 14 and 16, respectively, so we can construct a list showing the masses of possible combinations:

$$M(\mathrm{NO}) = 14 + 16 = 30\ \mathrm{g/mol} \tag{14.3.11}$$

$$M(\mathrm{N_2O}) = (2)(14) + 16 = 44\ \mathrm{g/mol} \tag{14.3.12}$$

$$M(\mathrm{NO_2}) = 14 + (2)(16) = 46\ \mathrm{g/mol} \tag{14.3.13}$$

The most likely choice is NO_2 which is in agreement with the data. The red-brown color of smog also results from the presence of NO_2 gas.

Exercise

You are in charge of interpreting the data from an unmanned space probe that has just landed on Venus and sent back a report on its atmosphere. The data are as follows: pressure, 90 atm; temperature, 557°C; density, 58 g/L. The major constituent of the atmosphere (>95%) is carbon. Calculate the molar mass of the major gas present and identify it.

Answer: 44 g/mol; CO_2

Summary

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the **ideal gas law**, *PV* = *nRT*. The proportionality constant, *R*, is called the **gas constant** and has the value 0.08206 (L·atm)/(K·mol), 8.3145 J/(K·mol), or 1.9872 cal/(K·mol), depending on the units used. The ideal gas law describes the behavior of an **ideal gas**, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. **Standard temperature and pressure (STP)** is 0°C and 1 atm. The volume of 1 mol of an ideal gas at STP is 22.41 L, the **standard molar volume**. All of the empirical gas relationships are special cases of the ideal gas law in which two of the four parameters are held constant. The ideal gas law allows us to calculate the value of the fourth quantity (P, V, T, or n) needed to describe a gaseous sample when the others are known and also predict the value of these quantities following a change in conditions if the original conditions (values of P, V, T, and n) are known. The ideal gas law can also be used to calculate the density of a gas if its molar mass is known or, conversely, the molar mass of an unknown gas sample if its density is measured.

Key Takeaway

- The ideal gas law is derived from empirical relationships among the pressure, the volume, the temperature, and the number of moles of a gas; it can be used to calculate any of the four properties if the other three are known.

Key Equations

Ideal gas law

Equation 6.3.1: $PV = nRT$

where $R = 0.08206 \dfrac{\mathrm{L \cdot atm}}{\mathrm{K \cdot mol}} = 8.3145 \dfrac{\mathrm{J}}{\mathrm{K \cdot mol}}$

Density of a gas

Equation 6.3.9: $d = \dfrac{MP}{RT}$

Conceptual Problems

1. For an ideal gas, is volume directly proportional or inversely proportional to temperature? What is the volume of an ideal gas at absolute zero?
2. What is meant by STP? If a gas is at STP, what further information is required to completely describe the state of the gas?
3. Given the following initial and final values, what additional information is needed to solve the problem using the ideal gas law?

Given	Solve for
V_1, T_1, T_2, n_1	n_2
P_1, P_2, T_2, n_2	n_1
T_1, T_2	V_2
P_1, n_1	P_2

4. Given the following information and using the ideal gas law, what equation would you use to solve the problem?

Given	Solve for
P_1, P_2, T_1	T_2
V_1, n_1, n_2	V_2
T_1, T_2, V_1, V_2, n_2	n_1

5. Using the ideal gas law as a starting point, derive the relationship between the density of a gas and its molar mass. Which would you expect to be denser—nitrogen or oxygen? Why does radon gas accumulate in basements and mine shafts?
6. Use the ideal gas law to derive an equation that relates the remaining variables for a sample of an ideal gas if the following are held constant.
   1. amount and volume
   2. pressure and amount
   3. temperature and volume

    4. temperature and amount
    5. pressure and temperature
7. Tennis balls that are made for Denver, Colorado, feel soft and do not bounce well at lower altitudes. Use the ideal gas law to explain this observation. Will a tennis ball designed to be used at sea level be harder or softer and bounce better or worse at higher altitudes?

Answer

1.
2.
3.
4.
5.
6.
    1. P/T = constant
    2. V/T = constant (Charles’ law)
    3. P/n = constant
    4. PV = constant (Boyle’s law)
    5. V/n = constant (Avogadro’s law)
7.

Numerical Problems

1. Calculate the number of moles in each sample at STP.
    1. 1580 mL of NO_2
    2. 847 cm^3 of HCl
    3. 4.792 L of H_2
    4. a 15.0 cm × 6.7 cm × 7.5 cm container of ethane
2. Calculate the number of moles in each sample at STP.
    1. 2200 cm^3 of CO_2
    2. 1200 cm^3 of N_2
    3. 3800 mL of SO_2
    4. 13.75 L of NH_3
3. Calculate the mass of each sample at STP.
    1. 36 mL of HI
    2. 550 L of H_2S
    3. 1380 cm^3 of CH_4
4. Calculate the mass of each sample at STP.
    1. 3.2 L of N_2O
    2. 65 cm^3 of Cl_2
    3. 3600 mL of HBr
5. Calculate the volume in liters of each sample at STP.
    1. 1.68 g of Kr
    2. 2.97 kg of propane (C_3H_8)
    3. 0.643 mg of $(CH_3)_2O$
6. Calculate the volume in liters of each sample at STP.
    1. 3.2 g of Xe
    2. 465 mg of CS_2
    3. 5.34 kg of acetylene (C_2H_2)
7. Calculate the volume of each gas at STP.

   1. 1.7 L at 28°C and 96.4 kPa
   2. 38.0 mL at 17°C and 103.4 torr
   3. 650 mL at −15°C and 723 mmHg

8. Calculate the volume of each gas at STP.
   1. 2.30 L at 23°C and 740 mmHg
   2. 320 mL at 13°C and 97.2 kPa
   3. 100.5 mL at 35°C and 1.4 atm

9. One method for preparing hydrogen gas is to pass HCl gas over hot aluminum; the other product of the reaction is $AlCl_3$. If you wanted to use this reaction to fill a balloon with a volume of 28,500 L at sea level and a temperature of 78°F, what mass of aluminum would you need? What volume of HCl at STP would you need?

10. An 3.50 g sample of acetylene is burned in excess oxygen according to the following reaction:

    $2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$

    At STP, what volume of $CO_2(g)$ is produced?

11. Calculate the density of ethylene (C_2H_4) under each set of conditions.
    1. 7.8 g at 0.89 atm and 26°C
    2. 6.3 mol at 102.6 kPa and 38°C
    3. 9.8 g at 3.1 atm and −45°C

12. Determine the density of O_2 under each set of conditions.
    1. 42 g at 1.1 atm and 25°C
    2. 0.87 mol at 820 mmHg and 45°C
    3. 16.7 g at 2.4 atm and 67°C

13. At 140°C, the pressure of a diatomic gas in a 3.0 L flask is 635 kPa. The mass of the gas is 88.7 g. What is the most likely identity of the gas?

14. What volume must a balloon have to hold 6.20 kg of H_2 for an ascent from sea level to an elevation of 20,320 ft, where the temperature is −37°C and the pressure is 369 mmHg?

15. What must be the volume of a balloon that can hold 313.0 g of helium gas and ascend from sea level to an elevation of 1.5 km, where the temperature is 10.0°C and the pressure is 635.4 mmHg?

16. The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at 20°C and 0.997 atm, how many moles of air does a person inhale each day? If the density of air is 1.19 kg/m^3, what is the average molecular mass of air?

Answers

1.
   1. 7.05×10^{-2} mol
   2. 3.78×10^{-2} mol
   3. 0.2138 mol
   4. 3.4×10^{-2} mol
2.
3.
   1. 0.21 g HI;
   2. 840 g H_2S;
   3. 0.988 g CH_4
4.
5.
   1. 0.449 L Kr
   2. 1510 L C_3H_8
   3. 3.13×10^{-4} L $(CH_3)_2O$
6.
7.
   1. 1.5 L

    2. 4.87 mL
    3. 650 mL
8.
9. 281 mmHg
10.
11.
12. 1. 1.0 g/L
    2. 1.1 g/L
    3. 4.6 g/L
13.
14.
15.
16. 2174
17.

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14.3.1: Real vs. Ideal Gases

Now, we need to expand on the qualifications with which we begin this chapter. We imagine that the results of a large number of experiments are available for our analysis. Our characterization of these results has been that all gases obey the same equations—Boyle's law, Charles' law, and the ideal gas equation—and do so exactly. This is an oversimplification. In fact they are always approximations. They are approximately true for all gases under all "reasonable" conditions, but they are not exactly true for any real gas under any condition. It is useful to introduce the idea of hypothetical gases that obey the classical gas equations exactly. In the previous section, we call the combination of Boyle's law and Charles' law the ideal gas equation. We call the hypothetical substances that obey this equation ***ideal gases***. Sometimes we refer to the classical gas laws collectively as the ***ideal gas laws***.

At very high gas densities, the classical gas laws can be very poor approximations. As we have noted, they are better approximations the lower the density of the gas. In fact, experiments show that the pressure—volume—temperature behavior of any real gasreal gas becomes arbitrarily close to that predicted by the ideal gas equation in the limit as the pressure goes to zero. This is an important observation that we use extensively.

At any given pressure and temperature, the ideal gas laws are better approximations for a compound that has a lower boiling point than they are for a compound with a higher boiling point. Another way of saying this is that they are better approximations for molecules that are weakly attracted to one another than they are for molecules that are strongly attracted to one another.

Forces between molecules cause them to both attract and repel one another. The net effect depends on the distance between them. If we assume that there are no intermolecular forcesintermolecular forces acting between gas molecules, we can develop exact theories for the behavior of macroscopic amounts of the gas. In particular, we can show that such substances obey the ideal gas equation. (We shall see that a complete absence of repulsive forces implies that the molecules behave as point masses.) Evidently, the difference between the behavior of a real gas and the behavior it would exhibit if it were an ideal gas is just a measure of the effects of intermolecular forces.

The ideal gas equation is not the only equation that gives a useful representation for the interrelation of gas pressure–volume–temperature data. There are many such ***equations of state***. They are all approximations, but each can be a particularly useful approximation in particular circumstances. We discuss ***van der Waal's equation*** equation and the ***virial equations*** later in this chapter. Nevertheless, we use the ideal gas equation extensively.

We will see that much of chemical thermodynamics is based on the behavior of ideal gases. Since there are no ideal gases, this may seem odd, at best. If there are no ideal gases, why do we waste time talking about them? After all, we don't want to slog through tedious, long-winded, pointless digressions. We want to understand how real stuff behaves! Unfortunately, this is more difficult. The charm of ideal gases is that we can understand their behavior; the ideal gas equation expresses this understanding in a mathematical model. Real gases are another story. We can reasonably say that we can best understand the behavior of a real gas by understanding how and why it is different from the behavior of a (hypothetical) ideal gas that has the same molecular structure.

14.4: Dalton's Law of Partial Pressure

Learning Objectives

- To determine the contribution of each component gas to the total pressure of a mixture of gases

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{14.4.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let’s suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressure, the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, ***the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases***. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as *Dalton’s law of partial pressures*. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots \tag{14.4.2}$$

$$= \sum_{i=1}^{n} P_i \tag{14.4.3}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

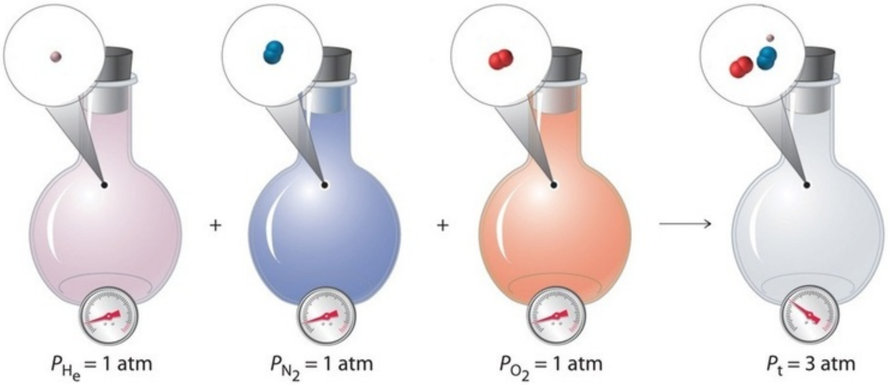


Figure 14.4.1: Dalton’s Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B \tag{14.4.4}$$

$$= n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) \tag{14.4.5}$$

$$= (n_A + n_B)\left(\frac{RT}{V}\right) \tag{14.4.6}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{14.4.7}$$

$$= \sum_{i=1}^{n} P_i\left(\frac{RT}{V}\right) \tag{14.4.8}$$

Equation 14.4.8 restates Equation 14.4.6 in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on only the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For Equation 14.4.8 to be valid, the identity of the particles present cannot have an effect. Thus an ideal gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 14.4.1.

✓ Example 14.4.1: The Bends

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called "the bends." At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of components, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A. Calculate the number of moles of He and O_2 present.
B. Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of He is

$$n_{\text{He}} = \frac{326.4\text{ g}}{4.003\text{ g/mol}} = 81.54\text{ mol}$$

The number of moles of O_2 is

$$n_{\text{O}_2} = \frac{51.2\text{ g}}{32.00\text{ g/mol}} = 1.60\text{ mol}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}}RT}{V} = \frac{81.54\text{ mol} \times 0.08206\,\dfrac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 293.15\text{ K}}{10.0\text{ L}} = 196.2\text{ atm}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{V} = \frac{1.60\text{ mol} \times 0.08206\,\dfrac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 293.15\text{ K}}{10.0\text{ L}} = 3.85\text{ atm}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85)\text{ atm} = 200.1\text{ atm}$$

Exercise 14.4.1

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer

$$P_{CH_4} = 137\ atm;\ P_{C_2H_6} = 13.4\ atm;\ P_{tot} = 151\ atm$$

Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction (χ) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_{tot}):

$$\chi_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{14.4.9}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $\chi_A = 1.0$, then the sample is pure A, not a mixture. If $\chi_A = 0$, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let's evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the ideal gas law to describe the pressures of both gas A and the mixture: $P_A = n_A RT/V$ and $P_{tot} = n_t RT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = \chi_A \tag{14.4.10}$$

Rearranging this equation gives

$$P_A = \chi_A P_{tot} \tag{14.4.11}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. By volume, Earth's atmosphere is about 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of gases such as CO_2, H_2O, and others. This means that 78% of the particles present in the atmosphere are N_2; hence the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using Equation 14.4.11, we therefore know that the partial pressure of N_2 is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of O_2 and Ar are 0.21 and 0.009 atm, respectively.

✓ Example 14.4.2: Exhaling Composition

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

the mole fractions of the gases

	Inhaled Air / mmHg	Exhaled Air / mmHg
P_{N_2}	597	568
P_{O_2}	158	116
P_{H_2O}	0.3	28
P_{CO_2}	5	48
P_{Ar}	8	8
P_{tot}	767	767

Given: pressures of gases in inhaled and exhaled air

Asked for: mole fractions of gases in exhaled air

Strategy:

Calculate the mole fraction of each gas using Equation 14.4.11.

Solution:

The mole fraction of any gas A is given by

$$\chi_A = \frac{P_A}{P_{tot}}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of CO_2 is given as:

$$\chi_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063$$

The following table gives the values of χ_A for the gases in the exhaled air.

Solutions to Example 10.6.2

Gas	Mole Fraction
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

? Exercise 14.4.2

Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.

Answer

$$P_{CO_2} = 86 \text{ atm}$$

$$P_{N_2} = 2.7 \text{ atm}$$

Summary

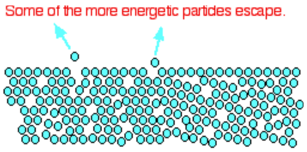
The partial pressure of each gas in a mixture is proportional to its mole fraction. The pressure exerted by each gas in a gas mixture (its **partial pressure**) is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (**Dalton's law of partial pressures**). The amount of gas present in a mixture may be described by its partial pressure or its mole fraction. The **mole fraction** of any component of a mixture is the ratio of the number of moles of that substance to the total number of moles of all substances present. In a mixture of gases, the partial pressure of each gas is the product of the total pressure and the mole fraction of that gas.

14.5: Vapor Pressure

This page looks at how the equilibrium between a liquid (or a solid) and its vapor leads to the idea of a saturated vapor pressure. It also looks at how saturated vapor pressure varies with temperature, and the relationship between saturated vapor pressure and boiling point.

Evaporation: Liquid/Vapor Equilibrium

The average energy of the particles in a liquid is governed by the temperature. The higher the temperature, the higher the average energy. But within that average, some particles have energies higher than the average, and others have energies lower than the average. Some of the more energetic particles on the surface of the liquid can be moving fast enough to escape from the attractive forces holding the liquid together. They evaporate. The diagram shows a small region of a liquid near its surface.

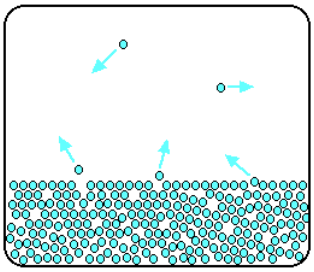


Notice that evaporation only takes place on the surface of the liquid. That's quite different from boiling which happens when there is enough energy to disrupt the attractive forces throughout the liquid. That's why, if you look at boiling water, you see bubbles of gas being formed all the way through the liquid.

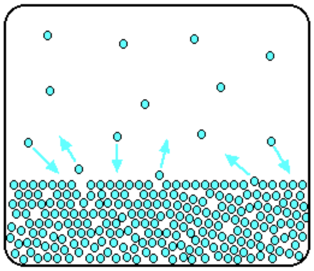
If you look at water which is just evaporating in the sun, you don't see any bubbles. Water molecules are simply breaking away from the surface layer. Eventually, the water will all evaporate in this way. The energy which is lost as the particles evaporate is replaced from the surroundings. As the molecules in the water jostle with each other, new molecules will gain enough energy to escape from the surface.

The evaporation of a liquid in a closed container

Now imagine what happens if the liquid is in a closed container. Common sense tells you that water in a sealed bottle does not seem to evaporate - or at least, it does not disappear over time. But there is constant evaporation from the surface. Particles continue to break away from the surface of the liquid - but this time they are trapped in the space above the liquid.



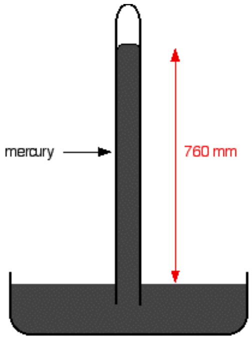
As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and be trapped there. There will rapidly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it.



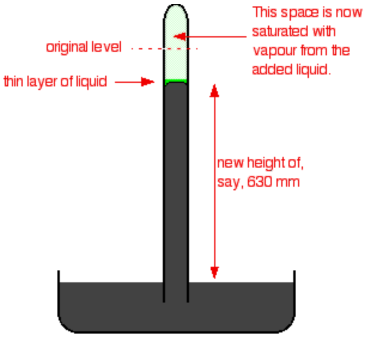
In this equilibrium, there will be a fixed number of the gaseous particles in the space above the liquid. When these particles hit the walls of the container, they exert a pressure. This pressure is called the saturated vapor pressure (also known as **saturation vapor pressure**) of the liquid.

Measuring the saturated vapor pressure

It is not difficult to show the existence of this saturated vapor pressure (and to measure it) using a simple piece of apparatus. If you have a mercury barometer tube in a trough of mercury, at 1 atmosphere pressure the column will be 760 mm tall. 1 atmosphere is sometimes quoted as 760 mmHg ("millimetres of mercury").



If you squirt a few drops of liquid into the tube, it will rise to form a thin layer floating on top of the mercury. Some of the liquid will evaporate and you will get the equilibrium we've just been talking about - provided there is still some liquid on top of the mercury. It is only an equilibrium if both liquid and vapor are present.



The saturated vapor pressure of the liquid will force the mercury level down a bit. You can measure the drop - and this gives a value for the saturated vapor pressure of the liquid at this temperature. In this case, the mercury has been forced down by a distance of 760 - 630 mm. The saturated vapor pressure of this liquid at the temperature of the experiment is 130 mmHg. You could convert this into proper SI units (pascals) if you wanted to. 760 mmHg is equivalent to 101,325 Pa.

A value of 130 mmHg is quite a high vapor pressure if we are talking about room temperature. Water's saturated vapor pressure is about 20 mmHg at this temperature. A high vapor pressure means that the liquid must be volatile - molecules escape from its surface relatively easily, and aren't very good at sticking back on again either.

That will result in larger numbers of them in the gas state once equilibrium is reached. The liquid in the example must have significantly weaker intermolecular forces than water.

The variation of saturated vapor pressure with temperature

The effect of temperature liquid/ vapor equilibrium

You can look at this in two ways. (1) There is a common sense way. If you increase the temperature, you are increasing the average energy of the particles present. That means that more of them are likely to have enough energy to escape from the surface of the liquid. That will tend to increase the saturated vapor pressure. (2) Or you can look at it in terms of Le Chatelier's Principle - which works just as well in this kind of physical situation as it does in the more familiar chemical examples.

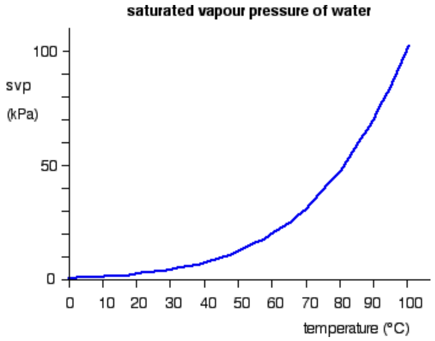
When the space above the liquid is saturated with vapor particles, you have this equilibrium occurring on the surface of the liquid:

$$\text{liquid} \rightleftharpoons \text{vapour} \qquad \Delta H \text{ is +ve}$$

The forward change (liquid to vapor) is endothermic. It needs heat to convert the liquid into the vapor. According to Le Chatelier, increasing the temperature of a system in a dynamic equilibrium favors the endothermic change. That means that increasing the temperature increases the amount of vapor present, and so increases the saturated vapor pressure.

The effect of temperature on the saturated vapor pressure of water

The graph shows how the saturated vapor pressure (svp) of water varies from 0°C to 100 °C. The pressure scale (the vertical one) is measured in kilopascals (kPa). 1 atmosphere pressure is 101.325 kPa.



Saturated vapor pressure and boiling point

A liquid boils when its saturated vapor pressure becomes equal to the external pressure on the liquid. When that happens, it enables bubbles of vapor to form throughout the liquid - those are the bubbles you see when a liquid boils.

If the external pressure is higher than the saturated vapor pressure, these bubbles are prevented from forming, and you just get evaporation at the surface of the liquid. If the liquid is in an open container and exposed to normal atmospheric pressure, the liquid boils when its saturated vapor pressure becomes equal to 1 atmosphere (or 101325 Pa or 101.325 kPa or 760 mmHg). This happens with water when the temperature reaches 100°C.

But at different pressures, water will boil at different temperatures. For example, at the top of Mount Everest the pressure is so low that water will boil at about 70°C. Whenever we just talk about "the boiling point" of a liquid, we always assume that it is being measured at exactly 1 atmosphere pressure. In practice, of course, that is rarely exactly true.

Sublimation: solid/vapor Equilibrium

Solids can also lose particles from their surface to form a vapor, except that in this case we call the effect sublimation rather than evaporation. Sublimation is the direct change from solid to vapor (or vice versa) without going through the liquid stage.

In most cases, at ordinary temperatures, the saturated vapor pressures of solids range from low to very, very, very low. The forces of attraction in many solids are too high to allow much loss of particles from the surface. However, there are some which do easily form vapors. For example, naphthalene (used in old-fashioned "moth balls" to deter clothes moths) has quite a strong smell. Molecules must be breaking away from the surface as a vapor, because otherwise you would not be able to smell it. Another fairly common example (discussed in detail on another page) is solid carbon dioxide - "dry ice". This never forms a liquid at atmospheric pressure and always converts directly from solid to vapor. That's why it is known as dry ice.

Contributors and Attributions

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14.6: Gas Stoichiometry

Learning Objectives

- Learn the ideal gas law.
- Apply the ideal gas law to any set of conditions of a gas.
- Apply the ideal gas law to molar volumes, density, and stoichiometry problems.

So far, the gas laws we have considered have all required that the gas change its conditions; then we predict a resulting change in one of its properties. Are there any gas laws that relate the physical properties of a gas at any given time? Consider a further extension of the combined gas law to include *n*. By analogy to Avogadro's law, *n* is positioned in the denominator of the fraction, opposite the volume. So,

$$\frac{PV}{nT} = constant$$

Because pressure, volume, temperature, and amount are the only four independent physical properties of a gas, the constant in the above equation is truly a constant. Indeed, because we do not need to specify the identity of a gas to apply the gas laws, this constant is the same for all gases. We define this constant with the symbol *R*, so the previous equation is written as

$$\frac{PV}{nT} = R$$

which is usually rearranged as

$$PV = nRT$$

This equation is called the **ideal gas law**. It relates the four independent properties of a gas at any time. The constant *R* is called the ideal gas law constant. Its value depends on the units used to express pressure and volume.

Table 14.6.1 - Values of the Ideal Gas Law Constant lists the numerical values of R.

Numerical Value	Units
0.08205	L·atmmol·K· $\frac{L.atm}{mol.K}$
62.36	L·torrmol·K=L·mmHgmol·K· $\frac{L.torr}{mol.K} = \frac{L.mmHg}{mol.K}$
8.314	$\frac{J}{mol.K}$

The ideal gas law is used like any other gas law, with attention paid to the unit and expression of the temperature in kelvins. However, *the ideal gas law does not require a change in the conditions of a gas sample*. The ideal gas law implies that if you know any three of the physical properties of a gas, you can calculate the fourth property.

Example 14.6.1:

A 4.22 mol sample of Ar has a pressure of 1.21 atm and a temperature of 34°C. What is its volume?

Solution

The first step is to convert temperature to kelvins:

34 + 273 = 307 K

Now we can substitute the conditions into the ideal gas law:

$$(1.21atm)(V) = (4.22\,mol)(0.08205\frac{L.\,atm}{mol.\,K})(307\,K)$$

The *atm* unit is in the numerator of both sides, so it cancels. On the right side of the equation, the *mol* and *K* units appear in the numerator and the denominator, so they cancel as well. The only unit remaining is *L*, which is the unit of volume that we are looking for. We isolate the volume variable by dividing both sides of the equation by 1.21:

$$V=\frac{(4.22)(0.08205)(307)}{1.21}L$$

Then solving for volume, we get V = 87.9 L

? Exercise 14.6.1

A 0.0997 mol sample of O_2 has a pressure of 0.692 atm and a temperature of 333 K. What is its volume?

Answer

3.94 L

✓ Example 14.6.2:

At a given temperature, 0.00332 g of Hg in the gas phase has a pressure of 0.00120 mmHg and a volume of 435 L. What is its temperature?

Solution

We are not given the number of moles of Hg directly, but we are given a mass. We can use the molar mass of Hg to convert to the number of moles.

$$0.00332\ g\,\cancel{Hg}\times\frac{1\,mol\,Hg}{200.59\ g\,\cancel{Hg}}=0.0000165\,mol=1.65\times10^{-5}mol$$

Pressure is given in units of millimeters of mercury. We can either convert this to atmospheres or use the value of the ideal gas constant that includes the mmHg unit. We will take the second option. Substituting into the ideal gas law,

$$(0.00332\,mm\,Hg)(435\,L)=(1.65\times10^{-5}mol)(62.36\frac{L.\,mmHg}{mol.\,K})T$$

The mmHg, L, and mol units cancel, leaving the K unit, the unit of temperature. Isolating T on one side, we get

$$T=\frac{(0.00332)(435)}{(1.65\times10^{-5})(62.36)}K$$

Then solving for K, we get T = 1,404 K

? Exercise 14.6.2

For a 0.00554 mol sample of H_2, P = 23.44 torr and T = 557 K. What is its volume?

Answer

8.21 L

The ideal gas law can also be used in stoichiometry problems.

✓ Example 14.6.3:

What volume of H_2 is produced at 299 K and 1.07 atm when 55.8 g of Zn metal react with excess HCl?

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Solution

Here we have a stoichiometry problem where we need to find the number of moles of H_2 produced. Then we can use the ideal gas law, with the given temperature and pressure, to determine the volume of gas produced. First, the number of moles of H_2 is calculated:

$$55.8\ g\,\cancel{Zn}\times\frac{1\ mol\,\cancel{Zn}}{65.41\ g\,\cancel{Zn}}\times\frac{1\ mol\ H_2}{1\ mol\,\cancel{Zn}}=0.853\ H_2$$

Now that we know the number of moles of gas, we can use the ideal gas law to determine the volume, given the other conditions:

$$(1.07atm)V=(0.853\,mol)(0.08205\frac{L.\,atm}{mol.\,K})(299\ K)$$

All the units cancel except for L, for volume, which means V = 19.6 L

? Exercise 14.6.3

What pressure of HCl is generated if 3.44 g of Cl_2 are reacted in 4.55 L at 455 K?

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

Answer

0.796 atm

It should be obvious by now that some physical properties of gases depend strongly on the conditions. What we need is a set of standard conditions so that properties of gases can be properly compared to each other. **Standard Temperature and Pressure (STP)** is defined as exactly 100 kPa of pressure (0.986 atm) and 273 K (0°C). For simplicity, we will use 1 atm as standard pressure. Defining STP allows us to more directly compare the properties of gases that differ from one another.

One property shared among gases is a molar volume. The **molar volume** is the volume of 1 mol of a gas. At STP, the molar volume of a gas can be easily determined by using the ideal gas law:

$$(1\,atm)V=(1\,mol)(0.08205\frac{L.\,atm}{mol.\,K})(273\,K)$$

All the units cancel except for L, the unit of volume. So V = 22.4 L

Note that we have not specified the identity of the gas; we have specified only that the pressure is 1 atm and the temperature is 273 K. This makes for a very useful approximation: *any gas at STP has a volume of 22.4 L per mole of gas*; that is, the molar volume at STP is 22.4 L/mol (Figure 14.6.1 Molar Volume). This molar volume makes a useful conversion factor in stoichiometry problems if the conditions are at STP. If the conditions are not at STP, a molar volume of 22.4 L/mol is not applicable. However, if the conditions are not at STP, the combined gas law can be used to calculate what the volume of the gas would be if at STP; then the 22.4 L/mol molar volume can be used.

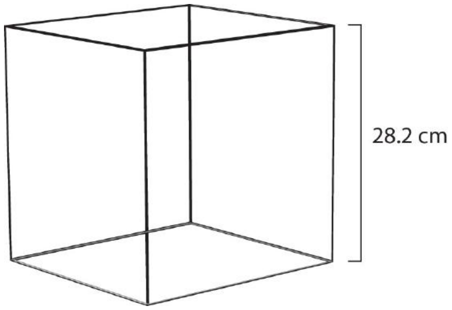


Figure 14.6.1: Molar Volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

✓ Example 14.6.4:

How many moles of Ar are present in 38.7 L at STP?

Solution

We can use the molar volume, 22.4 L/mol, as a conversion factor, but we need to reverse the fraction so that the L units cancel and mol units are introduced. It is a one-step conversion:

$$38.7\ \cancel{L} \times \frac{1\,mol}{22.4\ \cancel{L}} = 1.73\,mol$$

? Exercise 14.6.4

What volume does 4.87 mol of Kr have at STP?

Answer

109 L

✓ Example 14.6.5:

What volume of H_2 is produced at STP when 55.8 g of Zn metal react with excess HCl?

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Solution

This is a stoichiometry problem with a twist: we need to use the molar volume of a gas at STP to determine the final answer. The first part of the calculation is the same as in a previous example:

$$55.8\ g\,\cancel{Zn} \times \frac{1\ mol\,\cancel{Zn}}{65.41\ g\,\cancel{Zn}} \times \frac{1\,mol\,H_2}{1\ mol\,\cancel{Zn}} = 0.853\,H_2$$

Now we can use the molar volume, 22.4 L/mol, because the gas is at STP:

$$0.853\ mol\,\cancel{H_2} \times \frac{22.4\ L}{1\ mol\,\cancel{H_2}} = 19.1\ L\,H_2$$

Alternatively, we could have applied the molar volume as a third conversion factor in the original stoichiometry calculation.

? Exercise 14.6.5

What volume of HCl is generated if 3.44 g of Cl_2 are reacted at STP?

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Answer

2.17 L

The ideal gas law can also be used to determine the density of gases. Density, recall, is defined as the mass of a substance divided by its volume:

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

Assume that you have exactly 1 mol of a gas. If you know the identity of the gas, you can determine the molar mass of the substance. Using the ideal gas law, you can also determine the volume of that mole of gas, using whatever the temperature and pressure conditions are. Then you can calculate the density of the gas by using

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

✓ Example 14.6.6:

What is the density of N_2 at 25°C and 0.955 atm?

Solution

First, we must convert the temperature into kelvins:

25 + 273 = 298 K

If we assume exactly 1 mol of N_2, then we know its mass: 28.0 g. Using the ideal gas law, we can calculate the volume:

$$(0.955\,atm)V=(1\,mol)(0.08205\frac{L.\,atm}{mol.\,K})(298\,K)$$

All the units cancel except for L, the unit of volume. So V = 25.6 L

Knowing the molar mass and the molar volume, we can determine the density of N_2 under these conditions:

$$d=\frac{28.0\,g}{25.6\,L}=1.09\,g/L$$

? Exercise 14.6.6

What is the density of CO_2 at a pressure of 0.0079 atm and 227 K? (These are the approximate atmospheric conditions on Mars.)

Answer

0.019 g/L

Chemistry Is Everywhere: Breathing

Breathing (more properly called *respiration*) is the process by which we draw air into our lungs so that our bodies can take up oxygen from the air. Let us apply the gas laws to breathing.

Start by considering pressure. We draw air into our lungs because the diaphragm, a muscle underneath the lungs, moves down to reduce pressure in the lungs, causing external air to rush in to fill the lower-pressure volume. We expel air by the diaphragm pushing against the lungs, increasing pressure inside the lungs and forcing the high-pressure air out. What are the pressure changes involved? A quarter of an atmosphere? A tenth of an atmosphere? Actually, under normal conditions, it's only 1 or 2 torr of pressure difference that makes us breathe in and out.

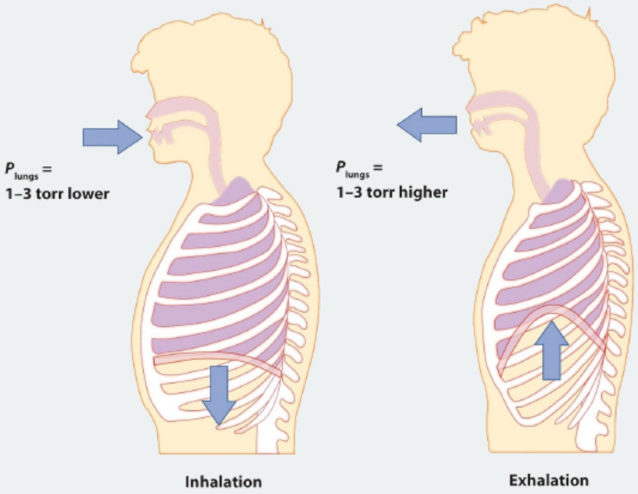


Figure 14.6.2 Breathing Mechanics. Breathing involves pressure differences between the inside of the lungs and the air outside. The pressure differences are only a few torr.

A normal breath is about 0.50 L. If room temperature is about 22°C, then the air has a temperature of about 295 K. With normal pressure being 1.0 atm, how many moles of air do we take in for every breath? The ideal gas law gives us an answer:

$$(1.0\,atm)(0.50\,L)=n(0.08205\frac{L.\,atm}{mol.\,K})(295\,K)$$

Solving for the number of moles, we get

n = 0.021 mol air

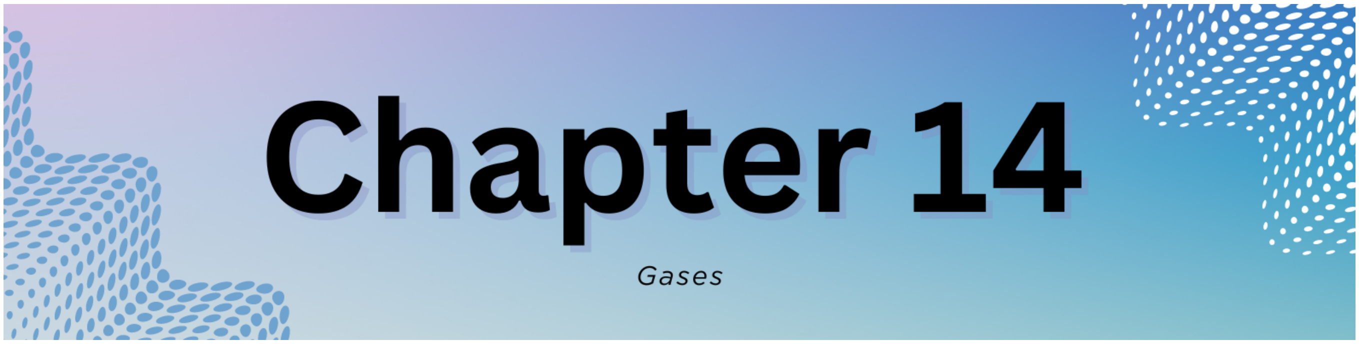
This ends up being about 0.6 g of air per breath—not much, but enough to keep us alive.

Summary

- The ideal gas law relates the four independent physical properties of a gas at any time.
- The ideal gas law can be used in stoichiometry problems whose chemical reactions involve gases.
- Standard temperature and pressure (STP) are a useful set of benchmark conditions to compare other properties of gases.
- At STP, gases have a volume of 22.4 L per mole.
- The ideal gas law can be used to determine the density of gases.

CHAPTER OVERVIEW

15: Gases and Gas Laws



15.1: Gas Pressure - a Result of Collisions

Learning Objectives

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears "pop" during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects (Figure $15.1.1$). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.

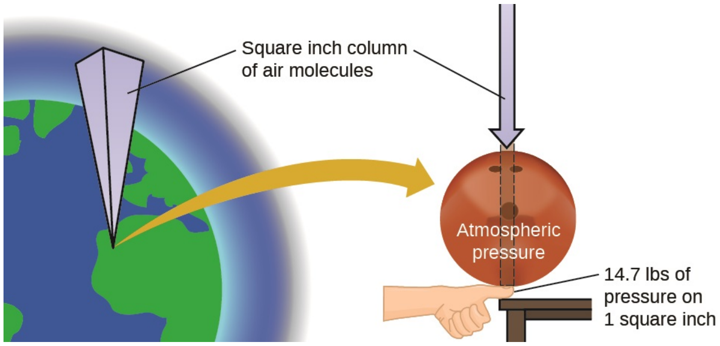


Figure **$15.1.1$** *: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.*

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car. 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.

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.

Pressure is defined as the force exerted on a given area:

$$P=\frac{F}{A} \tag{15.1.1}$$

> Since pressure is directly proportional to force and inversely proportional to area (Equation 15.1.1), pressure can be increased either by either **increasing** the amount of force or by **decreasing** the area over which it is applied. Correspondingly, pressure can be decreased by either **decreasing** the force or **increasing** the area.

Let's apply the definition of pressure (Equation 15.1.1) to determine which would be more likely to fall through thin ice in Figure 15.1.2—the elephant or the figure skater?

***Figure* 15.1.2** *: Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi).*

A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:

$$\text{pressure per elephant foot} = 14,000\frac{\text{lb}}{\text{elephant}} \times \frac{1\text{ elephant}}{4\text{ feet}} \times \frac{1\text{ foot}}{250\text{ in}^2} = 14\text{ lb/in}^2 \tag{15.1.2}$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:

$$\text{pressure per skate blade} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1\text{ skater}}{2\text{ blades}} \times \frac{1\text{ blade}}{2\text{ in}^2} = 30\text{ lb/in}^2 \tag{15.1.3}$$

Even though the elephant is more than one hundred-times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall though thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1\text{ skater}}{2\text{ feet}} \times \frac{1\text{ foot}}{30\text{ in}^2} = 2\text{ lb/in}^2 \tag{15.1.4}$$

The SI unit of pressure is the pascal (Pa), with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or bar (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—pounds per square inch (psi)—for example, in car tires. Pressure can also be measured using the unit atmosphere (atm), which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table 15.1.1 provides some information on these and a few other common units for pressure measurements

Table 15.1.1: Pressure Units

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
pascal (Pa)	1 Pa = 1 N/m^2	recommended IUPAC unit
kilopascal (kPa)	1 kPa = 1000 Pa	
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi	
atmosphere (atm)	1 atm = 101,325 Pa	air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly)	commonly used in meteorology
millibar (mbar, or mb)	1000 mbar = 1 bar	

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa	used by aviation industry, also some weather reports
torr	$1\ \text{torr} = \frac{1}{760}\ \text{atm}$	named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr	

Example 15.1.1: Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

a. torr
b. atm
c. kPa
d. mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 9.2.1.

a. $29.2\ \text{in}\ \cancel{\text{Hg}} \times \frac{25.4\ \cancel{\text{mm}}}{1\ \cancel{\text{in}}} \times \frac{1\ \text{torr}}{1\ \cancel{\text{mm Hg}}} = 742\ \text{torr}$

b. $742\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 0.976\ \text{atm}$

c. $742\ \cancel{\text{torr}} \times \frac{101.325\ \text{kPa}}{760\ \cancel{\text{torr}}} = 98.9\ \text{kPa}$

d. $98.9\ \cancel{\text{kPa}} \times \frac{1000\ \cancel{\text{Pa}}}{1\ \cancel{\text{kPa}}} \times \frac{1\ \cancel{\text{bar}}}{100,000\ \cancel{\text{Pa}}} \times \frac{1000\ \text{mbar}}{1\ \cancel{\text{bar}}} = 989\ \text{mbar}$

? Exercise 15.1.1

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Answer

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth’s surface, with a barometer (Figure 15.1.3). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.

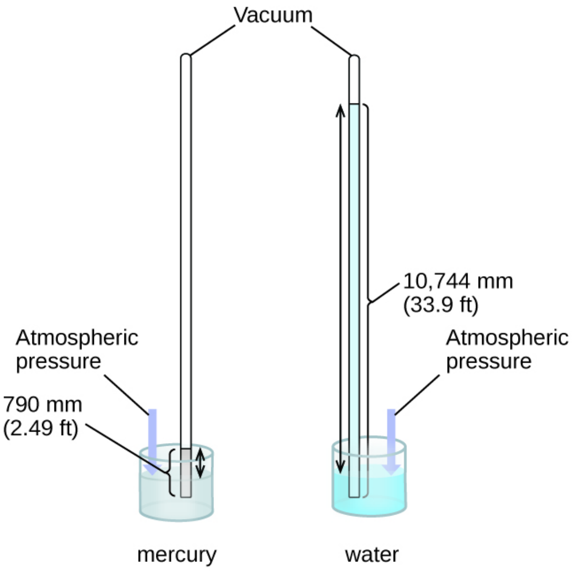


Figure **$15.1.3$** *: In a barometer, the height, h, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.*

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The torr was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as hydrostatic pressure, p:

$$p = h\rho g \tag{15.1.5}$$

where

- h is the height of the fluid,
- ρ is the density of the fluid, and
- g is acceleration due to gravity.

✓ Example 15.1.2: Calculation of Barometric Pressure

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = $13.6\ g/cm^3$.

Solution

The hydrostatic pressure is given by Equation 15.1.5, with $h = 760\ mm$, $\rho = 13.6\ g/cm^3$, and $g = 9.81\ m/s^2$. Plugging these values into the Equation 15.1.5 and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa:)

$$101,325\ N/\mathrm{m}^2 = 101,325\ \frac{\mathrm{kg}\cdot\mathrm{m/s}^2}{\mathrm{m}^2} = 101,325\ \frac{\mathrm{kg}}{\mathrm{m}\cdot\mathrm{s}^2} \tag{15.1.6}$$

$$\begin{aligned} p &= \left(760\ \mathrm{mm} \times \frac{1\ \mathrm{m}}{1000\ \mathrm{mm}}\right) \times \left(\frac{13.6\ \mathrm{g}}{1\ \mathrm{cm}^3} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} \times \frac{(100\ \mathrm{cm})^3}{(1\ \mathrm{m})^3}\right) \times \left(\frac{9.81\ \mathrm{m}}{1\ \mathrm{s}^2}\right) \\ &= (0.760\ \mathrm{m})(13,600\ \mathrm{kg/m}^3)(9.81\ \mathrm{m/s}^2) = 1.01 \times 10^5\ \mathrm{kg/ms}^2 = 1.01 \times 10^5\ N/\mathrm{m}^2 \\ &= 1.01 \times 10^5\ \mathrm{Pa} \end{aligned}$$

? Exercise 15.1.2

Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm^3.

Answer

10.3 m

A manometer is a device similar to a barometer that can be used to measure the pressure of a gas trapped in a container. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. As with a barometer, the distance between the liquid levels in the two arms of the tube (*h* in the diagram) is proportional to the pressure of the gas in the container. An open-end manometer (Figure 15.1.3) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.

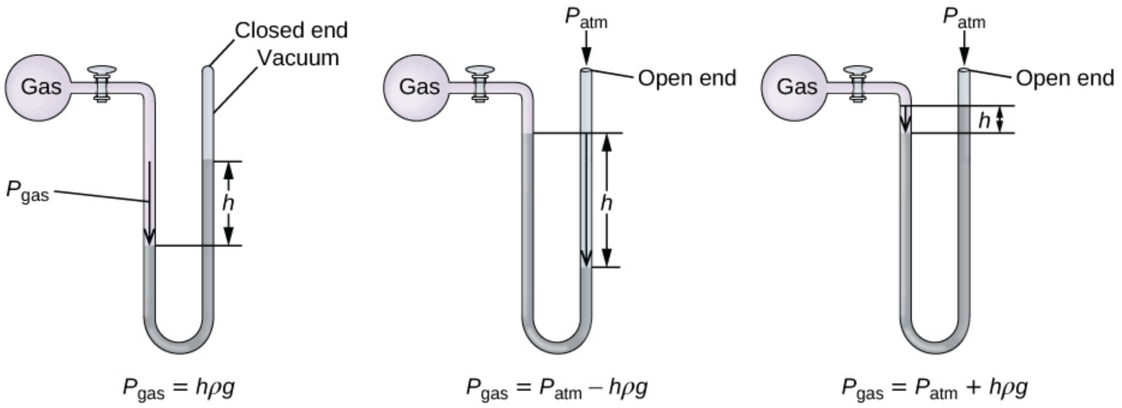
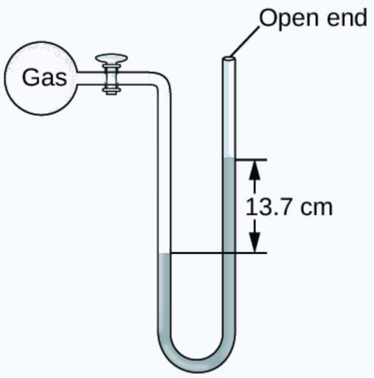


***Figure 15.1.4:** A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (h) is a measure of the pressure. Mercury is usually used because of its large density.*

Example 15.1.3: Calculation of Pressure Using an Open-End Manometer

The pressure of a sample of gas is measured at sea level with an open-end Hg (mercury) manometer, as shown below. Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



Solution

The pressure of the gas equals the hydrostatic pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 13.7 cm of Hg plus atmospheric pressure.)

a. In mm Hg, this is: 137 mm Hg + 760 mm Hg = 897 mm Hg

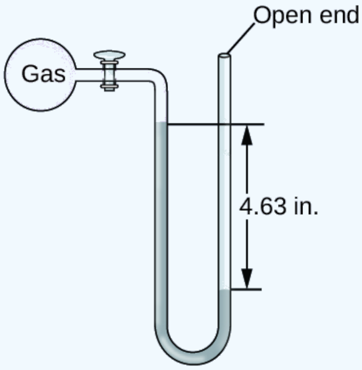
b. $897\ \cancel{\text{mmHg}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 1.18\ \text{atm}$

c. $1.18\ \cancel{\text{atm}} \times \frac{101.325\ \text{kPa}}{1\ \cancel{\text{atm}}} = 1.20 \times 10^2\ \text{kPa}$

? Exercise 15.1.3

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown below Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



Answer a

642 mm Hg

Answer b

0.845 atm

Answer c

85.6 kPa

Application: Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = “pulse”). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure 15.1.5). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff’s pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart’s ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).

Figure 15.1.5: *(a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)*

Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts (Figure 15.1.5) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

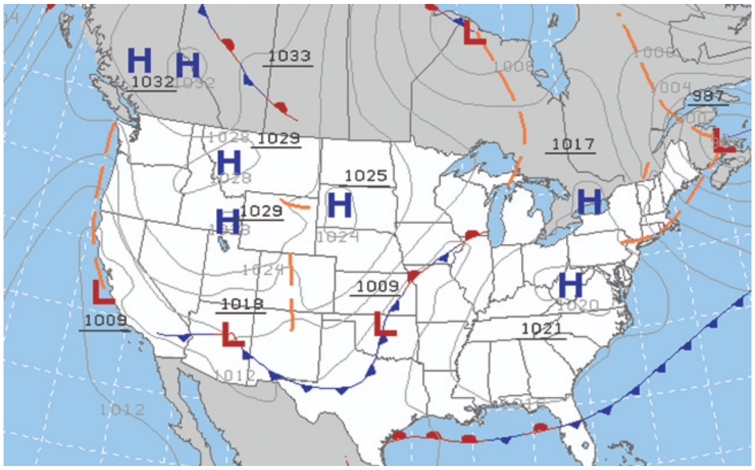


Figure 15.1.6: *Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration)*

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events.

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure 15.1.7: the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

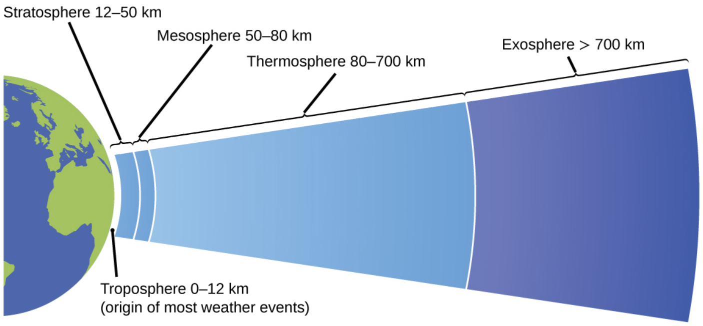


Figure 15.1.7: *Earth’s atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.*

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas pressures can be measured using one of several types of manometers.

Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$

Glossary

atmosphere (atm)
unit of pressure; 1 atm = 101,325 Pa

bar
(bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer
device used to measure atmospheric pressure

hydrostatic pressure
pressure exerted by a fluid due to gravity

manometer
device used to measure the pressure of a gas trapped in a container

pascal (Pa)
SI unit of pressure; 1 Pa = 1 N/m^2

pounds per square inch (psi)
unit of pressure common in the US

pressure
force exerted per unit area

torr

unit of pressure; $1 \text{ torr} = \frac{1}{760} \text{ atm}$

Contributors

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- Modified by Tom Neils (Grand Rapids Community College)

15.2: The Gas Laws

Learning Objectives

- Learn what is meant by the term *gas laws*.
- Learn and apply Boyle's law.
- Learn and apply Charles's law.

When seventeenth-century scientists began studying the physical properties of gases, they noticed some simple relationships between some of the measurable properties of the gas. Take pressure (P) and volume (V), for example. Scientists noted that for a given amount of a gas (usually expressed in units of moles [n]), if the temperature (T) of the gas was kept constant, pressure and volume were related: As one increases, the other decreases. As one decreases, the other increases. We say that pressure and volume are *inversely related*.

There is more to it, however: pressure and volume of a given amount of gas at constant temperature are *numerically* related. If you take the pressure value and multiply it by the volume value, the product is a constant for a given amount of gas at a constant temperature:

$$P \times V = \text{constant at constant } n \text{ and } T$$

If either volume or pressure changes while amount and temperature stay the same, then the other property must change so that the product of the two properties still equals that same constant. That is, if the original conditions are labeled P_1 and V_1 and the new conditions are labeled P_2 and V_2, we have

$$P_1V_1 = \text{constant} = P_2V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1V_1 = P_2V_2 \text{ at constant } n \text{ and } T$$

This equation is an example of a gas law. A **gas law** is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. This particular gas law is called **Boyle's law**, after the English scientist Robert Boyle, who first announced it in 1662. Figure 15.2.1 shows two representations of how Boyle's law works.

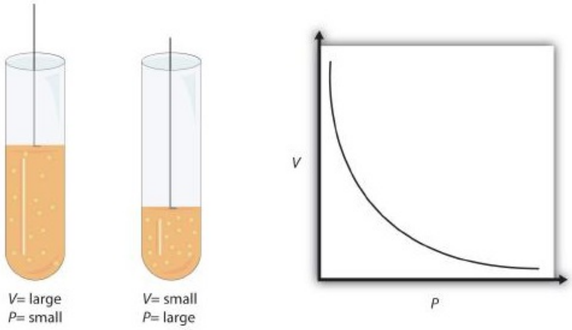


Figure 15.2.1: Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

Boyle's law is an example of a second type of mathematical problem we see in chemistry—one based on a mathematical formula. Tactics for working with mathematical formulas are different from tactics for working with conversion factors. First, most of the questions you will have to answer using formulas are word-type questions, so the first step is to identify what quantities are known and assign them to variables. Second, in most formulas, some mathematical rearrangements (i.e., algebra) must be performed to solve for an unknown variable. The rule is that to find the value of the unknown variable, you must mathematically isolate the unknown variable *by itself and in the numerator* of one side of the equation. Finally, units must be consistent. For example, in Boyle's law there are two pressure variables; they must have the same unit. There are also two volume variables; they also must have the same unit. In most cases, it won't matter *what* the unit is, but the unit must be the *same* on both sides of the equation.

✓ Example 15.2.1

A sample of gas has an initial pressure of 2.44 atm and an initial volume of 4.01 L. Its pressure changes to 1.93 atm. What is the new volume if temperature and amount are kept constant?

Solution

First, determine what quantities we are given. We are given an initial pressure and an initial volume, so let these values be P_1 and V_1:

$$P_1 = 2.44 \text{ atm and } V_1 = 4.01 \text{ L}$$

We are given another quantity, final pressure of 1.93 atm, but not a final volume. This final volume is the variable we will solve for.

$$P_2 = 1.93 \text{ atm and } V_2 = ? \text{ L}$$

Substituting these values into Boyle's law, we get

$$(2.44 \text{ atm})(4.01 \text{ L}) = (1.93 \text{ atm})V_2$$

To solve for the unknown variable, we isolate it by dividing both sides of the equation by 1.93 atm—both the number *and* the unit:

$$\frac{(2.44\,atm)(4.01\,L)}{1.93\,atm} = \frac{(1.93\,atm)\,V_2}{1.93\,atm}$$

Note that, on the left side of the equation, the unit *atm* is in the numerator and the denominator of the fraction. They cancel algebraically, just as a number would. On the right side, the unit *atm* and the number 1.93 are in the numerator and the denominator, so the entire quantity cancels:

$$\frac{(2.44\ \cancel{atm})(4.01\,L)}{1.93\ \cancel{atm}} = \frac{(1.93\ \cancel{atm})\,V_2}{1.93\ \cancel{atm}}$$

What we have left is

$$\frac{(2.44)(4.01\,L)}{1.93} = V_2$$

Now we simply multiply and divide the numbers together and combine the answer with the L unit, which is a unit of volume. Doing so, we get $V_2 = 5.07\,L$

Does this answer make sense? We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's law.

? Exercise 15.2.1

If P_1 = 334 torr, V_1 = 37.8 mL, and P_2 = 102 torr, what is V_2?

Answer

124 mL

As mentioned, you can use any units for pressure or volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

✓ Example 15.2.2

A sample of gas has an initial pressure of 722 torr and an initial volume of 88.8 mL. Its volume changes to 0.663 L. What is the new pressure?

Solution

We can still use Boyle's law to answer this, but now the two volume quantities have different units. It does not matter which unit we change, as long as we perform the conversion correctly. Let us change the 0.663 L to milliliters:

$$0.663\,L \times \frac{1000\,ml}{1\,L} = 663\,ml$$

Now that both volume quantities have the same units, we can substitute into Boyle's law:

$$(722\,torr)(88.8\,ml) = P_2(663\,ml)$$

$$\frac{(722\,torr)(88.8)\,ml}{(663\,ml)} = P_2$$

The mL units cancel, and we multiply and divide the numbers to get P_2 = 96.7 torr

The volume is increasing, and the pressure is decreasing, which is as expected for Boyle's law.

? Exercise 15.2.2

If V_1 = 456 mL, P_1 = 308 torr, and P_2 = 1.55 atm, what is V_2?

Answer

119 mL

There are other measurable characteristics of a gas. One of them is temperature (T). Perhaps one can vary the temperature of a gas sample and note what effect it has on the other properties of the gas. Early scientists did just this, discovering that if the amount of a gas and its pressure are kept constant, then changing the temperature changes the volume (V). As temperature increases, volume increases; as temperature decreases, volume decreases. We say that these two characteristics are *directly related*.

A mathematical relationship between V and T should be possible except for one thought: what temperature scale should we use? We know from Chapter 2 that science uses several possible temperature scales. Experiments show that the volume of a gas is related to its absolute temperature in Kelvin, *not its temperature in degrees Celsius*. If the temperature of a gas is expressed in kelvins, then experiments show that the *ratio* of volume to temperature is a constant:

$$\frac{V}{T} = constant$$

We can modify this equation as we modified Boyle's law: the initial conditions V_1 and T_1 have a certain value, and the value must be the same when the conditions of the gas are changed to some new conditions V_2 and T_2, as long as pressure and the amount of the gas remain constant. Thus, we have another gas law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}\ at\ constant\ P\ and\ n$$

This gas law is commonly referred to as **Charles's law**, after the French scientist Jacques Charles, who performed experiments on gases in the 1780s. The tactics for using this mathematical formula are similar to those for Boyle's law. To determine an unknown quantity, use algebra to isolate the unknown variable by itself and in the numerator; the units of similar variables must be the same. But we add one more tactic: all temperatures must be expressed in the absolute temperature scale (Kelvin). As a reminder, we review the conversion between the absolute temperature scale and the Celsius temperature scale:

K = °C + 273

where K represents the temperature in kelvins, and °C represents the temperature in degrees Celsius.

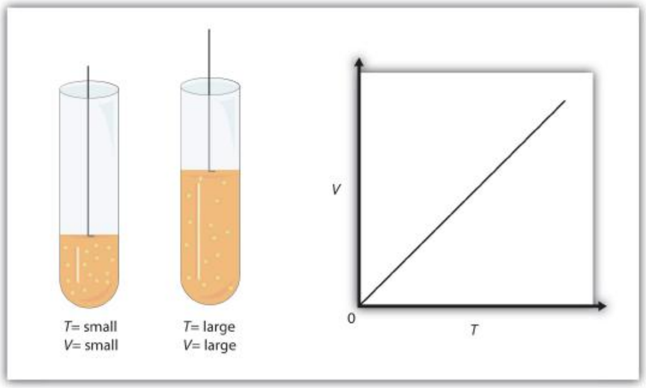


Figure 15.2.2: Charles's Law. A piston having a certain volume and temperature (left piston) will have twice the volume when its temperature is twice as much (right piston). One can also plot V versus T for a given amount of gas at a certain pressure; such a plot will look like the graph on the right.

✓ Example 15.2.3

A sample of gas has an initial volume of 34.8 mL and an initial temperature of 315 K. What is the new volume if the temperature is increased to 559 K? Assume constant pressure and amount for the gas.

Solution

First, we assign the given values to their variables. The initial volume is V_1, so V_1 = 34.8 mL, and the initial temperature is T_1, so T_1 = 315 K. The temperature is increased to 559 K, so the final temperature T_2 = 559 K. We note that the temperatures are already given in kelvins, so we do not need to convert the temperatures. Substituting into the expression for Charles's law yields

$$\frac{34.8\,ml}{315\;K}=\frac{V_2}{559\;K}$$

We solve for V_2 by algebraically isolating the V_2 variable on one side of the equation. We do this by multiplying both sides of the equation by 559 K (number and unit). When we do this, the temperature unit cancels on the left side, while the entire 559 K cancels on the right side:

$$\frac{(559\;\cancel{K})(34.8\,ml)}{315\;\;\cancel{K}}=\frac{V_2(\;\cancel{559\,K})}{\cancel{559\,K}}$$

The expression simplifies to

$$\frac{(559)(34.8\,ml)}{315}=V_2$$

By multiplying and dividing the numbers, we see that the only remaining unit is mL, so our final answer is

V_2 = 61.8 mL

Does this answer make sense? We know that as temperature increases, volume increases. Here, the temperature is increasing from 315 K to 559 K, so the volume should also increase, which it does.

? Exercise 15.2.3

If V_1 = 3.77 L and T_1 = 255 K, what is V_2 if T_2 = 123 K?

Answer

1.82 L

It is more mathematically complicated if a final temperature must be calculated because the *T* variable is in the denominator of Charles's law. There are several mathematical ways to work this, but perhaps the simplest way is to take the reciprocal of Charles's law. That is, rather than write it as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

write the equation as

$$\frac{T_1}{V_1} = \frac{T_2}{V_2}$$

It is still an equality and a correct form of Charles's law, but now the temperature variable is in the numerator, and the algebra required to predict a final temperature is simpler.

✓ Example 15.2.4

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must the temperature of the gas be for its volume to be 25.0 L?

Solution

Here, we are looking for a final temperature, so we will use the reciprocal form of Charles's law. However, the initial temperature is given in degrees Celsius, not kelvins. We must convert the initial temperature to kelvins:

−67°C + 273 = 206 K

In using the gas law, we must use T_1 = 206 K as the temperature. Substituting into the reciprocal form of Charles's law, we get

$$\frac{206\,K}{34.8\,L} = \frac{T_2}{25.0\,L}$$

Bringing the 25.0 L quantity over to the other side of the equation, we get

$$\frac{(25.0\,\cancel{L})(206\,K)}{34.8\,\cancel{L}} = T_2$$

The L units cancel, so our final answer is T_2 = 148 K

This is also equal to −125°C. As temperature decreases, volume decreases, which it does in this example.

? Exercise 15.2.4

If V_1 = 623 mL, T_1 = 255°C, and V_2 = 277 mL, what is T_2?

Answer

235 K, or −38°C

Summary

- The behavior of gases can be modeled with gas laws.
- Boyle's law relates a gas's pressure and volume at constant temperature and amount.
- Charles's law relates a gas's volume and temperature at constant pressure and amount.
- In gas laws, temperatures must always be expressed in kelvins.

15.3: Other Gas Relationships

Learning Objectives

- Review other simple gas laws.
- Learn and apply the combined gas law.

You may notice in Boyle's law and Charles's law that we actually refer to four physical properties of a gas: pressure (*P*), volume (*V*), temperature (*T*), and amount (in moles—*n*). We do this because these are the only four independent physical properties of a gas. There are other physical properties, but they are all related to one (or more) of these four properties.

Boyle's law is written in terms of two of these properties, with the other two being held constant. Charles's law is written in terms of two different properties, with the other two being held constant. It may not be surprising to learn that there are other gas laws that relate other pairs of properties—as long as the other two are held constant. In this section, we will mention a few.

Gay-Lussac's law relates pressure with absolute temperature. In terms of two sets of data, Gay-Lussac's law is

$$\frac{P_1}{T_1}=\frac{P_2}{T_2}$$

at constant V and n.

Note that it has a structure very similar to that of Charles's law, only with different variables—pressure instead of volume. **Avogadro's law** introduces the last variable for amount. The original statement of Avogadro's law states that equal volumes of different gases at the same temperature and pressure contain the same number of particles of gas. Because the number of particles is related to the number of moles (1 mol = 6.022 × 10^{23} particles), Avogadro's law essentially states that equal volumes of different gases, at the same temperature and pressure, contain the same *amount* (moles, particles) of gas. Put mathematically into a gas law, Avogadro's law is

$$\frac{V_1}{n_1}=\frac{V_2}{n_2}$$

at constant V and T.

(First announced in 1811, it was Avogadro's proposal that volume is related to the number of particles that eventually led to naming the number of things in a mole as Avogadro's number.) Avogadro's law is useful because for the first time we are seeing amount, in terms of the number of moles, as a variable in a gas law.

Example 15.3.1

A 2.45 L volume of gas contains 4.5 × 10^{21} gas particles. How many gas particles are there in 3.87 L if the gas is at constant pressure and temperature?

Solution

We can set up Avogadro's law as follows:

$$\frac{2.45\,L}{4.5\times10^{21}\,\text{particles}}=\frac{3.87\,L}{n_2}$$

We algebraically rearrange to solve for n_2:

$$n_2=\frac{(3.87\ \cancel{L})(4.5\times10^{21}\,\text{particles})}{2.45\ \cancel{L}}$$

The L units cancel, so we solve for n_2:

$$n_2=7.1\times10^{21}\,\text{particles}$$

? Exercise 15.3.1

A 12.8 L volume of gas contains 3.00 × 10^{20} gas particles. At constant temperature and pressure, what volume does 8.22 × 10^{18} gas particles fill?

Answer

0.351 L

The variable *n* in Avogadro's law can also stand for the number of moles of gas, in addition to number of particles.

One thing we notice about all gas laws, collectively, is that volume and pressure are always in the numerator, and temperature is always in the denominator. This suggests that we can propose a gas law that combines pressure, volume, and temperature. This gas law is known as the **combined gas law**, and its mathematical form is

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}\ at\ constant\ n$$

This allows us to follow changes in all three major properties of a gas. Again, the usual warnings apply about how to solve for an unknown algebraically (isolate it on one side of the equation in the numerator), units (they must be the same for the two similar variables of each type), and units of temperature must be in kelvins.

✓ Example 15.3.2

A sample of gas at an initial volume of 8.33 L, an initial pressure of 1.82 atm, and an initial temperature of 286 K simultaneously changes its temperature to 355 K and its volume to 5.72 L. What is the final pressure of the gas?

Solution

We can use the combined gas law directly; all the units are consistent with each other, and the temperatures are given in Kelvin. Substituting,

$$\frac{(1.82\,atm)(8.33\,L)}{286\,K}=\frac{P_2(5.72\,L)}{355\,K}$$

We rearrange this to isolate the P_2 variable all by itself. When we do so, certain units cancel:

$$\frac{(1.82\,atm)(8.33\ \cancel{L})(355\ \cancel{K})}{(286\ \cancel{K})(5.72\ \cancel{L})}=P_2$$

Multiplying and dividing all the numbers, we get

$$P_2=3.29\,atm$$

Ultimately, the pressure increased, which would have been difficult to predict because two properties of the gas were changing.

? Exercise 15.3.2

If P_1 = 662 torr, V_1 = 46.7 mL, T_1 = 266 K, P_2 = 409 torr, and T_2 = 371 K, what is V_2?

Answer

105 mL

As with other gas laws, if you need to determine the value of a variable in the denominator of the combined gas law, you can either cross-multiply all the terms, or just take the reciprocal of the combined gas law. Remember, the variable you are solving for must be in the numerator and all by itself on one side of the equation.

Summary

- There are gas laws that relate any two physical properties of a gas.
- The combined gas law relates pressure, volume, and temperature of a gas.

15.4: Ideal Gases and The Ideal Gas Law

Learning Objectives

- Explain all the quantities involved in the ideal gas law.
- Evaluate the gas constant R from experimental results.
- Calculate T, V, P, or n of the ideal gas law: $PV = nRT$.
- Describe the ideal gas law using graphics.

The Ideal Gas Law

The volume (*V*) occupied by *n* moles of any gas has a pressure (*P*) at temperature (*T*) in Kelvin. The relationship for these variables,

$$PV = nRT \tag{15.4.1}$$

where *R* is known as the gas constant, is called the **ideal gas law** or **equation of state**. Properties of the gaseous state predicted by the ideal gas law are within 5% for gases under ordinary conditions. In other words, given a set of conditions, we can predict or calculate the properties of a gas to be within 5% by applying the ideal gas law. How to apply such a law for a given set of conditions is the focus of general chemistry.

At a temperature much higher than the critical temperature and at low pressures, however, the ideal gas law is a very good model for gas behavior. When dealing with gases at low temperature and at high pressure, correction has to be made in order to calculate the properties of a gas in industrial and technological applications. One of the common corrections made to the ideal gas law is the van der Waal's equation, but there are also other methods dealing with the deviation of gas from ideality.

The Gas Constant *R*

Repeated experiments show that at standard temperature (273 K) and pressure (1 atm or 101325 N/m^2), one mole (*n* = 1) of gas occupies 22.4 L volume. Using this experimental value, you can evaluate the **gas constant *R*,**

$$R = \frac{PV}{nT} = \frac{1\text{ atm } 22.4\text{ L}}{1\text{ mol } 273\text{ K}} \tag{15.4.2}$$

$$\tag{15.4.3}$$

$$= 0.08205\ \frac{\text{L atm}}{\text{mol}\cdot\text{K}} \tag{15.4.4}$$

When SI units are desirable, *P* = 101325 N/m^2 (Pa for pascal) instead of 1 atm. The volume is 0.0224 m^3. The numerical value and units for *R* are

$$R = \frac{101325\ \frac{\text{N}}{\text{m}^2}\ 0.0224\text{ m}^3}{1\text{ mol } 273\text{ K}} \tag{15.4.5}$$

$$\tag{15.4.6}$$

$$= 8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}} \tag{15.4.7}$$

Note that $1\text{ L atm} = 0.001\text{ m}^3 \times 101325\ \frac{\text{N}}{\text{m}^2} = 101.325\text{ J (or N m)}$ Since energy can be expressed in many units, other numerical values and units for *R* are frequently in use.

The Gas Constant

For your information, the gas constant can be expressed in the following values and units.

$$R = 0.08205 \dfrac{\text{L atm}}{\text{mol} \cdot \text{K}} \quad \text{Notes:} \tag{15.4.8}$$

$$= 8.3145 \dfrac{\text{L kPa}}{\text{mol} \cdot \text{K}} \quad 1 \text{ atm} = 101.32 \text{ kPa} \tag{15.4.9}$$

$$= 8.3145 \dfrac{\text{J}}{\text{mol} \cdot \text{K}} \quad 1 \text{ J} = 1 \text{ L kPa} \tag{15.4.10}$$

$$= 1.987 \dfrac{\text{cal}}{\text{mol} \cdot \text{K}} \quad 1 \text{ cal} = 4.182 \text{ J} \tag{15.4.11}$$

$$= 62.364 \dfrac{\text{L torr}}{\text{mol} \cdot \text{K}} \quad 1 \text{ atm} = 760 \text{ torr} \tag{15.4.12}$$

The gas constant *R* is such a universal constant for all gases that its values are usually listed in the "Physical Constants" of textbooks and handbooks. It is also listed in Constants of our HandbookMenu at the left bottom. Although we try to use SI units all the time, the use of atm for pressure is still common. Thus, we often use R = 8.314 J / (mol·K) or 8.3145 J / mol·K.

The volume occupied by one mole, *n* = 1, of substance is called the **molar volume**, $V_{\text{molar}} = \dfrac{V}{n}$. Using the molar volume notation, the ideal gas law is:

$$PV_{\text{molar}} = RT$$

Applications of the Ideal Gas Law

The ideal gas law has four parameters and a constant, *R*,

$$PV = nRT\,,$$

and it can be rearranged to give an expression for each of *P*, *V*, *n* or *T*. For example,

$$P = \dfrac{nRT}{V} \text{ (Boyle's law)}$$

$$P = \left(\dfrac{nR}{V}\right) T \text{ (Charles's law)}$$

These equations are Boyle's law and Charles's law respectively. Similar expressions can be derived for *V*, *n* and *T* in terms of other variables. Thus, there are many applications. However, you must make sure that you use the proper numerical value for the gas constant *R* according to the units you have for the parameters.

Furthermore, $\dfrac{n}{V}$ is number of moles per unit volume, and this quantity has the same units as the concentration (*C*). Thus, the concentration is a function of pressure and temperature,

$$C = \dfrac{P}{RT}$$

At 1.0 atm pressure and room temperature of 298 K, the concentration of an ideal gas is 0.041 mol/L.

Avogadro's law can be further applied to correlate gas density ρ (weight per unit volume or *n M / V*) and molecular mass *M* of a gas. The following equation is easily derived from the ideal gas law:

$$PM = \dfrac{nM}{V} RT \tag{15.4.13}$$

Thus, we have

$$PM = \dfrac{dRT}{M} \tag{15.4.14}$$

$$\rho = \dfrac{nM}{V} \leftarrow \text{definition, and} \tag{15.4.15}$$

$$\rho = \dfrac{PM}{RT} \tag{15.4.16}$$

$$M = \dfrac{dRT}{P} \tag{15.4.17}$$

✓ Example 1

An air sample containing only nitrogen and oxygen gases has a density of 1.3393 g / L at STP. Find the weight and mole percentages of nitrogen and oxygen in the sample.

Solution
From the density ρ, we can evaluate an average molecular weight (also called molar mass).

$$\begin{aligned} PM &= dRT && (15.4.18) \\ M &= 22.4 \times d && (15.4.19) \\ &= 22.4 \text{ L/mol} \times 1.3393 \text{ g/L} && (15.4.20) \\ &= 30.0 \text{ g/mol} && (15.4.21) \end{aligned}$$

Assume that we have 1.0 mol of gas, and *x* mol of which is nitrogen, then (1 - *x*) is the amount of oxygen. The average molar mass is the mole weighted average, and thus,

$$28.0\,\mathrm{x} + 32.0(1-\mathrm{x}) = 30.0$$

$$-4\,\mathrm{x} = -2$$

$$\mathrm{x} = 0.50 \text{ mol of } \mathrm{N_2},\ \text{and } 1.0 - 0.50 = 0.50 \text{ mol } \mathrm{O_2}$$

Now, to find the weight percentage, find the amounts of nitrogen and oxygen in 1.0 mol (30.0 g) of the mixture.

$$\text{Mass of } 0.5 \text{ mol nitrogen} = 0.5 \times 28.0 = 14.0 \text{ g}$$

$$\text{Mass of } 0.5 \text{ mol oxygen} = 0.5 \times 32.0 = 16.0 \text{ g}$$

$$\text{Percentage of nitrogen} = 100 \times \frac{14.0}{30.0} = 46.7\%$$

$$\text{Percentage of oxygen} = 100 \times \frac{16.0}{30.0} = 100 - 46.7 = 53.3\%$$

DISCUSSION
We can find the density of pure nitrogen and oxygen first and evaluate the fraction from the density.

$$\rho \text{ of } \mathrm{N_2} = \frac{28.0}{22.4} = 1.2500 \text{ g/L}$$

$$\rho \text{ of } \mathrm{O_2} = \frac{32.0}{22.4} = 1.4286 \text{ g/L}$$

$$1.2500\,\mathrm{x} + 1.4286(1-\mathrm{x}) = 1.3393$$

Solving for x gives

$$\mathrm{x} = 0.50 \text{ (same result as above)}$$

? Exercise 1

Now, repeat the calculations for a mixture whose density is 1.400 g/L.

✓ Example 2

What is the density of acetone (C_3H_6O) vapor at 1.0 atm and 400 K?

Solution
The molar mass of acetone = 3*12.0 + 6*1.0 + 16.0 = 58.0. Thus,

$$\rho = \frac{PM}{RT} \tag{15.4.22}$$

$$\tag{15.4.23}$$

$$= \frac{1.0 \times 58.0 \text{ atm } \frac{\text{g}}{\text{mol}}}{0.08205 \frac{\text{L atm}}{\text{mol K}} \times 400 \text{ K}} \tag{15.4.24}$$

$$\tag{15.4.25}$$

$$= 1.767 \text{ g/L} \tag{15.4.26}$$

? Exercise 2

The density of acetone is 1.767 g/L; calculate its molar mass.

Confidence Building Questions

1. **What does the variable *n* stand for in the ideal gas law,**

   $PV = nRT$?

   Hint: number of moles of gas in a closed system.

   Skill:
   Describe the ideal gas law.

2. **A closed system means no energy or mass flow into or out of a system. In a closed system, how many independent variables are there among *n, T, V* and *P* for a gas?** Note: an independent variable can be of any arbitrary values.

   Hint: one

   Skill:
   The ideal gas equation shows the interdependence of the variables. Only one of them can be varied independently.

3. **What is the molar volume of an ideal gas at 2 atm and 1000 K?**

   Hint: 41.0

   Skill:
   Evaluate molar volume at any condition.

4. **A certain amount of a gas is enclosed in a container of fixed volume. If you let heat (energy) flow into it, what will increase?**
   (In a multiple choice, you may have volume, pressure, temperature, and any combination of these to choose from.)

   Hint: Both pressure and temperature will increase.

   Skill:
   Explain a closed system and apply ideal gas law.

5. **For a certain amount (*n* = constant) of gas in a closed system, how does volume *V* vary with the temperature? In the following, *k* is a constant depending on *n* and *P*.**

   a. $V = kT$
   b. $V = \frac{k}{T}$
   c. $TV = k$
   d. $V = kT^2$
   e. $V = k$

   Hint: a

   Skill:
   Explain Charles's law.

6. **Boyle's law is *P V* = constant. A sketch of *P* vs *V* on graph paper is similar to a sketch of the equation *x y* = 5. What curve(s) does this equation represent?**
   a. a parabola
   b. an ellipse
   c. a hyperbola
   d. a pair of hyperbolas
   e. a straight line
   f. a surface

   Hint: d

   Skill:
   Apply the skills acquired in math courses to chemical problem solving.

7. **For a certain amount of gas in a closed system, which one of the following equations is valid? Subscripts 1 and 2 refer to specific conditions 1 and 2 respectively.**
   a. $P_1 V_1 T_1 = P_2 V_2 T_2$
   b. $P_1 V_1 T_2 = P_2 V_2 T_1$
   c. $P_1 V_2 T_1 = P_2 V_1 T_2$
   d. $P_2 V_1 T_1 = P_1 V_2 T_2$
   e. $\dfrac{P_1 V_2}{T_1} = \dfrac{P_2 V_1}{T_2}$

   Hint: b

   Skill:
   Rearrange a mathematical equation.

8. **The gas constant *R* is 8.314 J / mol·K. Convert the numerical value of *R* so that its units are cal / (mol·K). A unit conversion table will tell you that 1 cal = 4.184 J. Make sure you know where to find it. During the exam, the conversion factor is given, but you should know how to use it.**

   Hint: 1.987 cal/(mol K).

   Skill:
   Use conversion factors, for example:

   $$8.314 \text{ J} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = ? \text{ cal}$$

9. **At standard temperature and pressure, how many moles of H_2 are contained in a 1.0 L container?**

   Hint: 0.045 mol/L

   Discussion:
   There are many methods for calculating this value.

10. **At standard temperature and pressure, how many grams of CO_2 are contained in a 3.0 L container? Molar mass of $CO_2 = 44$.**

    Hint: 5.89 g in 3 L

    One method:

    It contains $n = \dfrac{1 \text{ atm} \times 3 \text{ L}}{0.08205 \dfrac{\text{L atm}}{\text{mol} \cdot \text{K}} \times 273 \text{ K}}$

11. **What is the pressure if 1 mole of N_2 occupies 1 L of volume at 1000 K?**

    Hint: 82.1 atm

    Discussion:
    Depending on the numerical value and units of *R* you use, you will get the pressure in various units.
    At 1000 K, some of the N_2 molecules may dissociate. If that is true, the pressure will be higher!

12. **What is the temperature if 1 mole of N_2 occupying 100 L of volume has a pressure of 20 Pa (1 Pa = 1 Nm^{-2})?**

Hint: 240 K

Discussion:
At T = 240 K, ideal gas law may not apply to CO_2, because this gas liquifies at a rather high temperature. The ideal gas law is still good for N_2, H_2, O_2 etc, because these gases liquify at much lower temperatures.

15.5: Dalton's Law of Partial Pressures

Learning Objectives

- To determine the contribution of each component gas to the total pressure of a mixture of gases

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{15.5.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressure, the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, ***the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases***. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as *Dalton's law of partial pressures*. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots \tag{15.5.2}$$

$$= \sum_{i=1}^{n} P_i \tag{15.5.3}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

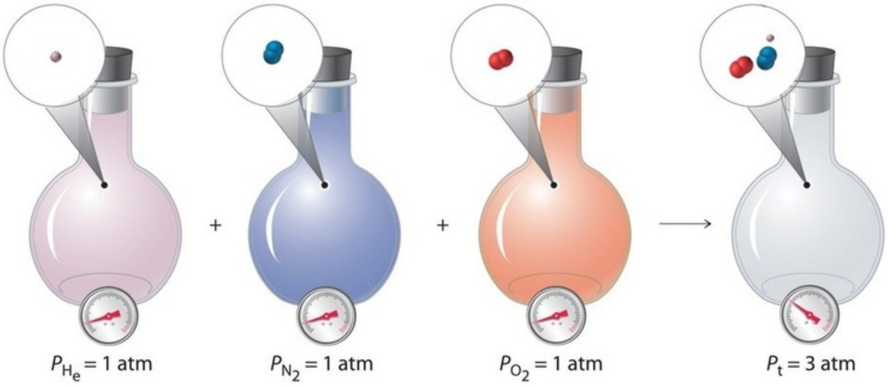


Figure 15.5.1: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B \tag{15.5.4}$$

$$= n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) \tag{15.5.5}$$

$$= (n_A + n_B)\left(\frac{RT}{V}\right) \tag{15.5.6}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{15.5.7}$$

$$= \sum_{i=1}^{n} P_i\left(\frac{RT}{V}\right) \tag{15.5.8}$$

Equation 15.5.8 restates Equation 15.5.6 in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on only the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For Equation 15.5.8 to be valid, the identity of the particles present cannot have an effect. Thus an ideal gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 15.5.1.

✓ Example 15.5.1: The Bends

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called "the bends." At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of components, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A. Calculate the number of moles of He and O_2 present.
B. Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of He is

$$n_{\mathrm{He}} = \frac{326.4\ \mathrm{g}}{4.003\ \mathrm{g/mol}} = 81.54\ \mathrm{mol}$$

The number of moles of O_2 is

$$n_{\mathrm{O_2}} = \frac{51.2\ \mathrm{g}}{32.00\ \mathrm{g/mol}} = 1.60\ \mathrm{mol}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\mathrm{He}} = \frac{n_{\mathrm{He}}RT}{V} = \frac{81.54\ \mathrm{mol} \times 0.08206\ \dfrac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 293.15\ \mathrm{K}}{10.0\ \mathrm{L}} = 196.2\ \mathrm{atm}$$

$$P_{\mathrm{O_2}} = \frac{n_{\mathrm{O_2}}RT}{V} = \frac{1.60\ \mathrm{mol} \times 0.08206\ \dfrac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 293.15\ \mathrm{K}}{10.0\ \mathrm{L}} = 3.85\ \mathrm{atm}$$

The total pressure is the sum of the two partial pressures:

$$P_{\mathrm{tot}} = P_{\mathrm{He}} + P_{\mathrm{O_2}} = (196.2 + 3.85)\ \mathrm{atm} = 200.1\ \mathrm{atm}$$

Exercise 15.5.1

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer

$P_{CH_4} = 137\ atm; P_{C_2H_6} = 13.4\ atm; P_{tot} = 151\ atm$

Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction (χ) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_{tot}):

$$\chi_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{15.5.9}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $\chi_A = 1.0$, then the sample is pure A, not a mixture. If $\chi_A = 0$, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let's evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the ideal gas law to describe the pressures of both gas A and the mixture: $P_A = n_A RT/V$ and $P_{tot} = n_t RT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = \chi_A \tag{15.5.10}$$

Rearranging this equation gives

$$P_A = \chi_A P_{tot} \tag{15.5.11}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. By volume, Earth's atmosphere is about 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of gases such as CO_2, H_2O, and others. This means that 78% of the particles present in the atmosphere are N_2; hence the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using Equation 15.5.11, we therefore know that the partial pressure of N_2 is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of O_2 and Ar are 0.21 and 0.009 atm, respectively.

Example 15.5.2: Exhaling Composition

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

the mole fractions of the gases

	Inhaled Air / mmHg	**Exhaled Air / mmHg**
P_{N_2}	597	568
P_{O_2}	158	116
P_{H_2O}	0.3	28
P_{CO_2}	5	48
P_{Ar}	8	8
P_{tot}	767	767

Given: pressures of gases in inhaled and exhaled air

Asked for: mole fractions of gases in exhaled air

Strategy:

Calculate the mole fraction of each gas using Equation 15.5.11.

Solution:

The mole fraction of any gas A is given by

$$\chi_A = \frac{P_A}{P_{tot}}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of CO_2 is given as:

$$\chi_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063$$

The following table gives the values of χ_A for the gases in the exhaled air.

Solutions to Example 10.6.2

Gas	**Mole Fraction**
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

Exercise 15.5.2

Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.

Answer

$$P_{CO_2} = 86 \text{ atm}$$

$$P_{\mathrm{N_2}} = 2.7\ \mathrm{atm}$$

Summary

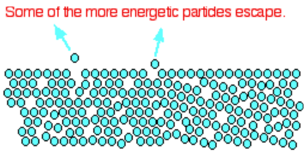
The partial pressure of each gas in a mixture is proportional to its mole fraction. The pressure exerted by each gas in a gas mixture (its **partial pressure**) is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (**Dalton's law of partial pressures**). The amount of gas present in a mixture may be described by its partial pressure or its mole fraction. The **mole fraction** of any component of a mixture is the ratio of the number of moles of that substance to the total number of moles of all substances present. In a mixture of gases, the partial pressure of each gas is the product of the total pressure and the mole fraction of that gas.

15.5.1: Vapor Pressure

This page looks at how the equilibrium between a liquid (or a solid) and its vapor leads to the idea of a saturated vapor pressure. It also looks at how saturated vapor pressure varies with temperature, and the relationship between saturated vapor pressure and boiling point.

Evaporation: Liquid/Vapor Equilibrium

The average energy of the particles in a liquid is governed by the temperature. The higher the temperature, the higher the average energy. But within that average, some particles have energies higher than the average, and others have energies lower than the average. Some of the more energetic particles on the surface of the liquid can be moving fast enough to escape from the attractive forces holding the liquid together. They evaporate. The diagram shows a small region of a liquid near its surface.

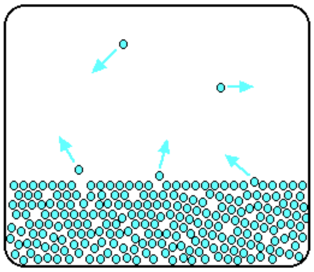


Notice that evaporation only takes place on the surface of the liquid. That's quite different from boiling which happens when there is enough energy to disrupt the attractive forces throughout the liquid. That's why, if you look at boiling water, you see bubbles of gas being formed all the way through the liquid.

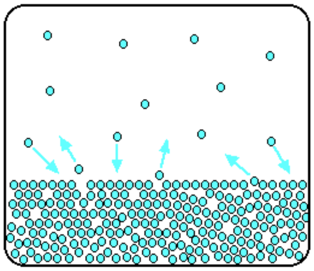
If you look at water which is just evaporating in the sun, you don't see any bubbles. Water molecules are simply breaking away from the surface layer. Eventually, the water will all evaporate in this way. The energy which is lost as the particles evaporate is replaced from the surroundings. As the molecules in the water jostle with each other, new molecules will gain enough energy to escape from the surface.

The evaporation of a liquid in a closed container

Now imagine what happens if the liquid is in a closed container. Common sense tells you that water in a sealed bottle does not seem to evaporate - or at least, it does not disappear over time. But there is constant evaporation from the surface. Particles continue to break away from the surface of the liquid - but this time they are trapped in the space above the liquid.



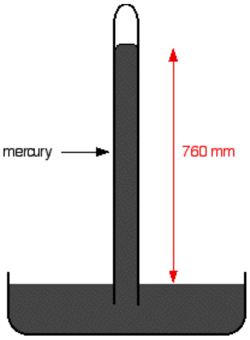
As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and be trapped there. There will rapidly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it.



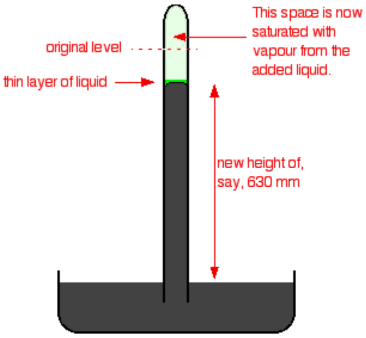
In this equilibrium, there will be a fixed number of the gaseous particles in the space above the liquid. When these particles hit the walls of the container, they exert a pressure. This pressure is called the saturated vapor pressure (also known as **saturation vapor pressure**) of the liquid.

Measuring the saturated vapor pressure

It is not difficult to show the existence of this saturated vapor pressure (and to measure it) using a simple piece of apparatus. If you have a mercury barometer tube in a trough of mercury, at 1 atmosphere pressure the column will be 760 mm tall. 1 atmosphere is sometimes quoted as 760 mmHg ("millimetres of mercury").



If you squirt a few drops of liquid into the tube, it will rise to form a thin layer floating on top of the mercury. Some of the liquid will evaporate and you will get the equilibrium we've just been talking about - provided there is still some liquid on top of the mercury. It is only an equilibrium if both liquid and vapor are present.



The saturated vapor pressure of the liquid will force the mercury level down a bit. You can measure the drop - and this gives a value for the saturated vapor pressure of the liquid at this temperature. In this case, the mercury has been forced down by a distance of 760 - 630 mm. The saturated vapor pressure of this liquid at the temperature of the experiment is 130 mmHg. You could convert this into proper SI units (pascals) if you wanted to. 760 mmHg is equivalent to 101,325 Pa.

A value of 130 mmHg is quite a high vapor pressure if we are talking about room temperature. Water's saturated vapor pressure is about 20 mmHg at this temperature. A high vapor pressure means that the liquid must be volatile - molecules escape from its surface relatively easily, and aren't very good at sticking back on again either.

That will result in larger numbers of them in the gas state once equilibrium is reached. The liquid in the example must have significantly weaker intermolecular forces than water.

The variation of saturated vapor pressure with temperature

The effect of temperature liquid/ vapor equilibrium

You can look at this in two ways. (1) There is a common sense way. If you increase the temperature, you are increasing the average energy of the particles present. That means that more of them are likely to have enough energy to escape from the surface of the liquid. That will tend to increase the saturated vapor pressure. (2) Or you can look at it in terms of Le Chatelier's Principle - which works just as well in this kind of physical situation as it does in the more familiar chemical examples.

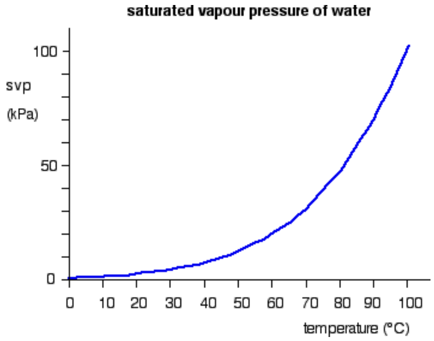
When the space above the liquid is saturated with vapor particles, you have this equilibrium occurring on the surface of the liquid:

$$\text{liquid} \rightleftharpoons \text{vapour} \qquad \Delta H \text{ is +ve}$$

The forward change (liquid to vapor) is endothermic. It needs heat to convert the liquid into the vapor. According to Le Chatelier, increasing the temperature of a system in a dynamic equilibrium favors the endothermic change. That means that increasing the temperature increases the amount of vapor present, and so increases the saturated vapor pressure.

The effect of temperature on the saturated vapor pressure of water

The graph shows how the saturated vapor pressure (svp) of water varies from 0°C to 100 °C. The pressure scale (the vertical one) is measured in kilopascals (kPa). 1 atmosphere pressure is 101.325 kPa.



Saturated vapor pressure and boiling point

A liquid boils when its saturated vapor pressure becomes equal to the external pressure on the liquid. When that happens, it enables bubbles of vapor to form throughout the liquid - those are the bubbles you see when a liquid boils.

If the external pressure is higher than the saturated vapor pressure, these bubbles are prevented from forming, and you just get evaporation at the surface of the liquid. If the liquid is in an open container and exposed to normal atmospheric pressure, the liquid boils when its saturated vapor pressure becomes equal to 1 atmosphere (or 101325 Pa or 101.325 kPa or 760 mmHg). This happens with water when the temperature reaches 100°C.

But at different pressures, water will boil at different temperatures. For example, at the top of Mount Everest the pressure is so low that water will boil at about 70°C. Whenever we just talk about "the boiling point" of a liquid, we always assume that it is being measured at exactly 1 atmosphere pressure. In practice, of course, that is rarely exactly true.

Sublimation: solid/vapor Equilibrium

Solids can also lose particles from their surface to form a vapor, except that in this case we call the effect sublimation rather than evaporation. Sublimation is the direct change from solid to vapor (or vice versa) without going through the liquid stage.

In most cases, at ordinary temperatures, the saturated vapor pressures of solids range from low to very, very, very low. The forces of attraction in many solids are too high to allow much loss of particles from the surface. However, there are some which do easily form vapors. For example, naphthalene (used in old-fashioned "moth balls" to deter clothes moths) has quite a strong smell. Molecules must be breaking away from the surface as a vapor, because otherwise you would not be able to smell it. Another fairly common example (discussed in detail on another page) is solid carbon dioxide - "dry ice". This never forms a liquid at atmospheric pressure and always converts directly from solid to vapor. That's why it is known as dry ice.

Contributors and Attributions

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15.6: Ideal Gases and Real Gases

Now, we need to expand on the qualifications with which we begin this chapter. We imagine that the results of a large number of experiments are available for our analysis. Our characterization of these results has been that all gases obey the same equations—Boyle's law, Charles' law, and the ideal gas equation—and do so exactly. This is an oversimplification. In fact they are always approximations. They are approximately true for all gases under all "reasonable" conditions, but they are not exactly true for any real gas under any condition. It is useful to introduce the idea of hypothetical gases that obey the classical gas equations exactly. In the previous section, we call the combination of Boyle's law and Charles' law the ideal gas equation. We call the hypothetical substances that obey this equation ***ideal gases***. Sometimes we refer to the classical gas laws collectively as the ***ideal gas laws***.

At very high gas densities, the classical gas laws can be very poor approximations. As we have noted, they are better approximations the lower the density of the gas. In fact, experiments show that the pressure—volume—temperature behavior of any real gasreal gas becomes arbitrarily close to that predicted by the ideal gas equation in the limit as the pressure goes to zero. This is an important observation that we use extensively.

At any given pressure and temperature, the ideal gas laws are better approximations for a compound that has a lower boiling point than they are for a compound with a higher boiling point. Another way of saying this is that they are better approximations for molecules that are weakly attracted to one another than they are for molecules that are strongly attracted to one another.

Forces between molecules cause them to both attract and repel one another. The net effect depends on the distance between them. If we assume that there are no intermolecular forcesintermolecular forces acting between gas molecules, we can develop exact theories for the behavior of macroscopic amounts of the gas. In particular, we can show that such substances obey the ideal gas equation. (We shall see that a complete absence of repulsive forces implies that the molecules behave as point masses.) Evidently, the difference between the behavior of a real gas and the behavior it would exhibit if it were an ideal gas is just a measure of the effects of intermolecular forces.

The ideal gas equation is not the only equation that gives a useful representation for the interrelation of gas pressure–volume–temperature data. There are many such ***equations of state***. They are all approximations, but each can be a particularly useful approximation in particular circumstances. We discuss ***van der Waal's equation*** equation and the ***virial equations*** later in this chapter. Nevertheless, we use the ideal gas equation extensively.

We will see that much of chemical thermodynamics is based on the behavior of ideal gases. Since there are no ideal gases, this may seem odd, at best. If there are no ideal gases, why do we waste time talking about them? After all, we don't want to slog through tedious, long-winded, pointless digressions. We want to understand how real stuff behaves! Unfortunately, this is more difficult. The charm of ideal gases is that we can understand their behavior; the ideal gas equation expresses this understanding in a mathematical model. Real gases are another story. We can reasonably say that we can best understand the behavior of a real gas by understanding how and why it is different from the behavior of a (hypothetical) ideal gas that has the same molecular structure.

- **2.8: Real Gases Versus Ideal Gases** by Paul Ellgen is licensed CC BY-SA 4.0. Original source: https://www.amazon.com/Thermodynamics-Chemical-Equilibrium-Paul-Ellgen/dp/1492114278.

15.7: Gas Stoichiometry

Learning Objectives

- Learn the ideal gas law.
- Apply the ideal gas law to any set of conditions of a gas.
- Apply the ideal gas law to molar volumes, density, and stoichiometry problems.

So far, the gas laws we have considered have all required that the gas change its conditions; then we predict a resulting change in one of its properties. Are there any gas laws that relate the physical properties of a gas at any given time? Consider a further extension of the combined gas law to include *n*. By analogy to Avogadro's law, *n* is positioned in the denominator of the fraction, opposite the volume. So,

$$\frac{PV}{nT} = constant$$

Because pressure, volume, temperature, and amount are the only four independent physical properties of a gas, the constant in the above equation is truly a constant. Indeed, because we do not need to specify the identity of a gas to apply the gas laws, this constant is the same for all gases. We define this constant with the symbol *R*, so the previous equation is written as

$$\frac{PV}{nT} = R$$

which is usually rearranged as

$$PV = nRT$$

This equation is called the **ideal gas law**. It relates the four independent properties of a gas at any time. The constant *R* is called the ideal gas law constant. Its value depends on the units used to express pressure and volume.

Table 15.7.1 - Values of the Ideal Gas Law Constant lists the numerical values of R.

Numerical Value	Units
0.08205	L·atmmol·K· $\frac{L.atm}{mol.K}$
62.36	L·torrmol·K=L·mmHgmol·K· $\frac{L.torr}{mol.K} = \frac{L.mmHg}{mol.K}$
8.314	$\frac{J}{mol.K}$

The ideal gas law is used like any other gas law, with attention paid to the unit and expression of the temperature in kelvins. However, *the ideal gas law does not require a change in the conditions of a gas sample*. The ideal gas law implies that if you know any three of the physical properties of a gas, you can calculate the fourth property.

Example 15.7.1:

A 4.22 mol sample of Ar has a pressure of 1.21 atm and a temperature of 34°C. What is its volume?

Solution

The first step is to convert temperature to kelvins:

34 + 273 = 307 K

Now we can substitute the conditions into the ideal gas law:

$$(1.21 atm)(V) = (4.22\, mol)(0.08205 \frac{L.\, atm}{mol.\, K})(307\ K)$$

The *atm* unit is in the numerator of both sides, so it cancels. On the right side of the equation, the *mol* and *K* units appear in the numerator and the denominator, so they cancel as well. The only unit remaining is *L*, which is the unit of volume that we are looking for. We isolate the volume variable by dividing both sides of the equation by 1.21:

$$V = \frac{(4.22)(0.08205)(307)}{1.21} L$$

Then solving for volume, we get V = 87.9 L

? Exercise 15.7.1

A 0.0997 mol sample of O_2 has a pressure of 0.692 atm and a temperature of 333 K. What is its volume?

Answer

3.94 L

✓ Example 15.7.2:

At a given temperature, 0.00332 g of Hg in the gas phase has a pressure of 0.00120 mmHg and a volume of 435 L. What is its temperature?

Solution

We are not given the number of moles of Hg directly, but we are given a mass. We can use the molar mass of Hg to convert to the number of moles.

$$0.00332 \; g \, \cancel{Hg} \times \frac{1 \, mol \, Hg}{200.59 \; g \, \cancel{Hg}} = 0.0000165 \, mol = 1.65 \times 10^{-5} mol$$

Pressure is given in units of millimeters of mercury. We can either convert this to atmospheres or use the value of the ideal gas constant that includes the mmHg unit. We will take the second option. Substituting into the ideal gas law,

$$(0.00332 \, mm \, Hg)(435 \; L) = (1.65 \times 10^{-5} mol)(62.36 \frac{L.mmHg}{mol.K})T$$

The mmHg, L, and mol units cancel, leaving the K unit, the unit of temperature. Isolating T on one side, we get

$$T = \frac{(0.00332)(435)}{(1.65 \times 10^{-5})(62.36)} K$$

Then solving for K, we get T = 1,404 K

? Exercise 15.7.2

For a 0.00554 mol sample of H_2, P = 23.44 torr and T = 557 K. What is its volume?

Answer

8.21 L

The ideal gas law can also be used in stoichiometry problems.

✓ Example 15.7.3:

What volume of H_2 is produced at 299 K and 1.07 atm when 55.8 g of Zn metal react with excess HCl?

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Solution

Here we have a stoichiometry problem where we need to find the number of moles of H_2 produced. Then we can use the ideal gas law, with the given temperature and pressure, to determine the volume of gas produced. First, the number of moles of H_2 is calculated:

$$55.8\ g\ \cancel{Zn} \times \frac{1\ mol\ \cancel{Zn}}{65.41\ g\ \cancel{Zn}} \times \frac{1\ mol\ H_2}{1\ mol\ \cancel{Zn}} = 0.853\ H_2$$

Now that we know the number of moles of gas, we can use the ideal gas law to determine the volume, given the other conditions:

$$(1.07 atm)V = (0.853\, mol)(0.08205 \frac{L.\, atm}{mol.\, K})(299\ K)$$

All the units cancel except for L, for volume, which means *V* = 19.6 L

? Exercise 15.7.3

What pressure of HCl is generated if 3.44 g of Cl_2 are reacted in 4.55 L at 455 K?

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

Answer

0.796 atm

It should be obvious by now that some physical properties of gases depend strongly on the conditions. What we need is a set of standard conditions so that properties of gases can be properly compared to each other. **Standard Temperature and Pressure (STP)** is defined as exactly 100 kPa of pressure (0.986 atm) and 273 K (0°C). For simplicity, we will use 1 atm as standard pressure. Defining STP allows us to more directly compare the properties of gases that differ from one another.

One property shared among gases is a molar volume. The **molar volume** is the volume of 1 mol of a gas. At STP, the molar volume of a gas can be easily determined by using the ideal gas law:

$$(1\ atm)V = (1\ mol)(0.08205 \frac{L.\, atm}{mol.\, K})(273\ K)$$

All the units cancel except for L, the unit of volume. So *V* = 22.4 L

Note that we have not specified the identity of the gas; we have specified only that the pressure is 1 atm and the temperature is 273 K. This makes for a very useful approximation: *any gas at STP has a volume of 22.4 L per mole of gas*; that is, the molar volume at STP is 22.4 L/mol (Figure 15.7.1 Molar Volume). This molar volume makes a useful conversion factor in stoichiometry problems if the conditions are at STP. If the conditions are not at STP, a molar volume of 22.4 L/mol is not applicable. However, if the conditions are not at STP, the combined gas law can be used to calculate what the volume of the gas would be if at STP; then the 22.4 L/mol molar volume can be used.

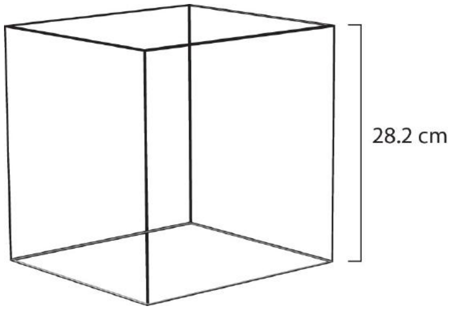


Figure 15.7.1: Molar Volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

✓ Example 15.7.4:

How many moles of Ar are present in 38.7 L at STP?

Solution

We can use the molar volume, 22.4 L/mol, as a conversion factor, but we need to reverse the fraction so that the L units cancel and mol units are introduced. It is a one-step conversion:

$$38.7\ \cancel{L} \times \frac{1\,mol}{22.4\ \cancel{L}} = 1.73\,mol$$

Exercise 15.7.4

What volume does 4.87 mol of Kr have at STP?

Answer

109 L

Example 15.7.5:

What volume of H_2 is produced at STP when 55.8 g of Zn metal react with excess HCl?

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Solution

This is a stoichiometry problem with a twist: we need to use the molar volume of a gas at STP to determine the final answer. The first part of the calculation is the same as in a previous example:

$$55.8\ g\,\cancel{Zn} \times \frac{1\ mol\,\cancel{Zn}}{65.41\ g\,\cancel{Zn}} \times \frac{1\,mol\,H_2}{1\ mol\,\cancel{Zn}} = 0.853\,H_2$$

Now we can use the molar volume, 22.4 L/mol, because the gas is at STP:

$$0.853\ mol\,\cancel{H_2} \times \frac{22.4\ L}{1\ mol\,\cancel{H_2}} = 19.1\ L\,H_2$$

Alternatively, we could have applied the molar volume as a third conversion factor in the original stoichiometry calculation.

Exercise 15.7.5

What volume of HCl is generated if 3.44 g of Cl_2 are reacted at STP?

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Answer

2.17 L

The ideal gas law can also be used to determine the density of gases. Density, recall, is defined as the mass of a substance divided by its volume:

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

Assume that you have exactly 1 mol of a gas. If you know the identity of the gas, you can determine the molar mass of the substance. Using the ideal gas law, you can also determine the volume of that mole of gas, using whatever the temperature and pressure conditions are. Then you can calculate the density of the gas by using

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

Example 15.7.6:

What is the density of N_2 at 25°C and 0.955 atm?

Solution

First, we must convert the temperature into kelvins:

25 + 273 = 298 K

If we assume exactly 1 mol of N_2, then we know its mass: 28.0 g. Using the ideal gas law, we can calculate the volume:

$$(0.955\,atm)V = (1\,mol)(0.08205\frac{L.\,atm}{mol.\,K})(298\,K)$$

All the units cancel except for L, the unit of volume. So V = 25.6 L

Knowing the molar mass and the molar volume, we can determine the density of N_2 under these conditions:

$$d = \frac{28.0\,g}{25.6\,L} = 1.09\,g/L$$

? Exercise 15.7.6

What is the density of CO_2 at a pressure of 0.0079 atm and 227 K? (These are the approximate atmospheric conditions on Mars.)

Answer

0.019 g/L

Chemistry Is Everywhere: Breathing

Breathing (more properly called *respiration*) is the process by which we draw air into our lungs so that our bodies can take up oxygen from the air. Let us apply the gas laws to breathing.

Start by considering pressure. We draw air into our lungs because the diaphragm, a muscle underneath the lungs, moves down to reduce pressure in the lungs, causing external air to rush in to fill the lower-pressure volume. We expel air by the diaphragm pushing against the lungs, increasing pressure inside the lungs and forcing the high-pressure air out. What are the pressure changes involved? A quarter of an atmosphere? A tenth of an atmosphere? Actually, under normal conditions, it's only 1 or 2 torr of pressure difference that makes us breathe in and out.

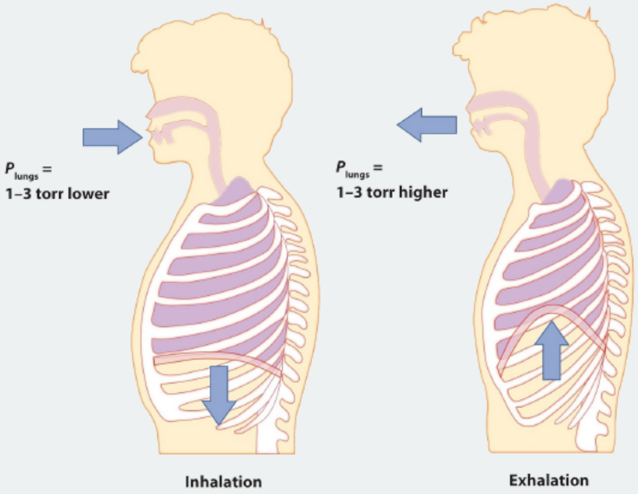


Figure 15.7.2 Breathing Mechanics. Breathing involves pressure differences between the inside of the lungs and the air outside. The pressure differences are only a few torr.

A normal breath is about 0.50 L. If room temperature is about 22°C, then the air has a temperature of about 295 K. With normal pressure being 1.0 atm, how many moles of air do we take in for every breath? The ideal gas law gives us an answer:

$$(1.0\,atm)(0.50\,L) = n(0.08205\frac{L.\,atm}{mol.\,K})(295\,K)$$

> Solving for the number of moles, we get
>
> $n = 0.021$ mol air
>
> This ends up being about 0.6 g of air per breath—not much, but enough to keep us alive.

Summary

- The ideal gas law relates the four independent physical properties of a gas at any time.
- The ideal gas law can be used in stoichiometry problems whose chemical reactions involve gases.
- Standard temperature and pressure (STP) are a useful set of benchmark conditions to compare other properties of gases.
- At STP, gases have a volume of 22.4 L per mole.
- The ideal gas law can be used to determine the density of gases.

CHAPTER OVERVIEW

16: Solids, Liquids, and Phase Changes

Here on Earth, we all live in a state of gravity. Not only us, but everything around us, including water, is being pulled towards the center of the planet by gravity. True, it is nice that our dogs don't float off into space, but when a child drops their ice cream (which is full of water, by the way) they don't have to know about gravity to be upset

***Floating Water in Zero Gravity**: Once again, astronauts on the International Space Station dissolved an effervescent tablet in a floating ball of water, and captured images using a camera capable of recording four times the resolution of normal high-definition cameras. The higher resolution images and higher frame rate videos can reveal more information when used on science investigations, giving researchers a valuable new tool aboard the space station. This footage is one of the first of its kind. The cameras are being evaluated for capturing science data and vehicle operations by engineers at NASA's Marshall Space Flight Center in Huntsville, Alabama.*

If you go far enough out in space, for instance, onto the International Space Station, gravity becomes negligible, and the laws of physics act differently than here on Earth. Just how might water act in a place of zero gravity? This video above from NASA gives you a good idea of how different water behaves when the effects if gravity are counteracted.

Actually, on the International Space Station, there is plenty of gravity—according to NASA scientists, the pull of Earth's gravity on the space station and its occupants is substantial: about 90 percent of the force at the Earth's surface. But since the space station is continuously falling around our planet, the astronauts and objects on board are in a kind of free-fall, too, and feel nearly weightless. Water on the space station behaves as if in a zero-gravity environment.

This unique picture shows not only a water drop but also an air bubble inside of the water drop. Notice they both behave the same....according to the laws of physics in space. They both form spheres. This makes sense, as without gravity to tug downward, the forces governing the objects are all the same. So, the water drop (and air bubble) form themselves so they occupy a shape having the least amount of surface area, which is a sphere. On Earth, gravity distorts the shape, but not in space.

Consider what would happen on Earth: The air bubble, lighter than water, would race upward to burst through the surface of the droplet. In space, the air bubble doesn't rise because it is no lighter than the water around it—there's no buoyancy. The droplet doesn't fall from the leaf because there's no force to pull it off. It's stuck there by molecular adhesion.

Sticky water. No buoyancy. These are some of the factors future space-dwellers must take into account when they plan their space gardens. If water is sprayed onto the base of the plant will it trickle down to the roots? More likely it will stick to the stem or adhere to the material in which the plant grows. As humans spend more time and go farther out in space in the future, the physics of "space water" will need to be well understood.

Chapter Sections

Attributions

- The Physics of Space Gardens, NASA.

16.1: The Phases - Solids, Liquids, and Gases

Learning Objectives

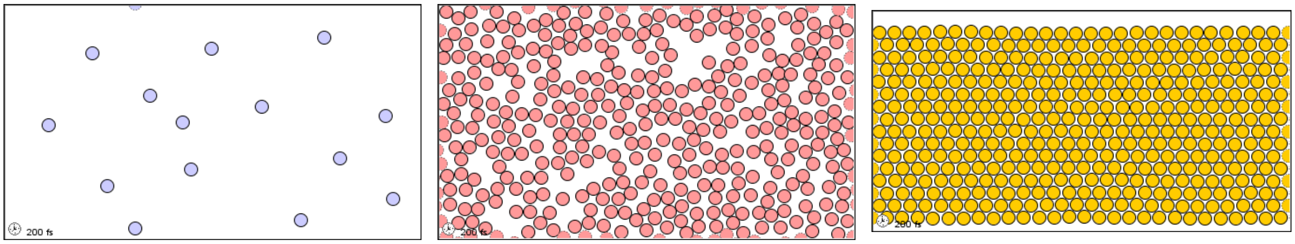
- To be familiar with the kinetic molecular description of liquids.

The *physical* properties of a substance depends upon its physical state. Water vapor, liquid water and ice all have the same *chemical* properties, but their *physical* properties are considerably different. In general *covalent bonds* determine: molecular shape, bond energies, *chemical* properties, while *intermolecular forces* (non-covalent bonds) influence the *physical* properties of liquids and solids. The kinetic molecular theory of gases gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

Figure 16.1.1: The three common states of matter. From the left, they are solid, liquid, and gas, represented by an ice sculpture, a drop of water, and the air around clouds, respectively. Images used with permission from Wikipedia.

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance. The intermolecular forces are attractive forces that try to draw the particles together (Figure $16.1.2$). A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces.

Molecular level picture of gases, liquids and solids.



(a) in the gaseous state

(b) as a liquid

(c) *in solid form*

Figure 16.1.2: Molecular level picture of gases, liquids and solids.

Below is an overview of the general properties of the three different phases of matter.

Properties of Gases

- A collection of widely separated molecules
- The kinetic energy of the molecules is greater than any attractive forces between the molecules
- The lack of any significant attractive force between molecules allows a gas to expand to fill its container
- If attractive forces become large enough, then the gases exhibit non-ideal behavior

Properties of Liquids

- The intermolecular attractive forces are strong enough to hold molecules close together
- Liquids are more dense and less compressible than gasses
- Liquids have a definite volume, independent of the size and shape of their container

- The attractive forces are ***not*** strong enough, however, to keep neighboring molecules in a fixed position and molecules are free to move past or slide over one another

> *Thus, liquids can be poured and assume the shape of their containers.*

Properties of Solids

- The intermolecular forces between neighboring molecules are strong enough to keep them locked in position
- Solids (like liquids) are not very compressible due to the lack of space between molecules
- If the molecules in a solid adopt a highly ordered packing arrangement, the structures are said to be ***crystalline***

> *Due to the strong intermolecular forces between neighboring molecules, solids are rigid.*

> - Cooling a gas may change the state to a liquid
> - Cooling a liquid may change the state to a solid
> - Increasing the pressure on a gas may change the state to a liquid
> - Increasing the pressure on a liquid may change the state to a solid

Video 16.1.1: Video highlighting the properties for the three states of matter. Source found at www.youtube.com/watch?v=s-KvoVzukHo.

Physical Properties of Liquids

In a gas, the distance between molecules, whether monatomic or polyatomic, is very large compared with the size of the molecules; thus gases have a low density and are highly compressible. In contrast, the molecules in liquids are very close together, with essentially no empty space between them. As in gases, however, the molecules in liquids are in constant motion, and their kinetic energy (and hence their speed) depends on their temperature. We begin our discussion by examining some of the characteristic properties of liquids to see how each is consistent with a modified kinetic molecular description.

The properties of liquids can be explained using a modified version of the kinetic molecular theory of gases described previously. This model explains the higher density, greater order, and lower compressibility of liquids versus gases; the thermal expansion of liquids; why they diffuse; and why they adopt the shape (but not the volume) of their containers. A kinetic molecular description of liquids must take into account both the nonzero volumes of particles and the presence of strong intermolecular attractive forces. Solids and liquids have particles that are fairly close to one another, and are thus called "**condensed phases**" to distinguish them from gases

- **Density**: The molecules of a liquid are packed relatively close together. Consequently, liquids are much denser than gases. The density of a liquid is typically about the same as the density of the solid state of the substance. Densities of liquids are therefore more commonly measured in units of grams per cubic centimeter (g/cm^3) or grams per milliliter (g/mL) than in grams per liter (g/L), the unit commonly used for gases.
- **Molecular Order:** Liquids exhibit short-range order because strong intermolecular attractive forces cause the molecules to pack together rather tightly. Because of their higher kinetic energy compared to the molecules in a solid, however, the molecules in a liquid move rapidly with respect to one another. Thus unlike the ions in the ionic solids, the molecules in liquids are not

arranged in a repeating three-dimensional array. Unlike the molecules in gases, however, the arrangement of the molecules in a liquid is not completely random.

- **Compressibility**: Liquids have so little empty space between their component molecules that they cannot be readily compressed. Compression would force the atoms on adjacent molecules to occupy the same region of space.
- **Thermal Expansion**: The intermolecular forces in liquids are strong enough to keep them from expanding significantly when heated (typically only a few percent over a 100°C temperature range). Thus the volumes of liquids are somewhat fixed. Notice from Table S1 (with a shorten version in Table 16.1.1) that the density of water, for example, changes by only about 3% over a 90-degree temperature range.

Table 16.1.1: The Density of Water at Various Temperatures

T (°C)	Density (g/cm^3)
0	0.99984
30	0.99565
60	0.98320
90	0.96535

- **Diffusion**: Molecules in liquids diffuse because they are in constant motion. A molecule in a liquid cannot move far before colliding with another molecule, however, so the mean free path in liquids is very short, and the rate of diffusion is much slower than in gases.
- **Fluidity**: Liquids can flow, adjusting to the shape of their containers, because their molecules are free to move. This freedom of motion and their close spacing allow the molecules in a liquid to move rapidly into the openings left by other molecules, in turn generating more openings, and so forth (Figure 16.1.3).

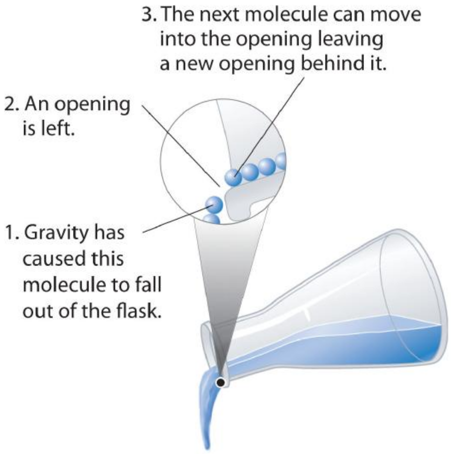


Figure 16.1.3: Why Liquids Flow. Molecules in a liquid are in constant motion. Consequently, when the flask is tilted, molecules move to the left and down due to the force of gravity, and the openings are occupied by other molecules. The result is a net flow of liquid out of the container. (CC BY-SA-NC; Anonymous vy request).

Contributors and Attributions

- Mike Blaber (Florida State University)

16.2: Phase Changes

We have previously described **evaporation**, the change of a liquid to a gas. This process is always endothermic, because energy is required to completely disrupt the IMFs of attraction between the particles. The reverse process of evaporation is **condensation**, which is always an exothermic process because IMFs of attraction form among the particles as they congregate into droplets. The phase changes involving solids are described below.

Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as **sublimation**. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms (Figure $16.2.1$). The reverse of sublimation is called **deposition**, a process in which gaseous substances directly change into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.

Figure* $16.2.1$*: *Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)*

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔHsub, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g) \quad \Delta H_{\text{sub}} = 26.1\ \mathrm{kJ/mol} \tag{16.2.1}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$\mathrm{CO_2}(g) \longrightarrow \mathrm{CO_2}(s) \quad \Delta H_{\text{dep}} = -\Delta H_{\text{sub}} = -26.1\ \mathrm{kJ/mol} \tag{16.2.2}$$

Fusion/Melting and Solidification/Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or melting. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure \(\PageIndex{2}\)).

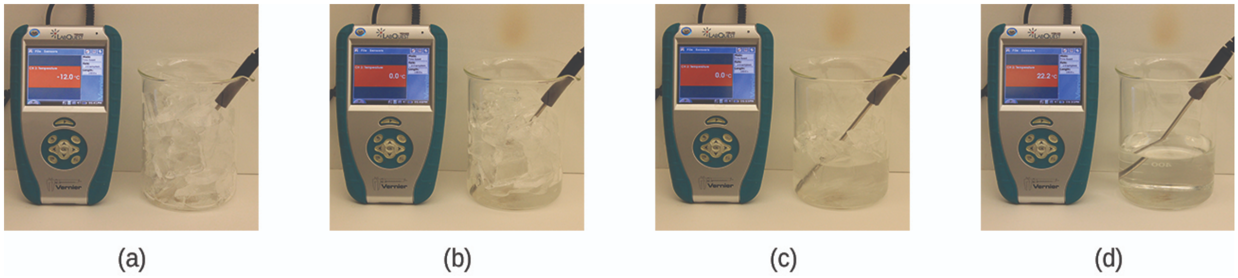


Figure 16.2.2: *(a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott).*

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal process of melting and freezing occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the melting point of the solid or the freezing point of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$\mathrm{H_2O}_{(s)} \rightarrow \mathrm{H_2O}_{(l)} \quad \Delta H_{\text{fus}} = 6.01 \text{ kJ/mol} \tag{16.2.3}$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$\mathrm{H_2O}_{(l)} \rightarrow \mathrm{H_2O}_{(s)} \quad \Delta H_{\text{frz}} = -\Delta H_{\text{fus}} = -6.01 \text{ kJ/mol} \tag{16.2.4}$$

Selected molar enthalpies of fusion are tabulated in Table 16.2.1. Solids like ice which have strong intermolecular forces have much higher values than those like CH_4 with weak ones. Note that the enthalpies of fusion and vaporization change with temperature.

Table 16.2.1: Molar Enthalpies of Fusion and Vaporization of Selected Substances.

Substance	**Formula**	**ΔH(fusion) / kJ mol^1**	**Melting Point / K**	**ΔH(vaporization) / kJ mol^{-1}**	**Boiling Point / K**	**$(\Delta H_v/T_b)$ / $\text{JK}^{-1}\ \text{mol}^{-1}$**
Neon	Ne	0.33	24	1.80	27	67
Oxygen	O_2	0.44	54	6.82	90.2	76
Methane	CH_4	0.94	90.7	8.18	112	73
Ethane	C_2H_6	2.85	90.0	14.72	184	80
Chlorine	Cl_2	6.40	172.2	20.41	239	85
Carbon tetrachloride	CCl_4	2.67	250.0	30.00	350	86
Water*	H_2O	6.00678 at 0°C, 101kPa 6.354 at 81.6 °C, 2.50 MPa	273.1	40.657 at 100 °C, 45.051 at 0 °C, 46.567 at -33 °C	373.1	109
n-Nonane	C_9H_{20}	19.3	353	40.5	491	82

Substance	Formula	ΔH(fusion) / kJ mol^{1}	Melting Point / K	ΔH(vaporization) / kJ mol^{-1}	Boiling Point / K	$(\Delta H_v/T_b)$ / JK^{-1} mol^{-1}
Mercury	Hg	2.30	234	58.6	630	91
Sodium	Na	2.60	371	98	1158	85
Aluminum	Al	10.9	933	284	2600	109
Lead	Pb	4.77	601	178	2022	88

*http://www1.lsbu.ac.uk/water/data.html

Energy Changes Associated with Phase Changes

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law.

$$\begin{array}{c} \text{solid} \longrightarrow \text{liquid} \quad \Delta H_{\text{fus}} \\ \underline{\text{liquid} \longrightarrow \text{gas} \quad \Delta H_{\text{vap}}} \\ \text{solid} \longrightarrow \text{gas} \quad \Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \end{array} \tag{16.2.5}$$

Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure $16.2.3$ For example:

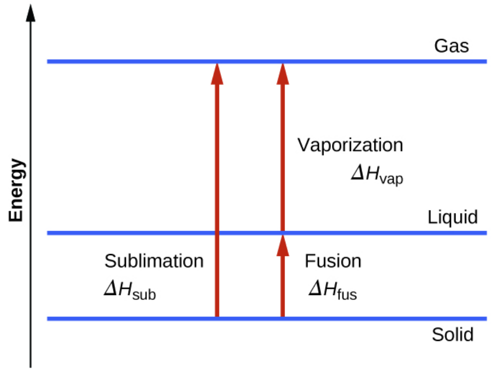


Figure $\mathbf{16.2.3}$ *: For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.*

Contributors

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16.3: Phase Change Diagrams

Freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure 16.3.3 shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

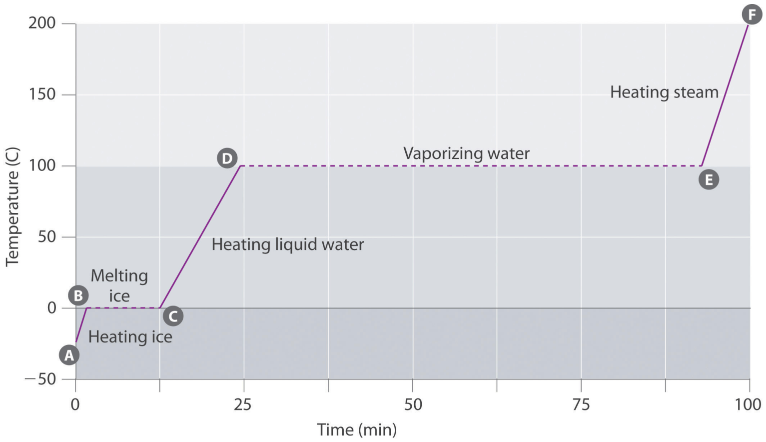


Figure 16.3.1: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure 16.3.3, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 16.3.3, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure 16.3.4 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 16.3.3, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

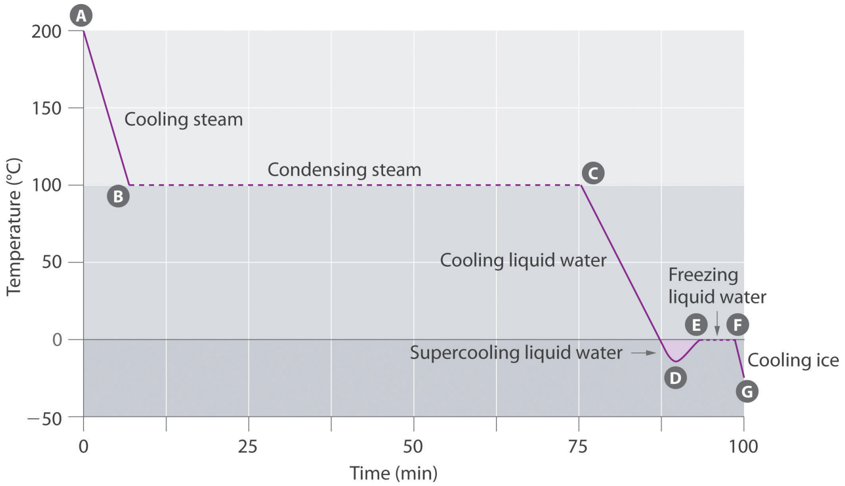


Figure 16.3.2: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth’s climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.

16.3.1 Example : Cooling Hot Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy:

Substitute the values given into the general equation relating heat gained to heat lost (Equation 5.39) to obtain the final temperature of the mixture.

Solution:

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T \tag{16.3.1}$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

16.3.1 Exercise : Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example 16.3.1

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

16.4: Phase Diagrams

Learning Objectives

- To understand the basics of a one-component phase diagram as a function of temperature and pressure in a closed system.
- To be able to identify the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical fluid.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure $16.4.1$). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure $16.4.1$) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

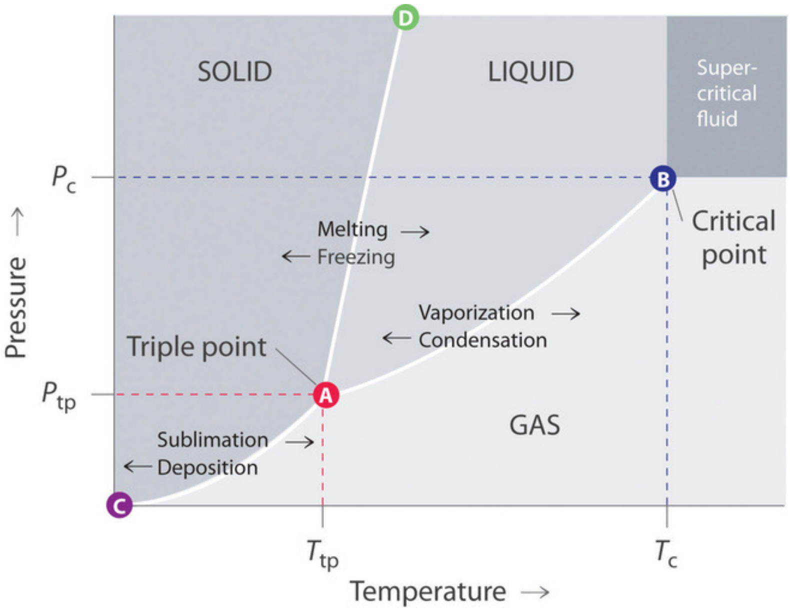


Figure 16.4.1: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

> The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure $16.4.1$, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure $16.4.1$, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure 16.4.2 shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to “freeze-dry” foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

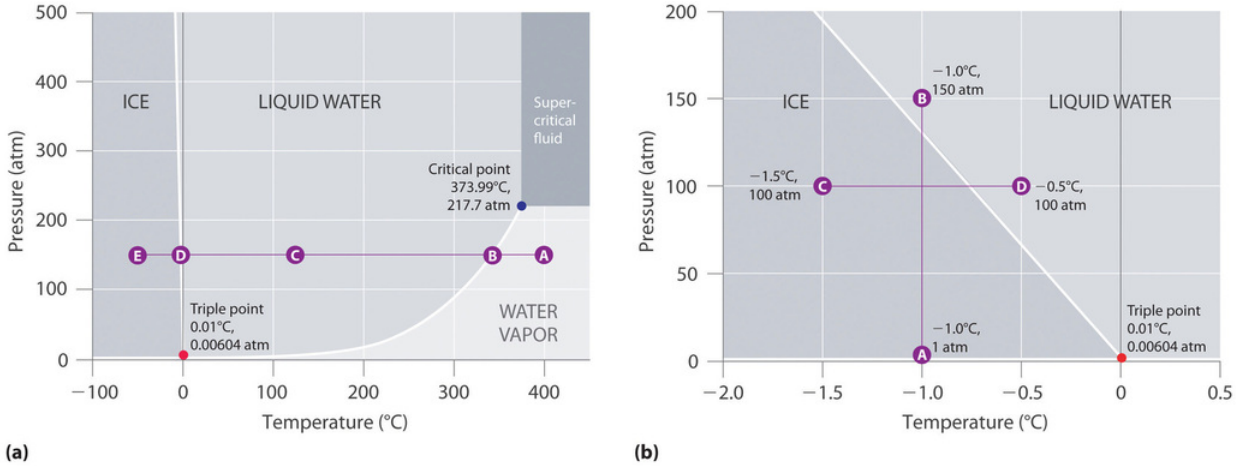


Figure 16.4.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 16.4.1).

The phase diagram for water illustrated in Figure 16.4.2b shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure 16.4.1; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure 16.4.2b point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Ice Skating: An Incorrect Hypothesis of Phase Transitions

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater’s blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively satisfying, it is incorrect, as we can show by a simple calculation.

Pressure from ice skates on ice. from wikihow.com.

Recall that pressure (*P*) is the force (*F*) applied per unit area (*A*):

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

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

$$F = mg$$

where *m* is the mass and *g* is the acceleration due to Earth's gravity (9.81 m/s^2). Thus the force is

$$F = (75.0\ kg)(9.81\ m/s^2) = 736\ (kg \bullet m)/s^2 = 736 N$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

$$A = (2.0 \times 10^{-3}\ m)(25 \times 10^{-2}\ m) = 5.0 \times 10^{-4} m^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

$$P = \frac{736\ N}{5.0 \times 10^{-4}\ m^2} = 1.5 \times 10^6\ N/m^2 = 1.5 \times 10^6\ Pa = 15\ atm$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C, and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water. These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about −7°C, when the number of lubricating surface water layers decreases.

✓ Example 16.4.1: Water

Referring to the phase diagram of water in Figure $16.4.2$:

a. predict the physical form of a sample of water at 400°C and 150 atm.
b. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A. Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.
B. Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

a. **A** Locate the starting point on the phase diagram in part (a) in Figure $16.4.2$. The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at *T* = 400°C and *P* = 150 atm is a gas.

b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure 16.4.2. At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At P = 150 atm and T = −50°C, therefore, the sample is solid ice.

? Exercise 16.4.2

Referring to the phase diagram of water in Figure 16.4.2, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer

The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure 16.4.3) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.

Dry ice ($CO_2(s)$) sublimed in air under room temperature and pressure. from Wikipedia.

Also notice the critical point at 30.98°C and 72.79 atm. Supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

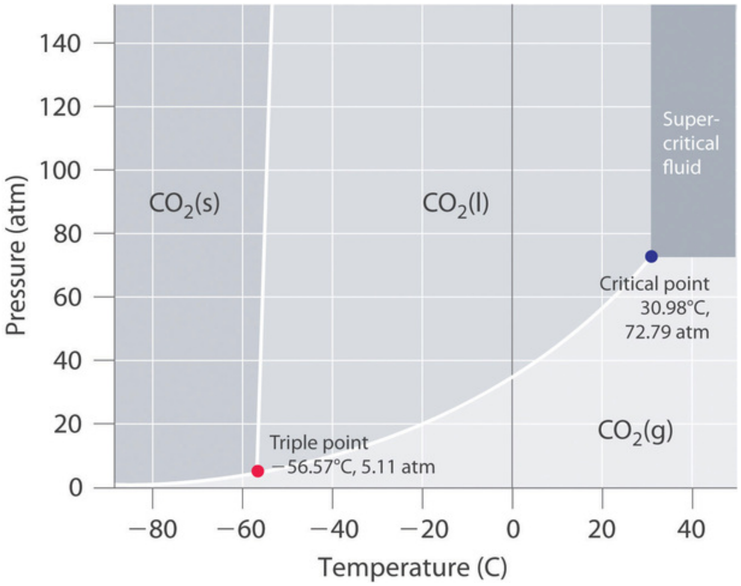


Figure 16.4.3: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

The triple point is at -57.57 degrees C and 5.11 atm. The critical point is at 30.98 degree C and 72.79 atm.

The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure 16.4.1.

Figure 16.4.1: Critical Temperatures and Pressures of Some Simple Substances

Substance	**T_c (°C)**	**P_c (atm)**
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

> High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.

Supercritical Fluids

A Video Discussing Phase Diagrams. Video Source: Phase Diagrams(opens in new window) [youtu.be]

16.5: Intermolecular Forces

Learning Objectives

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

> *The properties of liquids are intermediate between those of gases and solids, but are more similar to solids.*

Intermolecular forces determine bulk properties, such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures.

In this section, we explicitly consider three kinds of intermolecular interactions. There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding, and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure 16.5.1a.

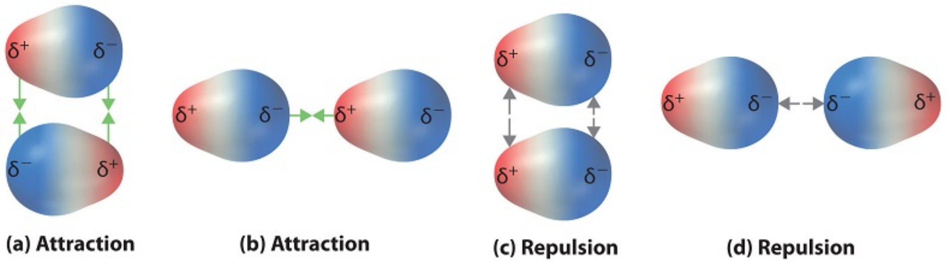


Figure 16.5.1: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions. (CC BY-SA-NC; anonymous)

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure 16.5.1c). Hence dipole–dipole interactions, such as those in Figure 16.5.1b, are *attractive intermolecular interactions*, whereas those in Figure 16.5.1d are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 16.5.2. On average, however, the attractive interactions dominate.

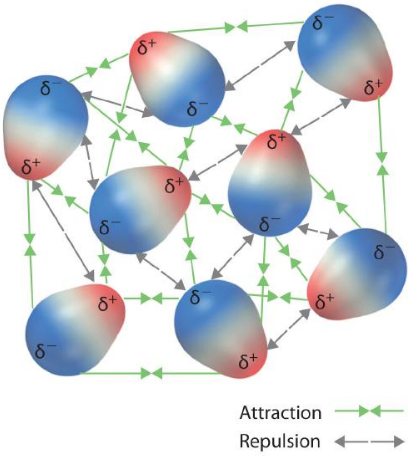


Figure 16.5.2: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules. (CC BY-SA-NC; anonymous)

The green arrows pointing towards each other represent attraction. The gray arrows pointing away from each other represent repulsion

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^3$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^3, or 8-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure. Conversely, NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 16.5.1.

Table 16.5.1: Relationships Between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

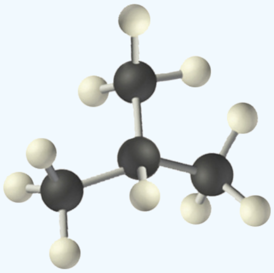
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*

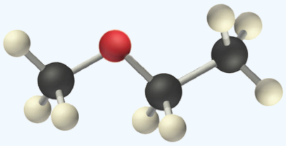
Video Discussing Dipole Intermolecular Forces. Source: Dipole Intermolecular Force, YouTube(opens in new window) [youtu.be]

✓ Example 16.5.1

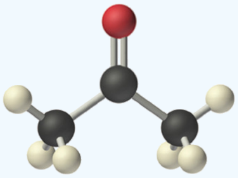
Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



2-Methylpropane



Ethyl methyl ether



Acetone

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds.

The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point.

Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point.

Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.

Thus we predict the following order of boiling points:

2-methylpropane < ethyl methyl ether < acetone

This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

? Exercise 16.5.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far, we have considered only interactions between polar molecules. Other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature; why others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 16.5.2).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 16.5.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 16.5.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

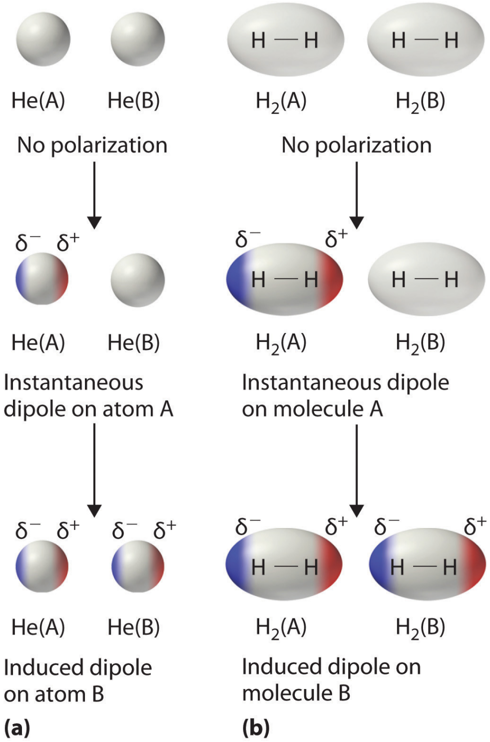
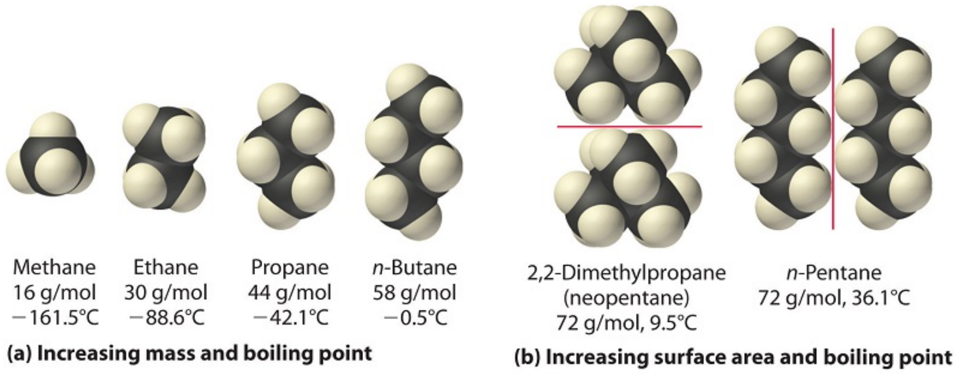


Figure 16.5.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 16.5.3, tends to become more pronounced as atomic and molecular masses increase (Table 16.5.2). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus, London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 16.5.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 16.5.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).



(a) Increasing mass and boiling point

(b) Increasing surface area and boiling point

Figure 16.5.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Video Discussing London/Dispersion Intermolecular Forces. Source: Dispersion Intermolecular Force, YouTube(opens in new window) [youtu.be]

✓ Example 16.5.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds, and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

? Exercise 16.5.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent, Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 16.5.5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

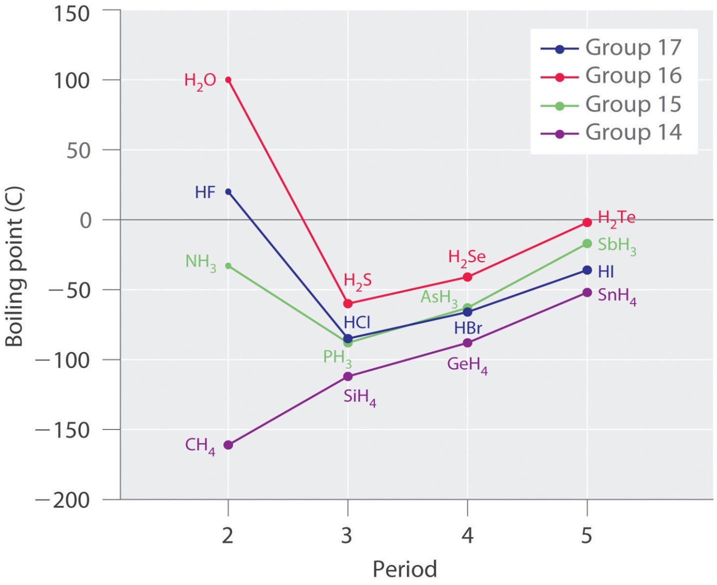


Figure 16.5.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Group 14 is in purple, group 15 is in green, group 16 is red, and group 17 is blue. Graph of boiling point against period.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 16.5.6. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O⋯H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water, rather than sinks.

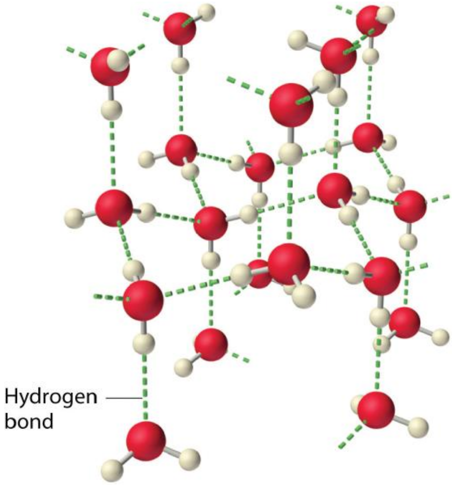


Figure 16.5.6: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cage like structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

> *Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.*

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Video Discussing Hydrogen Bonding Intermolecular Forces. Source: Hydrogen Bonding Intermolecular Force, YouTube(opens in new window) [youtu.be]

✓ Example 16.5.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

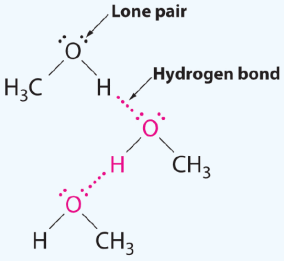
Strategy:

A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A. Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B. The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



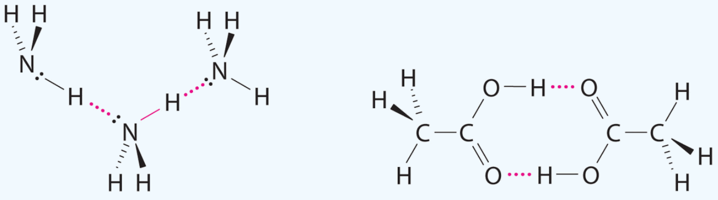
Hydrogen bonding in methanol

? Exercise 16.5.3

Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia

Hydrogen bonding in acetic acid

Hydrogen bonding in ammonia between nitrogen and hydrogen. hydrogen bonding in acetic acid is between oxygen and hydrogen.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

✓ Example 16.5.4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$\text{He } (-269°\text{C}) < \text{Ar } (-185.7°\text{C}) < N_2O\ (-88.5°\text{C}) < C_{60}\ (>280°\text{C}) < \text{NaCl } (1465°\text{C}).$$

? Exercise 16.5.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

✓ Example 16.5.5

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.
b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.
c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

? Exercise 16.5.6

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

> dipole-dipole interactions

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid, or the liquid and gas phases, are due to changes in intermolecular interactions, but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^3$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules; their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones, because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O⋯H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cage like structure that is less dense than liquid water.

16.6: Properties of Liquids

Learning Objectives

- To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions:

- surface tension,
- capillary action, and
- viscosity.

Surface Tension

If liquids tend to adopt the shapes of their containers, then why do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of 7.29 x 10^{-2} J/m^2 (at 20°C), while mercury with metallic bonds has as surface tension that is 15 times higher: 4.86 x 10^{-1} J/m^2 (at 20°C).

Figure $16.6.1$ presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

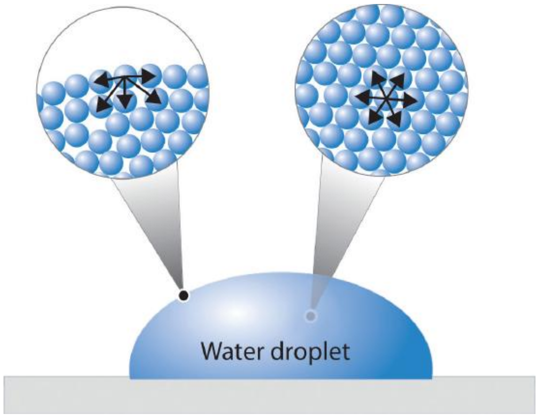


Figure 16.6.1: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it “floats,” even though steel is much denser than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is even observable in the zero gravity conditions of space as shown in Figure $16.6.2$ (and more so in the video link) where water wrung from a wet towel continues to float along the towel's surface!

Figure 16.6.2: The Effects of the High Surface Tension of Liquid Water. The full video can be found at www.youtube.com/watch?v=9jB7rOC5kG8.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2) or dyne per centimeter (dyn/cm), where 1 dyn = 1×10^{-5} N. The values of the surface tension of some representative liquids are listed in Table 16.6.1. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

Table 16.6.1: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension ($\times 10^{-3}$ J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure $16.6.3$. When a glass capillary is is placed in liquid water, water rises up into the capillary. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

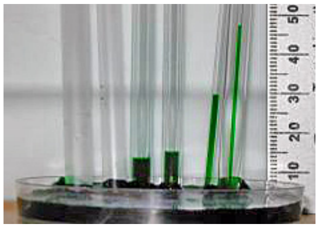


Figure $16.6.3$: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.

> - Cohesive forces bind molecules of the same type together
> - Adhesive forces bind a substance to a surface

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (Figure $16.6.4$). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure $16.6.4$).

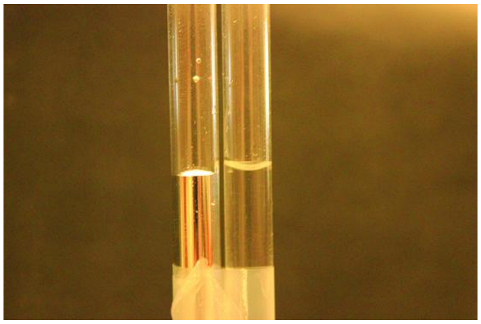


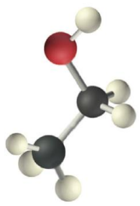
Figure $16.6.4$: The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

> Polar substances are drawn up a glass capillary and generally have a concave meniscus.

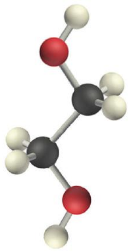
Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and “wick” the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 11.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



Ethanol



Ethylene glycol

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

> *Viscosity increases as intermolecular interactions or molecular size increases.*

Video Discussing Surface Tension and Viscosity. Video Link: Surface Tension, Viscosity, & Melting Point, YouTube(opens in new window) [youtu.be]

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures.

Figure 16.6.5: Oil being drained from a car

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity (Figure 16.6.5). So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives “for improved engine performance” are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

✓ Example 16.6.1

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A. Identify the cohesive forces in the motor oil.
B. Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains.

B Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

? Exercise 16.6.1

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer

Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Summary

Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. **Surface tension** is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

16.7: Solids

Learning Objectives

- To understand the correlation between bonding and the properties of solids.
- To classify solids as ionic, molecular, covalent (network), or metallic, where the general order of increasing strength of interactions.

Crystalline solids fall into one of four categories. All four categories involve packing discrete molecules or atoms into a lattice or repeating array, though *network solids* are a special case. The categories are distinguished by the nature of the interactions holding the discrete molecules or atoms together. Based on the nature of the forces that hold the component atoms, molecules, or ions together, solids may be formally classified as ionic, molecular, covalent (network), or metallic. The variation in the relative strengths of these four types of interactions correlates nicely with their wide variation in properties.

Table 16.7.1: Solids may be formally classified as ionic, molecular, covalent (network), or metallic

Type of Solid	Interaction	Properties	Examples
Ionic	Ionic	High Melting Point, Brittle, Hard	NaCl, MgO
Molecular	Hydrogen Bonding, Dipole-Dipole, London Dispersion	Low Melting Point, Nonconducting	H_2, CO_2
Metallic	Metallic Bonding	Variable Hardness and Melting Point (depending upon strength of metallic bonding), Conducting	Fe, Mg
Network	Covalent Bonding	High Melting Point, Hard, Nonconducting	C (diamond), SiO_2 (quartz)

In ionic and molecular solids, there are no chemical bonds between the molecules, atoms, or ions. The solid consists of discrete chemical species held together by intermolecular forces that are **electrostatic** or **Coulombic** in nature. This behavior is most obvious for an ionic solid such as $NaCl$, where the positively charged Na^+ ions are attracted to the negatively charged Cl^- ions. Even in the absence of ions, however, electrostatic forces are operational. For polar molecules such as CH_2Cl_2, the positively charged region of one molecule is attracted to the negatively charged region of another molecule (dipole-dipole interactions). For a nonpolar molecule such as CO_2, which has no permanent dipole moment, the random motion of electrons gives rise to temporary polarity (a temporary dipole moment). Electrostatic attractions between two temporarily polarized molecules are called London Dispersion Forces.

Hydrogen bonding is a term describing an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. (See the IUPAC Provisional Recommendation on the definition of a hydrogen bond.) Dots are employed to indicate the presence of a hydrogen bond: X–H•••Y. The attractive interaction in a hydrogen bond typically has a strong electrostatic contribution, but dispersion forces and weak covalent bonding are also present.

In metallic solids and network solids, however, chemical bonds hold the individual chemical subunits together. The crystal is essential a single, macroscopic molecule with continuous chemical bonding throughout the entire structure. In metallic solids, the valence electrons are no longer exclusively associated with a single atom. Instead these electrons exist in molecular orbitals that are delocalized over many atoms, producing an electronic band structure. The metallic crystal essentially consists of a set of metal cations in a sea of electrons. This type of chemical bonding is called metallic bonding.

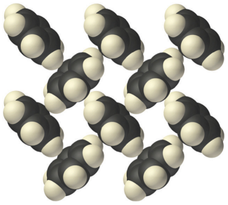
Ionic Solids

You learned previously that an ionic solid consists of positively and negatively charged ions held together by electrostatic forces. The strength of the attractive forces depends on the charge and size of the ions that compose the lattice and determines many of the physical properties of the crystal.

The **lattice energy** (i.e., the energy required to separate 1 mol of a crystalline ionic solid into its component ions in the gas phase) is directly proportional to the product of the ionic charges and inversely proportional to the sum of the radii of the ions. For example, NaF and CaO both crystallize in the face-centered cubic (fcc) sodium chloride structure, and the sizes of their component ions are about the same: Na^+ (102 pm) versus Ca^{2+} (100 pm), and F^- (133 pm) versus O^{2-} (140 pm). Because of the higher charge on the ions in CaO, however, the lattice energy of CaO is almost four times greater than that of NaF (3401 kJ/mol versus 923 kJ/mol). The forces that hold Ca and O together in CaO are much stronger than those that hold Na and F together in NaF, so the heat of fusion of CaO is almost twice that of NaF (59 kJ/mol versus 33.4 kJ/mol), and the melting point of CaO is 2927°C versus 996°C for NaF. In both cases, however, the values are large; that is, simple ionic compounds have high melting points and are relatively hard (and brittle) solids.

Molecular Solids

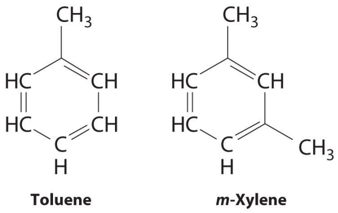
Molecular solids consist of atoms or molecules held to each other by dipole–dipole interactions, London dispersion forces, or hydrogen bonds, or any combination of these. The arrangement of the molecules in solid benzene is as follows:



The structure of solid benzene. In solid benzene, the molecules are not arranged with their planes parallel to one another but at 90° angles. (CC BY-NC-SA; Anonymous by request).

Because the intermolecular interactions in a molecular solid are relatively weak compared with ionic and covalent bonds, molecular solids tend to be soft, low melting, and easily vaporized (ΔH_{fus} and ΔH_{vap} are low). For similar substances, the strength of the London dispersion forces increases smoothly with increasing molecular mass. For example, the melting points of benzene (C_6H_6), naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$), with one, two, and three fused aromatic rings, are 5.5°C, 80.2°C, and 215°C, respectively. The enthalpies of fusion also increase smoothly within the series: benzene (9.95 kJ/mol) < naphthalene (19.1 kJ/mol) < anthracene (28.8 kJ/mol). If the molecules have shapes that cannot pack together efficiently in the crystal, however, then the melting points and the enthalpies of fusion tend to be unexpectedly low because the molecules are unable to arrange themselves to optimize intermolecular interactions. Thus toluene ($C_6H_5CH_3$) and m-xylene [m-$C_6H_4(CH_3)_2$] have melting points of −95°C and −48°C, respectively, which are significantly lower than the melting point of the lighter but more symmetrical analog, benzene.

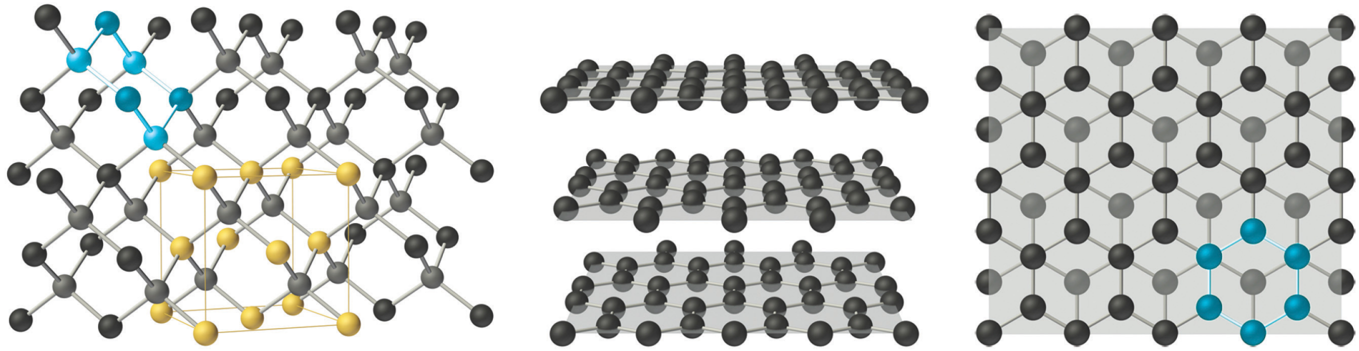
Self-healing rubber is an example of a molecular solid with the potential for significant commercial applications. The material can stretch, but when snapped into pieces it can bond back together again through reestablishment of its hydrogen-bonding network without showing any sign of weakness. Among other applications, it is being studied for its use in adhesives and bicycle tires that will self-heal.



Toluene and m-xylene. The methyl groups attached to the phenyl ring in toluene and m-xylene prevent the rings from packing together as in solid benzene. (CC BY-NC-SA; Anonymous by request).

Covalent Network Solids

Covalent solids are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure 16.7.1, consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.



(a) Diamond **(b) Graphite**

Figure 16.7.1: The Structures of Diamond and Graphite. (a) Diamond consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer. (CC BY-NC-SA; Anonymous by request).

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in Section 12.3, except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (SiO_2), shown in Section 12.1, can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in Figure $16.7.1$. It contains planar networks of six-membered rings of sp2 hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized 2pz orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in Chapter 9. In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimes at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the "lead" in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other hand, is colorless when pure because it has no delocalized electrons. Table $16.7.2$ compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table 16.7.2: A Comparison of Intermolecular (ΔH_{sub}) and Intramolecular Interactions

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
phosphorus (s)	58.98	201
sulfur (s)	64.22	226

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
iodine (s)	62.42	149

Carbon: An example of an Covalent Network Solid

In network solids, conventional chemical bonds hold the chemical subunits together. The bonding between chemical subunits, however, is identical to that within the subunits, resulting in a continuous network of chemical bonds. One common examples of network solids are diamond (a form of pure carbon) Carbon exists as a pure element at room temperature in three different forms: graphite (the most stable form), diamond, and fullerene.

Diamonds

The structure of diamond is shown at the right in a "ball-and-stick" format. The balls represent the carbon atoms and the sticks represent a covalent bond. Be aware that in the "ball-and-stick" representation the size of the balls do not accurately represent the size of carbon atoms. In addition, a single stick is drawn to represent a covalent bond irrespective of whether the bond is a single, double, or triple bond or requires resonance structures to represent. In the diamond structure, all bonds are single covalent bonds (σ bonds). The "space-filling" format is an alternate representation that displays atoms as spheres with a radius equal to the van der Waals radius, thus providing a better sense of the size of the atoms.

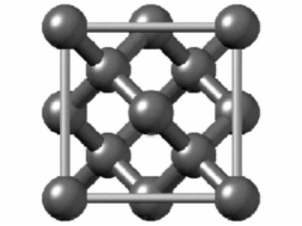


Figure 16.7.2: Rotating model of diamond cubic. Figure used with permission from Wikipedia

Notice that diamond is a network solid. The entire solid is an "endless" repetition of carbon atoms bonded to each other by covalent bonds. (In the display at the right, the structure is truncated to fit in the display area.)

Questions to consider

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in diamond?
- The diamond structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- Diamond are renowned for its hardness. Explain why this property is expected on the basis of the structure of diamond.

Graphite

The most stable form of carbon is graphite. Graphite consists of sheets of carbon atoms covalently bonded together. These sheets are then stacked to form graphite. Figure 16.7.3 shows a ball-and-stick representation of graphite with sheets that extended "indefinitely" in the xy plane, but the structure has been truncated for display purposed. Graphite may also be regarded as a network solid, even though there is no bonding in the z direction. Each layer, however, is an "endless" bonded network of carbon atoms.

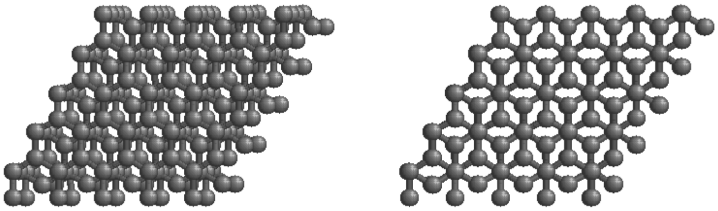


Figure 16.7.3: Animation of a rotating graphite structure. This is a stereogram and can be viewed in 3D if a viewer's eyes are crossed slightly to overlap the two panels. Images used with permission from Wikipedia.

Questions to consider

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in graphite?
- The a layer of the graphite structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- What force holds the carbon sheets together in graphite?
- Graphite is very slippery and is often used in lubricants. Explain why this property is expected on the basis of the structure of graphite.
- The slipperiness of graphite is enhanced by the introduction of impurities. Where would such impurities be located and why would they make graphite a better lubricant?

Fullerenes

Until the mid 1980's, pure carbon was thought to exist in two forms: graphite and diamond. The discovery of C_{60} molecules in interstellar dust in 1985 added a third form to this list. The existence of C_{60}, which resembles a soccer ball, had been hypothesized by theoreticians for many years. In the late 1980's synthetic methods were developed for the synthesis of C_{60}, and the ready availability of this form of carbon led to extensive research into its properties.

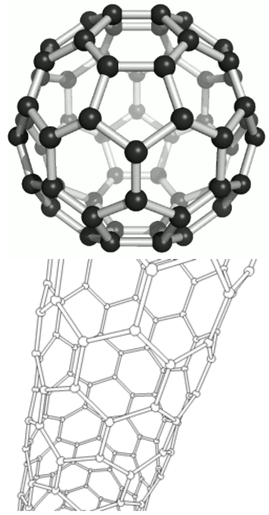


Figure 16.7.4: Example of fullerenes: a buckyball (C_{60} *on left and an extended bucktube. Images used with permission from Wikipedia.*

The C_{60} molecule (Figure $16.7.4$; left), is called buckminsterfullerene, though the shorter name fullerene is often used. The name is a tribute to the American architect R. Buckminster Fuller, who is famous for designing and constructing geodesic domes which bear a close similarity to the structure of C_{60}. As is evident from the display, C_{60} is a sphere composed of six-member and five-member carbon rings. These balls are sometimes fondly referred to as "Bucky balls". It should be noted that fullerenes are an entire class of pure carbon compounds rather than a single compound. A distorted sphere containing more than 60 carbon atoms have also been found, and it is also possible to create long tubes (Figure $16.7.4$; right). All of these substances are pure carbon.

Questions to Consider

- What is the bonding geometry around each carbon? (Note that this geometry is distorted in C_{60}.)
- What is the hybridization of carbon in fullerene?
- A single crystal of C60 falls into which class of crystalline solids?
- It has been hypothesized that C60 would make a good lubricant. Why might C60 make a good lubricant?

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure $16.7.5$. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials.

Metals are characterized by their ability to reflect light, called luster, their high electrical and thermal conductivity, their high heat capacity, and their malleability and ductility. Every lattice point in a pure metallic element is occupied by an atom of the same metal. The packing efficiency in metallic crystals tends to be high, so the resulting metallic solids are dense, with each atom having as many as 12 nearest neighbors.

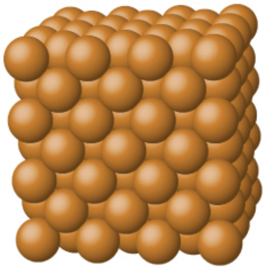


Figure* $16.7.5$*: Copper is a metallic solid. (CC BY; OpenStax).

Bonding in metallic solids is quite different from the bonding in the other kinds of solids we have discussed. Because all the atoms are the same, there can be no ionic bonding, yet metals always contain too few electrons or valence orbitals to form covalent bonds with each of their neighbors. Instead, the valence electrons are delocalized throughout the crystal, providing a strong cohesive force that holds the metal atoms together.

> *Valence electrons in a metallic solid are delocalized, providing a strong cohesive force that holds the atoms together.*

The strength of metallic bonds varies dramatically. For example, cesium melts at 28.4°C, and mercury is a liquid at room temperature, whereas tungsten melts at 3680°C. Metallic bonds tend to be weakest for elements that have nearly empty (as in Cs) or nearly full (Hg) valence subshells, and strongest for elements with approximately half-filled valence shells (as in W). As a result, the melting points of the metals increase to a maximum around group 6 and then decrease again from left to right across the d block. Other properties related to the strength of metallic bonds, such as enthalpies of fusion, boiling points, and hardness, have similar periodic trends.

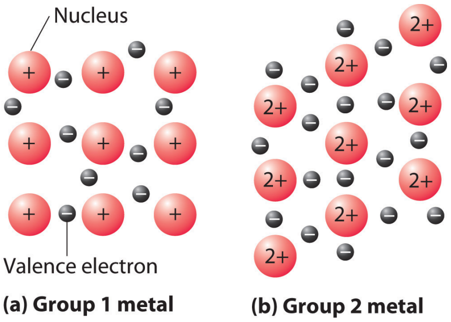


Figure 16.7.6: The Electron-Sea Model of Bonding in Metals. Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a “sea” of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting point.

A somewhat oversimplified way to describe the bonding in a metallic crystal is to depict the crystal as consisting of positively charged nuclei in an electron sea (Figure $16.7.6$). In this model, the valence electrons are not tightly bound to any one atom but are distributed uniformly throughout the structure. Very little energy is needed to remove electrons from a solid metal because they are not bound to a single nucleus. When an electrical potential is applied, the electrons can migrate through the solid toward the positive electrode, thus producing high electrical conductivity. The ease with which metals can be deformed under pressure is attributed to the ability of the metal ions to change positions within the electron sea without breaking any specific bonds. The transfer of energy through the solid by successive collisions between the metal ions also explains the high thermal conductivity of metals. This model does not, however, explain many of the other properties of metals, such as their metallic luster and the observed trends in bond strength as reflected in melting points or enthalpies of fusion. Some general properties of the four major classes of solids are summarized in Table 16.7.2

Table 16.7.2: Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous

*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.

> The general order of increasing strength of interactions in a solid is:
>
> $$\textit{molecular solids} < \textit{ionic solids} \approx \textit{metallic solids} < \textit{covalent solids}$$

✓ Example 16.7.1

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

A. Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.
B. Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

A Germanium lies in the p block just under Si, along the diagonal line of semimetallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a covalent solid. RbI contains a metal from group 1 and a nonmetal from group 17, so it is an ionic solid containing Rb^+ and I^- ions. The compound C6(CH3)6 is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form a molecular solid with no covalent bonds between them. Zn is a d-block element, so it is a metallic solid.

B Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is $C_6(CH_3)_6$ < Zn ~ RbI < Ge. The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

? Exercise 16.7.1

Classify C_{60}, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer

> C_{60} (molecular) < AgZn (metallic) ~ $BaBr_2$ (ionic) < GaAs (covalent). The actual melting points are C60, about 300°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

Summary

The major types of solids are ionic, molecular, covalent, and metallic. Ionic solids consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to have high melting points and are rather hard. Molecular solids are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. As a result, they tend to be rather soft and have low melting points, which depend on their molecular structure. Covalent solids consist of two- or three-dimensional networks of atoms held together by covalent bonds; they tend to be very hard and have high melting points. Metallic solids have unusual properties: in addition to having high thermal and electrical conductivity and being malleable and ductile, they exhibit luster, a shiny surface that reflects light. An alloy is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (substitutional alloys), by inserting smaller atoms into holes in the metal lattice (interstitial alloys), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form intermetallic compounds with unique properties.

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